QUANTUM CHEMICAL STUDY OF THERMAL DEHYDROCHLORINATION OF POLY(VINYL CHLORIDE) CONTAINING ALDEHYDE GROUPS*

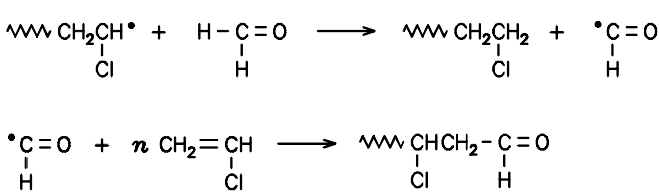
Jaroslav BURDA

Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

Received September 26, 1994
Accepted June 15, 1995

Thermal dehydrochlorination of syndiotactic oligomeric models of PVC with aldehyde groups is studied using semiempirical quantum chemical methods AM1 and MNDO. The possibility of both radical and ionic mechanism of HCl elimination is examined. From the results it follows that the homolytic detachment of chlorine from the carbon in β-position to the aldehyde group is preferred, followed by hydrogen splitting off. Hydrogen atom detachment from the carbon in α-position to the aldehyde group as the first step is found energetically less convenient. The dehydrochlorination of aldehyde-containing PVC model, especially of the first molecule from the chain, is remarkably easier in comparison with regular PVC model. However, the energetical preference is smaller for further HCl splitting off and, from the kinetic point of view, this process seems to be slower. The influence of the aldehyde group inductive effect on the driving force potential $\mu(C^{\alpha}–C^{\omega})$ is apparent from the partial charge distributions.

The last work in the series on thermal dehydrochlorination of PVC deals with the chains with CHO endgroups. Such aldehyde structures are formed in the course of polymerization of vinyl chloride by copolymerization with molecular oxygen, which is built into the polymer chain as peroxide. The peroxide further decomposes, under the polymerization conditions, to hydrogen chloride, carbon monoxide and formaldehyde[1]. The last mentioned compound can react with the radical end of growing polymer chain, creating formaldehyde radical. The following step is polymerization of vinyl chloride



* Part VI in the series Thermal Dehydrochlorination of Poly(vinyl chloride); Part V: see ref.[5].

initiated by this radical. Formaldehyde acts here as a so-called chain-transfer agent[2]. The β-chloroaldehyde results as a product of above mentioned reaction.

Aldehyde groups together with other structure defects considerably influence dehydrochlorination of PVC chains. The goal of this work is to find out how the CHO group changes the situation in its neighbourhood and what leads to easier elimination of HCl molecules.

CALCULATIONS

Stepwise splitting off of HCl molecules by both radical and ionic mechanisms, activated by the presence of aldehyde groups, is simulated using the semiempirical quantum-chemistry methods MNDO and AM1, similarly to previous PVC model systems studied[3–5]. In the present case the detached chlorine atom is localized on the carbon in β-position to the aldehyde group. The following step is hydrogen splitting off from the carbon in the α-position. As an alternative process, hydrogen detachment (activation in α-position) followed by dechlorination in the next step was considered. Only the MNDO method is used for this alternative activation. All structures studied are based on "tetramer" of vinyl chloride, 3,5,7,9-tetrachlorodecan-1-al (*I*) in trans–trans ("syndio") conformation. After the geometry optimization of this species, the dechlorination (or dehydrogenation) is performed, followed again by complete optimization of the new structure. This algorithm is stopped when the third double bond is created.

RESULTS AND DISCUSSION

The modelling reactions can be divided into the overall reaction – (*A*) giving rise to unsaturated structures

$$\text{R–CHCl–CH}_2\text{–R}' \longrightarrow \text{R–CH=CH–R}' + \text{HCl} \qquad (A)$$

and into reaction steps leading to radical or ionic intermediates:

$$\text{R–CHCl–CH}_2\text{–R}' \longrightarrow \text{R–CH}\bullet\text{–CH}_2\text{–R}' + \text{Cl}\bullet \qquad (B)$$

$$\text{R–CHCl–CH}_2\text{–R}' \longrightarrow \text{R–CH}^+\text{–CH}_2\text{–R}' + \text{Cl}^- \qquad (B')$$

$$\text{R–CHCl–CH}_2\text{–R}' \longrightarrow \text{R–CHCl–CH}\bullet\text{–R}' + \text{H}\bullet \qquad (C)$$

$$\text{R–CHCl–CH}_2\text{–R}' \longrightarrow \text{R–CHCl–CH}^-\text{–R}' + \text{H}^+ \qquad (\text{C}')$$

The reaction energies are summed up in Table I. It can be seen from the comparison of energies of the reactions (*B*) and (*C*) and (*B′*) and (C′) that aldehyde group does not make the activation of the hydrogen in α-position more favourable than that of chlorine atom in neither of the mechanisms considered. Therefore, further discussion is focused only on the results of reactions and species from schemes (*A*), (*B*) and (B′).

From the second column of Table I, one can notice the dependence of reaction energy differences ΔE_A on the number of double bonds. Considering the MNDO method, these differences are nearly the same as in similar structures without CHO groups. The same comparison, using the AM1 method, leads to the prediction of a slightly higher energetical preference of the dehydrochlorination reaction (*A*) in the presence of aldehyde group, especially for the detachment of the first HCl molecule (about 20 kJ/mol).

A similar conclusion can be drawn for the first chlorine detachment by radical mechanism using both methods. MNDO predicts the same course of dechlorination as in the absence of CHO groups. On the contrary, AM1 results lead to different conclusions. First, the energies ΔE_A slightly increase with the length of π-electron system. This is the opposite behaviour in comparison with the models without CHO groups. Second, all the values ΔE_B for splitting off further chlorine atoms are higher than ΔE_B for the corresponding models of regular PVC: ΔE_B(2 Cl → 1 Cl) = 2.64 eV against 2.87 eV here. This may lead to slowing down the reaction (*B*) according to the Eyring theory of absolute reaction rates for the case of radical mechanism.

The predictions of energy for ionic mechanism $\Delta E_{B'}$ using both methods are similar. In comparison with the aldehyde-free chains even the detachment of the first chloride

TABLE I

Energetical balances (eV) of the HCl elimination (*A*), Cl• (*B*) and Cl^- detachment (B′), and H• (*C*) and H^+ detachment (C′) from *I* and its unsaturated derivatives

Reaction step[a]	ΔE_A		ΔE_B		$\Delta E_{B'}$		ΔE_C	$\Delta E_{C'}$
	MNDO	AM1	MNDO	AM1	MNDO	AM1	MNDO	MNDO
$I \rightarrow I$(3 Cl)	0.555	–0.023	2.563	2.840	6.897	7.469	3.421	9.249
I(3 Cl) → I(2 Cl)	0.524	–0.103	2.549	2.853	6.691	7.299	3.264	9.037
I(2 Cl) → I(1 Cl)	0.550	–0.109	2.573	2.866	6.568	7.168	3.221	8.918

[a] $I(n\ \text{Cl}) \rightarrow I(n-1)\ \text{Cl}$ means dehydrochlorination, dechlorination or dehydrogenation reaction of the unsaturated structure with *n* Cl atoms to that with (*n* – 1) Cl atoms.

anion is less favoured, approximately by about 0.2 eV. Further energies $\Delta E_{B'}$ decrease with the number of double bonds only slowly, so that in the third dechlorination the difference is more than 1 eV.

The conclusions for energetical balances from Table I are confirmed by the results of energy values of frontier orbitals. HOMO energy level of the system with 4 chlorine atoms (Table II) lies higher than that of the corresponding model without CHO group, i.e., it can be considered less stabile (e.g., by AM1 method –10.7 vs –11.0 eV), whereas the levels of the next systems with 3 and less chlorine atoms are already lower than those of equivalent models without CHO. This means that a greater amount of energy is necessary for making a more stabile system react. This fact correlates well with the dependence of ΔE_B on the length of π-electron system, where ΔE_B increases with the number of double bonds.

The energy level of SOMO of radical species (Table II) increases with the decreasing number of chlorine atoms in the system. This demonstrates the growth of lability of described radical species and thus a faster completion of the dehydrochlorination process. Regarding AM1 method, this fact is in contrast to the models without CHO groups. The values of SOMO energies are lower than those of the regular PVC models. This means that activation by aldehyde group is, in this step, lower than activation by allylic structure.

TABLE II
Frontier orbital energies (eV) of *I*, its unsaturated derivatives and its radical and cationic intermediates

Structure	MNDO	AM1
	HOMO/LUMO	
I	–11.11/0.15	–10.70/0.54
I(3 Cl)	–10.64/–0.34	–10.44/–0.33
I(2 Cl)	–9.62/–0.72	–9.43/–0.80
I(1 Cl)	–9.06/–0.90	–8.84/–1.09
Radicals	HDOMO/SOMO/LUMO	
I(3 Cl)	–10.92/–4.82/0.27	–10.72/–4.46/0.76
I(2 Cl)	–10.50/–4.73/–0.19	–10.52/–4.39/–0.18
I(1 Cl)	–9.50/–4.61/–0.41	–9.55/–4.28/–0.63
Cations	HOMO/LUMO	
I(3 Cl)	–14.15/–8.29	–13.03/–7.74
I(2 Cl)	–14.14/–8.03	–13.92/–7.50
I(1 Cl)	–12.89/–7.80	–12.72/–7.48

Only mild growth of LUMO spectral values can be observed in the ionic mechanism (Table II), compared to the similar models without CHO groups. The completion of the dehydrochlorination process by ionic mechanism also does not run so fast as for activation by allylic groupings and so it can be considered relatively slowed down.

With regard to previous works[3–5], the dependence of the electron density distribution on the decreasing number of chlorine atoms in the system is not typical of the basic systems (Fig. 1*a*). The presence of aldehyde group induces alternating partial charges in its neighbourhood. This can be seen from the considerable similarity of the curves describing the distribution of partial charges on carbons in all systems. In the case of the curves describing systems with 3 or less chlorine atoms, when there is no electronegative chlorine atom on the 8th carbon, partial charge of this carbon remains, due to the inductive effect, considerably shifted towards positive values and is nearly the same as the corresponding charge in the system with 4 chlorine atoms. This inductive effect

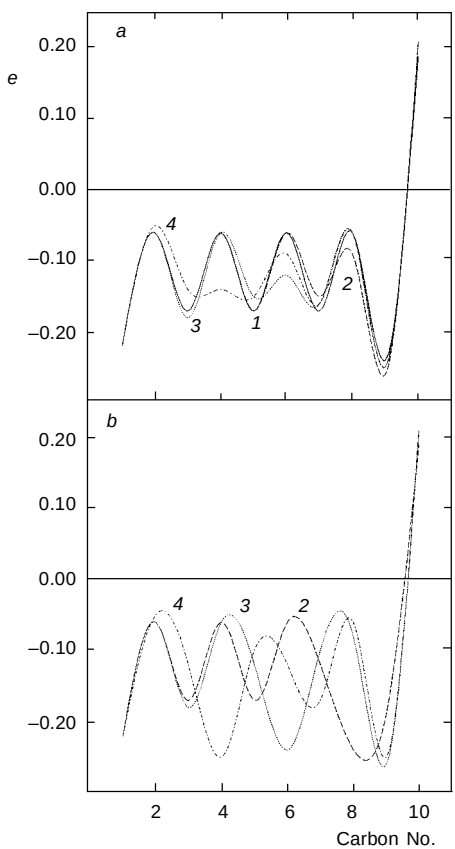


FIG. 1
Partial electron charge (*e*) distribution on the carbon atoms in structure *I* and its unsaturated derivatives (*a*) and their radical intermediates (*b*) as obtained by AM1 method. *1* Saturated system, *2* system with single double bond, *3* system with two double bonds, *4* system with three double bonds

substantially cancels existing driving force potential* $\mu(C^{\alpha}–C^{\omega})$ (see ref.[3]) for the basic systems. This is the explanation, why the radical forming step (*B*) is not activated to the extent of the models without CHO group and it correlates with the slight increase in ΔE_B. The potential $\mu(C^{\alpha}–C^{\omega})$ is apparent only in the case of radical structures (see Fig. 1*b*), where its existence supports energetical prediction of kinetics of the completion of dehydrochlorination and of slightly lower reaction energies ΔE_A for further elimination of HCl molecules.

CONCLUSIONS

From the energetical balances, one can summarize that the elimination of the first HCl molecule is more favoured in aldehyde-containing models than in the models without aldehyde group. In spite of the fact that the dehydrochlorination energies ΔE_A are slightly more favourable (at least using AM1 method), further growth of unsaturated structure is more or less curbed judging from the energy ΔE_B and HOMO spectral values. Vanishing of the potential $\mu(C^{\alpha}–C^{\omega})$ does not predict higher activation by aldehyde groups for basic systems. Only the transformation of radical intermediates to unsaturated structures (H detachment) can be considered activated as a consequence of both SOMO energies and the existence of potential $\mu(C^{\alpha}–C^{\omega})$. Nevertheless, this activation is smaller in comparison with corresponding allylic activation. Similar situation exists for the ionic mechanism, where the values $\Delta E_{B'}$ do not show an increased activation of chloride anion, not even in the first step.

Another interesting consequence should be mentioned. In the case of the models with aldehyde groups the radical mechanism will be energetically more favoured due to the formation of longer π-electron system than for the models of regular PVC. The fast fall of energy of ionic systems $\Delta E_{B'}$ with the number of double bonds enables a gradual transition from the radical to ionic mechanism depending on the environment polarity. Here, on the contrary, this possibility is less probable, thanks to a mild decrease in activation energies $\Delta E_{B'}$ in dependence on the length of π-electron system.

REFERENCES

1. Braun D., Sonderhof D.: Eur. Polym. J. *18*, 141 (1982).
2. Lukas R.: Makromol. Chem., Macromol. Symp. *29*, 21 (1989).
3. Burda J., Lukas R.: Collect. Czech. Chem. Commun. *57*, 93 (1992).
4. Burda J., Lukas R.: Collect. Czech. Chem. Commun. *58*, 343 (1993).
5. Burda J., Lukas R.: Collect. Czech. Chem. Commun. *60*, 1303 (1995).

* In fact, the superscript α should be replaced by β, since there is a greater β-activation in aldehyde models.