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ON THERMAL DEHYDROCHLORINATION OF MODEL COMPOUNDS FOR POLY(VINYL CHLORIDE)—II

EXTENDED HÜCKEL AND ITERATIVE EXTENDED HÜCKEL CALCULATIONS ON THE β-*CIS*-DEHYDROCHLORINATION OF ETHYL CHLORIDE

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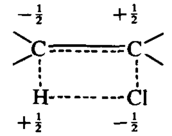
Abstract—The semiempirical methods of molecular orbital—extended Hückel (EHT) and iterative extended Hückel theory (IEHT)—were used to the study of the mechanism of β-*cis*-elimination of hydrogen chloride from ethyl chloride. The geometrical and electronic structure of transition state was determined and the change in the distribution of electronic density along the reaction path was investigated by means of the Mulliken population analysis.

INTRODUCTION

One approach to the investigation of thermal destruction of poly(vinyl chloride) (PVC) is the study of the decomposition of low-molecular chloroalkanes which represent individual units of the chain of PVC.[1-5] The dehydrochlorination of these substances proceeds mostly as a β - *cis* - elimination. In spite of a great deal of experimental data concerning the decomposition of alkyl chlorides[6] there is no uniform and general view of the mechanism of this reaction.

Maccol and Thomas[6,7] suggested that the formation of a ion pair should be a step controlling the reaction rate and correlated the activation energy of reaction with the heterolytic dissociation energy of C—Cl bond. Benson *et al*[8-11] assume a semiionic character of the four-centre transition state (TS) and calculated the activation energies of hydrogen chloride addition to different olefins by means of an electrostatic model of point dipols. Setser and Hasler[12,13] calculated the rate constants and preexponential factors of ethyl chloride decomposition on the basis of the Rice - Ramsperger - Kassel - Marcus (RRKM) theory of unimolecular reactions.[14]



The aim of this study is to investigate the mechanism of β - *cis* - elimination of hydrogen chloride and to determine the geometrical and electronic structure of the TS of reaction by using the semiempirical quantum chemical EHT and IEHT methods.

Reaction model

Ethyl chloride was chosen as a model substance for the study of the mechanism of β - *cis* - elimination. Its choice was due to the possibility of comparing the structure of TS established by us with the structures stated by other authors[8-13] as well as to its relative simplicity when compared with other alkyl chlorides. In spite of this "simplicity" a molecule of ethyl chloride possesses 18 degrees of freedom and a construction of total energetic hypersurface would be very intricate. Therefore on the basis of the foregoing views of the structure of TS[8-13] and the known structures of initial substance and products we have used the reaction model of unimolecular elimination of hydrogen chloride which is drawn in Fig 1. We have selected the subsequent geometridal parameters as the most important for the reaction path

Bond lengths:

$R_{C_1-Cl} \equiv R_1$: $R_{C_2-H_4} \equiv R_2$; $R_{C_1-C_2} \equiv R_3$; $R_{H_4-Cl} \equiv R_4$;

Bond angles:

$\measuredangle\, H_4C_2C_1 \equiv \beta$; $\measuredangle\, ClC_1C_2 \equiv \alpha$; $\measuredangle\, H_7C_1C_2 \equiv \delta$
dihedral angle $\measuredangle\, Cl—C_1—C_2—H_5 \equiv \gamma$

which were gradually changed from the initial

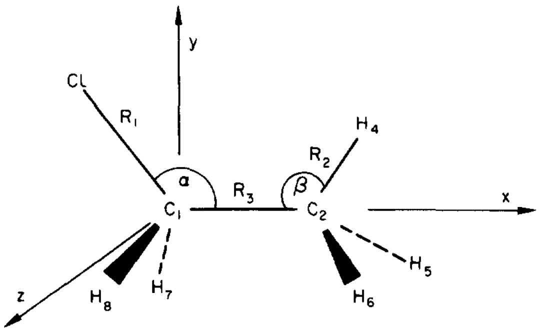


Fig 1. The coordinate for the reacting system.

substance to the product in accordance with the principle of least motion.[15] As regards the problems which we are interested in, we paid the main attention to the initial reaction stage until the formation of transition state. In the initial stage of reaction these parameters represent a gauche conformation which is the most stable conformation of ethyl chloride in gaseous phase.[16] Owing to a small value of the energetic difference of *cis-gauche* conformations (3·68 kcal/mol)[17] we assume that the $H_4C_2C_1Cl$ atoms are in the first point of the model reaction path (RC1) in one plane (xy). Also Tee's calculations[15] on this particular reaction suggest an effective dihedral angle very close to zero. During the reaction the distances R_1 and R_2 increase, i.e. the C_1—Cl and C_2—H bonds weaken and the ethyl chloride molecule decomposed into ethylene and hydrogen chloride at the same time the hybridization of carbons change from sp^3 to sp^2 and the remaining H atoms (H_5, H_6, H_7, H_8) come into one plane (xz) with the C atoms. The values of this set of parameters in particular points of the reaction path thus simulated as well as the geometry of ethyl chloride, ethylene, and hydrogen chloride are given in Table 1.

The solution of secular problem of particular points of reaction path has been performed by the EHT and IEHT methods at a usual parametrization.[18–20] For the denotation of atomic orbitals (AO) the following symbols have been used. The symbols S_{C_1}, X_{C_1}, Y_{C_1}, Z_{C_1} and S_{C_2}, X_{C_2}, Y_{C_2}, Z_{C_2} denote 2s, $2p_y$, and $2p_z$ AO of the carbons 1 and 2. H stands for 1s AO of hydrogen. S_{Cl}, X_{Cl}, Y_{Cl}, and Z_{Cl} denote 3s, $3p_x$, $3p_y$, and $3p_z$ AO of chlorine. The changes in the electronic structure along the model reaction path have been studied by investigating the value of particular populations according to Mulliken.[21]

Changes in the electronic structure of ethyl chloride along the reaction path

The values of the total energy of particular points of the reaction path calculated according to EHT and IEHT are presented in Table 2. The calculated values show that the total energy increases to a maximum which is in RC9. The investigation of the course of particular populations enables us to have a detailed insight into the character of the changes in electronic structure along the reaction path. Though the AO populations are not invariant with respect to the rotation of coordinate system, they are a valuable aid for the investigation of the trend of the changes in electronic density along the reaction path.

The distribution of electronic structure in a molecule is characterized by the gross charge q(A).[21] The gross charge of all atoms calculated by both the methods are presented in Fig 2. It should be noted that the q(H) values of the H atoms which have less direct concern with the reaction, i.e., $H_6(=H_5)$ and $H_8(=H_7)$ are almost unchanged. The most conspicuous change in the gross charge on Cl

Table 1. Values of geometrical parameters in the points of model reaction path[a]

RC	R_1	R_2	R_3	R_4	β	α	γ	δ
C_2H_5Cl	1·78	1·09	1·54	3·66	109·46	109·46	120·0	109·46
1	1·82	1·13	1·52	2·55	108·0	109·0	116·5	110·5
2	1·88	1·19	1·50	2·51	107·0	108·0	113·0	112·0
3	1·94	1·25	1·48	2·48	106·0	107·0	109·5	113·5
4	2·00	1·31	1·46	2·44	105·0	106·0	106·0	115·0
5	2·06	1·37	1·44	2·40	104·0	105·0	102·5	116·5
6	2·12	1·43	1·42	2·35	103·0	104·0	99·0	118·0
7	2·18	1·49	1·40	2·27	102·0	103·0	95·5	119·5
8	2·24	1·55	1·38	2·06	98·0	99·0	92·0	121·0
9	2·30	1·60	1·38	1·80	94·0	95·0	90·0	121·8
10	2·36	1·75	1·34	1·47	90·0	90·0	90·0	121·8
11	2·46	1·91	1·34	1·27	90·0	90·0	90·0	121·8
12	2·56	2·56	1·34	1·27	90·0	90·0	90·0	121·8
13	3·06	3·59	1·34	1·27	90·0	90·0	90·0	121·8
C_2H_4, HCl			1·34	1·27				121·8

[a] Distances are in Å, angles in degrees.

Table 2. Course of the total energy along the reaction path calculated by the EHT and IEHT[a] method

RC	E_{Tot}(EHT)	E_{Tot}(IEHT)
1	−8 150·25	−7 920·86
2	−8 148·06	−7 911·88
3	−8 143·81	−7 904·17
4	−8 138·15	−7 891·80
5	−8 131·11	−7 877·14
6	−8 123·38	−7 862·49
7	−8 113·93	−7 850·86
8	−8 098·76	−7 844·24
9	−8093·54	−7 841·48
10	−8 099·83	−7 893·40
11	−8 133·07	−7 928·67
12	−8 151·61	−7 958·94
13	−8 176·27	−7 989·34

[a] In kcal/mol.

and C_1 takes place in the initial stage of reaction when the charge transfer from C_1 to Cl sets in. Between RC8 and RC10 charge transfer from H to C_2 (it is H_4 if not stated otherwise) and between RC10 and RC11 the charge transfer from the atom of Cl to the atom of H starts to be effective. This transfer is due to the interaction between Cl–H and plays together with the C_1–C_2 interaction the main part in the TS stabilization when the system passes from the TS configuration towards the products.

The course of charge distribution and the trend of the change of electronic density along the reaction path enables us to investigate the gross populations N(r)[21] for all AO's atoms, which direct concern with the reaction. From the course of N(r) (Fig 3) it is obvious that the changes in charge distribution along the reaction path appear in the space characteristic of these AO's:

$$Y_{C_1}, Y_{C_2}, S_{Cl}, X_{Cl}, Y_{Cl}, H$$

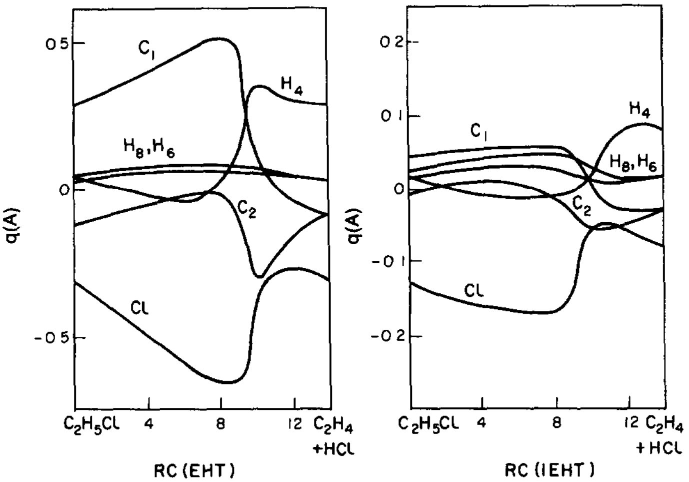


Fig 2. The change of the gross charge, q(A), of the atoms in the reaction processes.

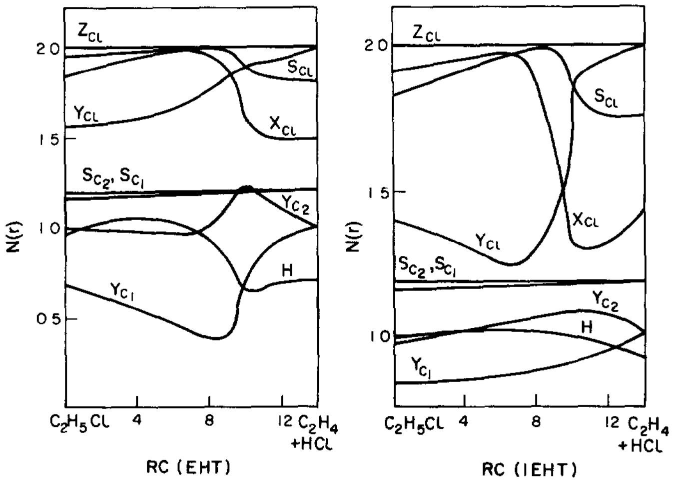


Fig 3. The change of AO gross population, N(r), of the C_1, C_2, Cl, H atoms in the reaction processes.

while the electronic density outside this space is almost unchanged. From the course of populations of AO's of the chlorine atom it is possible to draw conclusions on the electronic processes which occur inside the Cl atom. During the reaction AO Y_{Cl} turns into a free electron pair. The atomic orbital X_{Cl} shows the character of free electron pair in the initial state of reaction but it looses this character because of the interaction with hydrogen (charge transfer to hydrogen) during the reaction. The atomic orbital S_{Cl} is of great importance for the stabilization of system after RC9. $N(S_{Cl})$ reaches its maximum value in RC9 while AO S_{Cl} assumes the character of free electron pair.

From the populations N(r) for each 2s, $2p_x$, $2p_y$, and $2p_z$ AO of C atom we can obtain "hybridization relations" on individual atoms.[21,22] The C atoms in ethyl chloride show the subsequent relations:

$$\begin{aligned} C_1 \ \text{IEHT} \ & S^{1\cdot18} X^{0\cdot97} Y^{0\cdot83} Z^{0\,98}, && \text{i.e. } S^{1\cdot18} P^{2\,78} \\ \text{EHT} \ & S^{1\cdot16} X^{0\,91} Y^{0\cdot68} Z^{0\cdot96}, && \text{i.e. } S^{1\,16} P^{2\,55} \\ C_2 \ \text{IEHT} \ & S^{1\,15} X^{0\cdot94} Y^{0\,96} Z^{0\cdot96}, && \text{i.e. } S^{1\,15} P^{2\,68} \\ \text{EHT} \ & S^{1\cdot19} X^{0\,97} Y^{0\cdot98} Z^{0\,98}, && \text{i.e. } S^{1\,19} P^{2\cdot93} \end{aligned}$$

while for ethylene we obtain

$$\begin{aligned} C_1, C_2 \ \text{IEHT} \ & S^{1\,18} X^{0\cdot94} Y^{1\,00} Z^{0\cdot94}, \ \text{i.e. } S^{1\cdot18} (XZ)^{1\,88} Y^{1\cdot00} \\ \text{EHT} \ & S^{1\cdot20} X^{0\,94} Y^{1\,00} Z^{0\cdot95}, \ \text{i.e. } S^{1\cdot20} (XZ)^{1\cdot89} Y^{1\,00} \end{aligned}$$

These relations may be compared with tetragonal SP^3, $S(XYZ)^3$, and trigonal SP^2, $S(XZ)^2$ hybrid atomic orbital (HAO). All "hybridization relations" manifest a higher 2s character than it would correspond to tetragonal and trigonal HAO.

The overlap population between atoms M(A—B)[21] (Fig 4) is a measure of electronic density in the region between two atoms and may be considered to be the order of bond.[21,23] It is obvious from Fig 4 that the order of bonds which do not take part in the origination of transition state does hardly change at all. In the region between RC8 and RC9 the electrons participating in reaction are delocalized over the whole four-center complex and the character of this delocalization is asymmetrical (Fig 4).

DISCUSSION

The changes in energy and in populations along the reaction path show that the configuration of reaction system at the top of reaction barrier (RC9) may be considered to be a transition state. The geometrical parameters of TS for unimolecular elimination of hydrogen chloride following from the EHT and IEHT calculations of model reaction path are as follows:

$$R_1 = 2\cdot30\ \text{Å}, R_2 = 1\cdot60\ \text{Å}, R_3 = 1\cdot38\ \text{Å}, R_4 = 1\cdot80\ \text{Å}$$
$$\beta = 94\cdot0^\circ \quad \alpha = 95\cdot0^\circ \quad \gamma = 90\cdot0^\circ \quad \delta = 121\cdot8^\circ$$

The calculated parameters characterizing TS may be compared with the values of parameters which have been suggested for the TS of the elimination of hydrogen chloride from ethyl chloride by other methods (Tables 3, 4). Haugen and Benson[8,9] used a simple electrostatic model of point dipols which enables us to calculate the activation energies of *cis*-addition of HX molecules on double bond. Since the *cis*-elimination is a reverse reaction with respect to *cis*-addition, the TS structure is equal for both the reactions.

Hasler and Setser[12] calculated on the basis of the RRKM theory of unimolecular reactions the values of rate constants and preexponential factors for several TS structures and among them for the Benson–Haugen structure too. The calculated rate constants and preexponential factors of the Hasler–Setser models HS-1 and HS-2 (Tables 3, 4) comply with experimental data but high preexpo-

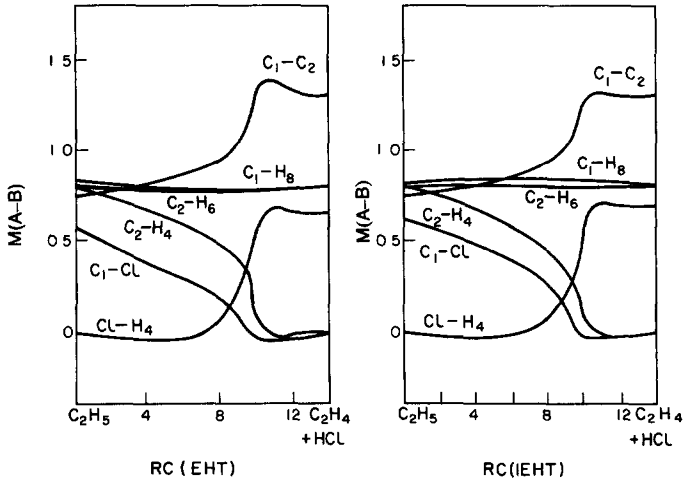


Fig 4. The change of the overlap population between atoms, M(A–B), in the reaction processes.

Table 3. Values of the geometrical parameters of TS

Model TS	R_1	R_2	R_3	R_4
RC9[a]	2·30	1·60	1·38	1·80
B[b]	2·78	2·09	1·40	1·67
HS-1[c]	1·86	1·59	1·32	1·78
HS-2[c]	2·00	1·36	1·37	1·49
HS-3[c]	2·44	1·74	1·37	1·54

[a] Present work; [b] Ref 8; [c] Ref 12.

Table 4. Values of the orders of bonds in TS

Model TS	n_{C_1-Cl}	n_{C_2-H}	$n_{C_1-C_2}$	n_{H-Cl}
RC9-IEHT[a,b]	0·20	0·38	1·02	0·25
RC9-EHT[a,b]	0·12	0·43	1·00	0·24
B[c]	0·18	0·18	1·50	0·50
HS-1[d]	0·80	0·20	1·80	0·20
HS-2[d]	0·50	0·50	1·50	0·50
HS-3[d]	0·12	0·12	1·50	0·43

[a] Present work; [b] M(A–B); [c] Ref 8; [d] Ref 12.

nential factors and thus high values of activation entropy ($\Delta S^{\ddagger}$)[12] are obtained with the Benson–Haugen model (B) and the Hasler–Setser model HS-3. The comparison of geometrical parameters shows that the TS (RC9) structure calculated by us is reasonable and it is geometrically more similar to the kinetic models of Setser and Hasler than to the electrostatic model of Benson and Haugen.

According to Miller,[24] the Woodward–Hoffmann rules of the conservation of orbital symmetry[25] would lead to the conclusion that the four-centre β-*cis*-eliminations (additions) in which the so-called σ–π switch occurs cannot proceed as synchronous reactions i.e. without any formation of some intermediate of biradical or ionic type. In these reactions is a net gain (loss) of a π–MO and loss (gain) of a σ–MO. Recently Goddard, however, demonstrated[26] on the basis of orbital phase continuity principle that the β - *cis* - eliminations of hydrogen halogenides can proceed as synchronous reactions when the free electron pair of halogen plays an important role. The course of populations along the reaction path confirms the important role of the free electron pair on the Cl atom (it follows from the course of populations that this is the free electron pair in the AO X_{Cl} direction). During the reaction it turns into the MO of hydrogen chloride the σ bonding pair C_1–Cl turns into the free electron pair (Y_{Cl}). If we denote the free electron pair with n, the course of the reaction may be described by the following scheme

$$\sigma^2_{CH} + \sigma^2_{CCl} + n^2_{X_{Cl}} \rightleftarrows \pi^2_{CC} + n^2_{Y_{Cl}} + \sigma^2_{HCl}$$

The course of populations on the atoms which do not participate direct in the formation of transition state changes very little during the reaction Therefore we may assume in the first approxima tion that the charge distribution of the ground stat of atoms (outside transition state) and adjacen bonds is not disturbed during the reaction. Suc assumption was postulated by Benson an Haugen[9,10] for their model.

From the comparison of individual population (Fig 2, 3) may well be seen that there ar considerable differences between their value calculated by EHT and IEHT methods. The charg distribution obtained by EHT method appears to b exaggerated because EHT methods does no involve explicitly electronic repulsion and propos too great a ionic structure. In IEHT version used b us the parameters are assumed to depend o molecular charge distribution according t Cusachs.[19,20] Such a dependence allows one t correct, in first-order way for interelectroni repulsion effects and thus to obtain a more rea charge distribution in the molecule. Despite of th different values, the course of the changes o population proves to be very similar during th reaction and consequently, the qualitative descrip tion of the reaction mechanism of ethyl chlorid dehydrochlorination obtained on the basis on EH and IEHT calculations of the model reaction path i equal.

The comparison of the orbital energies of th highest occupied molecular orbital (HO MO) wit the ionisation potential (IP) of ethyl chloride (in th scope of Koompans theorem) shows that the valu of HO MO energy calculated by IEHT metho (− 11·90 eV) is close to the value of IP (11·18 eV) while the value calculated according to EH (−13·43 eV) is more remote from the experiment value.

It is quite interesting to compare the values c reaction barrier ($E^{\ddagger}$) and the energetic difference between the *cis* and *gauche* conformer (ΔE) c ethyl chloride calculated by EHT and IEH methods with experimental values.

$E^{\ddagger}_{exp} = 56{\cdot}5\text{–}69{\cdot}8$ kcal/mol[6]; $E^{\ddagger}_{IEHT} = 92{\cdot}44$ kcal/mo
$E^{\ddagger}_{EHT} = 60{\cdot}25$ kcal/mol.

$\Delta E_{exp} = 3{\cdot}68$ kcal/mol[16]; $\Delta E_{IEHT} = 5{\cdot}32$ kcal/mol;
$\Delta E_{EHT} = 4{\cdot}49$ kcal/mol.

There is however a paradox: whereas th *energetic* values calculated by the EHT method ar closer to experimental than those from the IEH method, it is the latter method which obtains considerably more realistic *charge distributio* (*and* also, incidentally, a better ionisation potenti for ethyl chloride). We presume that the betterin of the charge distribution by iteration is most likel detrimental to exactness of the EHT method in th proposition of energetic characteristics. The agree ment of the reaction barrier calculated by EHT method with the experimental value is probably quite an accidental one which is also witnessed by the fact that the energetic values calculated for both methods characterize the reaction as an exothermic (Table 2) one which oppose the experiment ($\Delta H = 16 \cdot 5$ kcal/mol[10]). In the method used, Hamiltonian does not include any nuclear repulsion therms, it takes account of interelectron repulsion using a very specious $H\mu\nu$ recipe and it pays little attention to electron - others - nucleus attractive forces.[28] We can, therefore not expect the methods to be apt of giving a quantitative description of the energetic reaction surface.

Owing to the semiempirical EHT and IEHT methods and simplifications done in the modelling of the reaction path we cannot state that the reaction path which has been established is real, i.e. corresponds to the points of reaction path on the potential hypersurface of the decomposition of ethyl chloride. Whereas the energetic results must be considered sceptically, the qualitative conclusions on the mechanism of unimolecular elimination of hydrogen chloride from ethyl chloride and TS structure are more likely to endure and to provide a practical basis for the further study of reactions of present type.

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