

THEORETICAL ANALYSIS OF STEREOSELECTIVITY IN BIMOLECULAR ELIMINATION REACTIONS

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Properties of the chloroethane molecule in the initial stage of its bimolecular elimination reaction were computed by the CNDO/2 method. For $C_\alpha R_1 R_2 X - C_\beta R_3 R_4 H$ -type compounds the results were generalized by analyzing the interaction between sp^3 hybrid orbitals of the α - and β -carbon. This analysis explained the energetical preference of antiperiplanar and synperiplanar conformations which had been established experimentally for bimolecular elimination reaction of compounds of the given type.

Stereoselectivity belongs to general features of bimolecular elimination reaction of the $C_\alpha R_1 R_2 X - C_\beta R_3 R_4 H$ -type compounds (where $X = \text{halogen, OH, NH}_2$). As a rule these reactions proceed as *trans*-eliminations not only in the liquid phase¹, but also on the surface of solid catalysts². Many authors have tried to explain this effect. According to *e.g.* Reutov³, this effect is brought about by a minimum repulsion of electron pairs which take part in splitting $C_\alpha - X$ and $C_\beta - H$ bonds in a conformation when the mutual position of these bonds is antiperiplanar. Obviously, this would mean that the dependence of the feasibility of the reaction on the conformation of splitting bonds should be sinusoidal with a maximum for the antiperiplanar position and minimum for the synperiplanar one. However, quantum chemical computations indicated that the extent of activation of the synperiplanar hydrogen is not negligible⁴⁻⁷ (the computed dependence possesses two extremes of the same type for both positions). Theoretical computations⁴⁻⁶ agree well with experimental findings; however, up to now no analysis has been performed of reasons for the stability of the activated complex for both mutual positions of the key bonds.

A next step in the solution of the problem was made by Klopman⁸, who interpreted the reaction as an interaction between an electron donor (the $C_\beta - H$ bond) and an electron acceptor (the $C_\alpha - X$ bond). He arrived at the conclusion that the most favourable conformations for the interaction of these bonds are just antiperiplanar and synperiplanar ones due to maximum values of overlap integrals of the HOMO $C_\beta - H$ and LUMO $C_\alpha - X$ bonds. Further, due to purely steric reasons, he suggested the preference of the antiperiplanar conformation, which leads to *trans*-elimination. His qualitative conclusions agree well with the cited computations⁴⁻⁷.

This work starts from our earlier attempt to analyze bimolecular elimination reactions⁷ and explains their course by using more fundamental conceptions of the quantum chemistry. Chloroethane was selected as the model system and hydroxyl anion as the base attacking the hydrogen atom.

METHODS AND RESULTS

The computations were performed by the CNDO/2 method⁹ for several conformations of the chloroethane molecule itself and for a structure which models one point of the reaction coordinate as an interaction between the hydrogen of the β -carbon and the hydroxyl anion. A standard geometry was used for the chloroethane molecule¹⁰ (tetrahedral bond angles; bond lengths: C—C 0.154 nm, C—H 0.109 nm, and C—Cl 0.178 nm⁴). The geometry of the model of the point on the reaction coordinate is obvious from Fig. 1a: the distance between C_β and O is equal to the sum of standard C—H and hydrogen bridge bond length¹¹: 0.109 nm + 0.160 nm = 0.269 nm; O—H bond has standard length¹⁰ 0.096 nm; the C_β —H(...OH⁻) and C_α —Cl bonds are elongated⁴ by 7%; all bond angles of both elongated bonds are diminished⁴ to 105°.

The following quantities were selected for the discussion of our results: a) relative total energy, E (tot) [J], related to one molecule with $\omega = 0^\circ$; b) relative charge on atom A, $Q(A)$ [$10^{-2} \cdot e$], related to one molecule with $\omega = 0^\circ$; c) relative Wiberg bond index¹² of bond A—B, $W(A-B)$ [-], related to one molecule with $\omega = 0^\circ$; d) frontier electron density⁴ in the LUMO, FED [-]. The dependence of computed values of the selected quantities on the dihedral angle ω (for its definition see Fig. 1b) is illustrated on Figs 2—7.

For evaluating the effect of the mutual interaction of two sp^3 hybrid orbitals of single-bonded carbon atoms, a computation analogous to the HMO method was performed (we assumed a proportionality between the resonance and overlap integrals and the latter was determined from values computed by a CNINDO program⁹). The results are illustrated on Fig. 8.

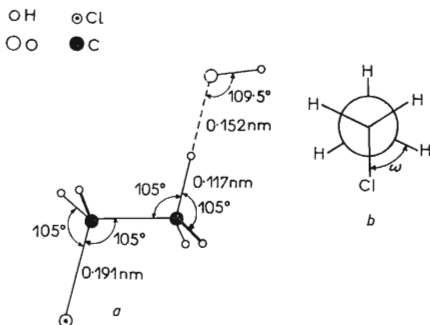


FIG. 1

The Geometry of the Model and the Definition of the Dihedral Angle

DISCUSSION

Significance of two positions – synperiplanar and antiperiplanar ones ($\omega = 0^\circ$ and $\omega = 180^\circ$) – is obvious at first sight from Figs 2–7, which illustrate the dependence of several quantities describing the degree of activation of the molecule on angle ω . The fact, that already in the chloroethane molecule the hydrogen atoms on β -carbon are not equivalent, is documented on Fig. 2. According to the value of the frontier electron density in the LUMO approximation, the most easily base attackable is the antiperiplanar hydrogen whereas the synperiplanar hydrogen is somewhat less attackable. As indicated by the dependences of other quantities, these conformations are favourable also in the course of the reaction itself. This is proved directly on Fig. 3 by the change of the total energy of one point on the reaction coordinate during the rotation around the $C_\alpha-C_\beta$ bond. Fig. 4, which illustrates the dependence of the charge of the chloride atom, yields a similar pattern. This atom possesses a significantly higher negative charge if its position with respect to the attacked hydrogen is antiperiplanar (according to common conceptions¹ of the reaction mechanism, the chlorine atom splits off as anion).

A proof of the easiest elimination of the antiperiplanar hydrogen is also provided by Figs 5–7 whence it can be derived that a weakening of the $C_\alpha-Cl$ (Fig. 5) and $C_\beta-H$ (Fig. 6) bonds and a strengthening of the $C_\alpha-C_\beta$ bond (Fig. 7) at one point of the reaction coordinate is most significant just for this conformation. Simultaneously, these – for an elimination typical changes of strengths of key bonds – occur also for the synperiplanar position, though to a lesser extent. This is how our com-

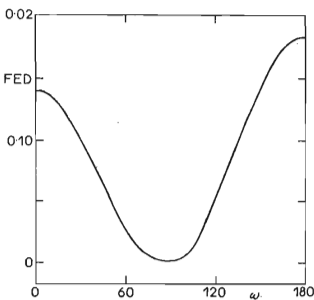


FIG. 2

The Dependence of the Frontier Electron Density (FED) of LUMO for the H_β Atom in $CH_2Cl.CH_3$ on the Dihedral Angle

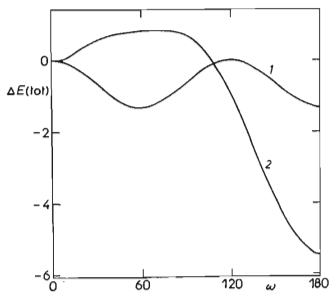


FIG. 3

The Dependence of the Relative Total Energy (in 10^{-20} J) of $CH_2Cl.CH_3$ 1 and $CH_2Cl.CH_2H...OH^-$ 2 on the Dihedral Angle

putations interpret the experimentally observed preference of the *trans*-elimination. If this reaction path is out of any reason blocked, the reaction may proceed as the less favourable *cis*-elimination¹. It is interesting to note that the preference of *trans*-elimination follows from properties of the activated complex and not from a higher frequency of occurrence of reactant molecules in a definite conformation as assumed by Klopman⁸.

Here, questions arise why just these two and not some other conformations of the activated complex are favourable and, further, why the antiperiplanar mutual position of splitting bonds is more favourable of the two. The first one may be answered in terms of the interaction through space¹³. The attack of the base weakens key bonds of the reactant molecule (*cf.* Figs 5 and 6). Consequently, the bond saturation of two hybrid orbitals oriented in the direction of these bonds decreases. At favourable conditions these orbitals can interact with one another (*cf.* curve 3 on Fig. 7), which leads to a stabilization of the system, *i.e.* of the activated complex. The energetic effect of this interaction is approximately proportional to the overlap integral of both orbitals¹⁴. This, for a given geometry of the model and with the Slater orbital exponents⁹, may be expressed by the relation $S = 0.0015 + 0.1533 \cos \omega$, where ω is the above defined dihedral angle. The absolute value of the overlap integral is maximal for $\omega = 0^\circ$ and $\omega = 180^\circ$ – that means for the synperiplanar and anti-

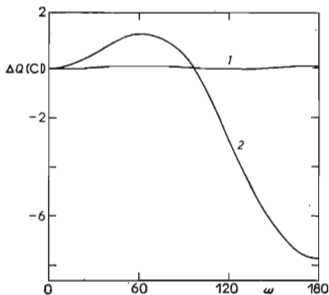


FIG. 4
The Dependence of the Relative Charge for the Cl Atom (in $10^{-2} e$) in $\text{CH}_2\text{Cl}.\text{CH}_3$ 1 and in $\text{CH}_2\text{Cl}.\text{CH}_2\text{H} \dots \text{OH}^-$ 2 on the Dihedral Angle

The absolute values at $\omega = 0^\circ$ are for curve 1 equal to $-0.1458 e$, for curve 2 to $-0.2496 e$.

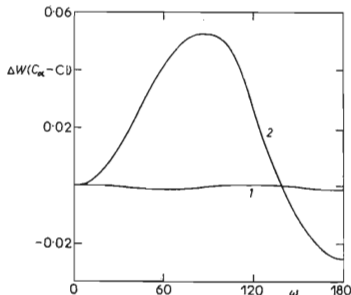


FIG. 5
The Dependence of the Relative Wiberg Index for the $\text{C}_\alpha - \text{Cl}$ Bond in $\text{CH}_2\text{Cl}.\text{CH}_3$ 1 and in $\text{CH}_2\text{Cl}.\text{CH}_2\text{H} \dots \text{OH}^-$ 2 on the Dihedral Angle

The absolute values at $\omega = 0^\circ$ are for curve 1 equal to 1.0555, for curve 2 to 0.9306.

periplanar mutual positions of both hybrid orbitals. Thus, their direct interaction constitutes the reason for the preference of the *trans*- and *cis*-elimination.

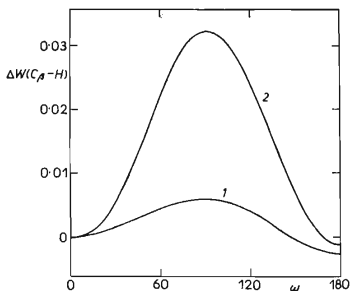


FIG. 6

The Dependence of the Relative Wiberg Index for the C_β -H Bond in $\text{CH}_2\text{Cl}.\text{CH}_3$ 1 and for the C_β -H(...OH⁻) Bond in $\text{CH}_2\text{Cl}.\text{CH}_2\text{H}...\text{OH}^-$ 2 on the Dihedral Angle

The absolute values at $\omega = 0^\circ$ are for curve 1 equal to 0.9737, for curve 2 to 0.7245.

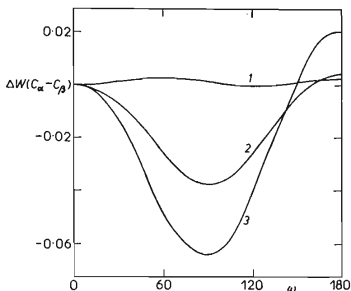


FIG. 7

The Dependence of the Relative Wiberg Index for the C_α - C_β Bond on the Dihedral Angle ω in $\text{CH}_2\text{Cl}.\text{CH}_3$ 1 and in $\text{CH}_2\text{Cl}.\text{CH}_2\text{H}...\text{OH}^-$ 2 together with the Relative Contribution to the Wiberg Index for this Bond Due to Hybrid Orbitals Oriented in the Direction of the C_α -Cl and C_β -H(...OH⁻) Bonds 3

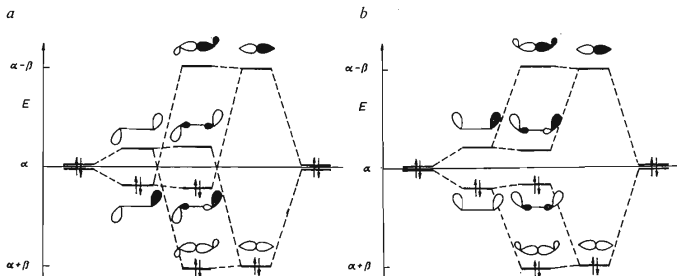


FIG. 8

The Scheme of the Interaction for Four sp^3 Orbitals of Two Neighbouring Carbon Atoms; Two Orbitals Form the C-C Bond and Two Are in Mutually a) Antiperiplanar; b) Synperiplanar Positions

If only this interaction existed in the system, the *cis*-elimination should be preferred, because the absolute value of overlap of the hybrid orbitals considered is higher for this reaction path than for the *trans*-elimination. To explain the observed preference of the *trans*-elimination, we must take into account a further interaction, usually denoted as the interaction through bond¹³, which is brought about by a nonzero overlap between the hybrid orbitals considered and those creating the bonding (σ) and antibonding (σ^*) molecular orbitals of the $C_\alpha-C_\beta$ bond. To estimate the effect of this interaction, we performed a computation for the hybrid sp^3 orbitals by a method analogous to the HMO method. These results are illustrated schematically on Fig. 8, whose right-hand part refers to the formation of the σ and σ^* orbitals of the $C_\alpha-C_\beta$ bond, its left-hand part corresponds to the direct (through-space) interaction of the hybrid orbitals considered, and its middle part describes the relatively weaker changes due to the interaction through bond. With the employed approximations, the interaction through bond exhibits no influence on the total energy of the synperiplanar conformation as two interacting orbitals are occupied and the other two empty. A different situation is encountered in the antiperiplanar position, where the total energy decreases, because the interaction through bond stabilizes the occupied orbitals.

As indicated by our computations, the effect of the interaction through bond is sufficiently strong to change the order of energy levels of both conformations, which follows in the first approximation from the interaction through space, and thereby to prefer the *trans*-elimination to the required extent. Thus, the steric path of bimolecular elimination reactions can be explained by employing exclusively the quantum chemistry conceptions — the interaction through space or through bond.

REFERENCES

1. Banthorpe D. V.: *Elimination Reactions*, Chapter 1. Elsevier, Amsterdam 1963.
2. Pines H., Manassen J.: *Advan. Catal. Relat. Subj.* 16, 49 (1966).
3. Reutov O.: *Theoretical Principles of Organic Chemistry*, p. 195. Mir, Moscow 1967.
4. Fujimoto H., Yamabe S., Fukui K.: *Bull. Chem. Soc. Jap.* 44, 971 (1971).
5. Fujimoto H., Fukui K. in the book: *Chemical Reactivity and Reaction Paths* (G. Klopman, Ed.), p. 23. Wiley, New York 1974.
6. Sedláček J., Kraus M.: *React. Kinet. Catal. Letters* 2, 57 (1975).
7. Sedláček J.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1975.
8. Klopman G. in the book: *Chemical Reactivity and Reaction Paths* (G. Klopman, Ed.), p. 55. Wiley, New York 1974.
9. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*, p. 163. McGraw Hill, New York 1970.
10. Ref. 9, p. 110.
11. Ref. 8, p. 30.
12. Wiberg K.: *Tetrahedron* 24, 1083 (1968).
13. Hoffmann R.: *Accounts Chem. Res.* 4, 1 (1971).
14. Hoffmann R., Imamura A., Hehre W. J.: *J. Amer. Chem. Soc.* 90, 1499 (1968).

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