

SIMPLE THEORETICAL MODELS FOR ELIMINATION REACTIONS ON POLAR CATALYSTS; THE REACTIVITY OF HALOGENO-, HYDROXY-, AMINO- AND MERCAPTOPROPANE

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CNDO/2 calculations have been made for simple models of the adsorption of $(\text{CH}_3)_2\text{CHZ}$ molecules ($\text{Z} = \text{Cl}, \text{OH}, \text{NH}_2$, and SH) on the surface of polar catalysts. The results of these calculations and their interpretation by the method of configuration analysis in terms of uniformly localized molecular orbitals made it possible to explain satisfactorily a series of experimental facts. The mechanism and stereoselectivity of the reaction as well as reactivity trends for the series of the molecules studied are discussed.

Polar catalysts (oxides, aluminosilicates and salts) are known to activate the decomposition of halogenoalkanes, alcohols, amines and thiols to olefin and hydrogen halide, water, ammonia or hydrogen sulphide^{1,2}. Especially, the behaviour of alcohols has been studied in detail. Besides a number of experimental works³, several attempts have been made at quantum chemical interpretation of phenomena⁴⁻⁶. Comparison of characteristics of the elimination reaction for the above reactants revealed close analogies in the regularities controlling this process.

Current ideas about the course of this reaction can be summarized in the following way: The reaction proceeds with participation of a pair of acid and base catalytic centre^{3,7-9}. With respect to the timing of the key bonds cleavage, we can differentiate the type of mechanism in a continuous series starting from E1-like *via* E2-like up to E1cB-like mechanism^{1,2}. The acid catalytic centre seems to be most likely the surface hydroxyl group (Bronsted acid). One cannot, however, exclude that under certain conditions also metal cation (Lewis acid) can act as the acid centre. The suitable base centre is assumed to be oxygen anion.

Besides the mechanism involving molecular adsorption, also that involving dissociative adsorption has been proposed by some authors^{1,2}. However, it has been recently proved that the dissociative adsorption leads to dehydrogenation reaction^{10,11}. The same conclusion has been arrived at also on the basis of the earlier quantum chemical studies¹².

The present work deals with the quantum chemical interpretation of some common features of the behaviour of chloroalkanes, alcohols, amines and thiols in the elimination reaction taking place on the surface of polar catalysts.

EXPERIMENTAL

Methods

Calculations for $(\text{CH}_3)_2\text{CHZ}$ molecules ($Z = \text{Cl}, \text{OH}, \text{NH}_2$ and SH) and their protonated and deprotonated forms (models of adsorption) were made by semi-empirical CNDO/2 quantum chemical method without considering d -orbitals¹³. The molecules were constructed with the use of standard bond lengths¹⁴ ($\text{Cl}-\text{H} \dots \dots 128 \text{ pm}$; $\text{Cl}-\text{C} \dots 178 \text{ pm}$; $\text{S}-\text{H} \dots 134.5 \text{ pm}$; $\text{S}-\text{C} \dots 180.8 \text{ pm}$), tetrahedral bond angles and staggered conformations. Tetrahedral arrangement of bonds and free electron pairs was adopted for hetero atoms.

Molecular adsorption on acid centre was modelled by protonation of the molecule¹⁵, while dissociative adsorption was modelled by deprotonation¹². The direction and extent of activation caused by adsorption were estimated from changes in charge distribution and from relative changes in bond strength (Wiberg bond index¹⁶). In the case of the model of molecular adsorption, *i.e.* of interaction with proton, a more detailed analysis of electron redistribution has been performed by the method of configuration analysis¹⁷.

This method is based on the fact that manyelectron function belonging to two interacting molecules, approximated by Slater determinant, can be expressed as the linear combination of the functions corresponding to the ground state and to all the possible inter- and intramolecular excited states of isolated molecules

$$\Psi = c_0\Psi_0 + \sum_a c_a\Psi_{i \rightarrow j, k \rightarrow l} \dots$$

$$c_0^2 + \sum_a c_a^2 = 1. \quad (1)$$

The squares of expansion coefficients are then the measure of the contribution of the given electron configuration to the electron redistribution caused by the interaction studied.

In order to discuss electron transfers in terms of common ideas about localized chemical bonds, canonical MO's obtained by CNDO/2 calculation were transformed into MO's uniformly localized on individual bonds¹⁸, before performing conformation analysis. This transformation was made with the aim to minimize the quantity

$$P_{\text{occ}} = \sum_i^{\text{occ}} P_{i, \text{A-B}} \quad (\text{resp.} \quad P_{\text{unocc}} = \sum_i^{\text{unocc}} P_{i, \text{A-B}}), \quad (2)$$

where

$$P_{i, \text{A-B}} = \sum_{\mu \in \text{A}} \sum_{\nu \in \text{B}} c_{\mu i} c_{\nu i} S_{\mu\nu} \quad (3)$$

which are the suitable measure of the localization of MO in the molecule. MO's expressed in the LCAO approximation ($\varphi_i = \sum_{\mu} c_{\mu i} \chi_{\mu}$; $S_{\mu\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle$) were transformed in pairs according to the relations

$$\varphi'_i = \varphi_i \cos \vartheta + \varphi_j \sin \vartheta \quad (4)$$

$$\varphi'_j = -\varphi_i \sin \vartheta + \varphi_j \cos \vartheta$$

in which ϑ was chosen such that the quantity defined by Eq. (2) was minimized. By substitution of Eqs (4) into Eq. (3) and Eq. (2) and by derivation with respect to ϑ , one obtains the following relations

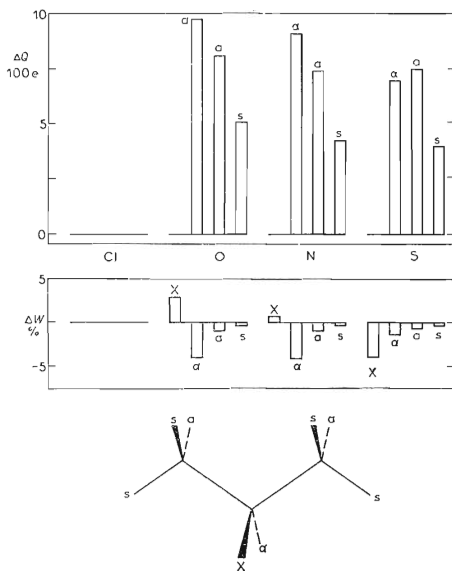


FIG. 1

Changes in charge distribution and relative changes in the strength of selected bonds in modelling dissociative adsorption by deprotonation of $(CH_3)_2CHZ$ molecules ($Z = OH, NH_2$ and SH). The scheme in the lower part of the figure defines the designation of atoms

$$\begin{aligned}
 dP/d\vartheta &= X \sin 2\vartheta - Y \cos 2\vartheta & (5) \\
 X &= \sum_{\mu \in A} \sum_{\nu \in B} S_{\mu\nu} (c_{\mu j} c_{\nu j} - c_{\mu i} c_{\nu i}) + \\
 &\quad + \sum_{\rho \in C} \sum_{\sigma \in D} S_{\rho\sigma} (c_{\rho i} c_{\sigma i} - c_{\rho j} c_{\sigma j}) \\
 Y &= \sum_{\rho \in C} \sum_{\sigma \in D} S_{\rho\sigma} (c_{\rho j} c_{\sigma j} + c_{\rho i} c_{\sigma i}) - \\
 &\quad - \sum_{\mu \in A} \sum_{\nu \in B} S_{\mu\nu} (c_{\mu j} c_{\nu i} + c_{\mu i} c_{\nu j}) .
 \end{aligned}$$

For the local extreme¹⁸ it holds that

$$\operatorname{tg} 2\vartheta = Y/X . \quad (6)$$

In addition to local minima, the above conditions hold, however, also for maxima. For finding the expression which would be valid only for required minima, further derivation was performed and after modification the following relation was obtained

$$\cos 2\vartheta/X > \theta , \quad (7)$$

the application of which to Eq. (5) leads to the following expressions

$$\begin{aligned}
 \cos 2\vartheta &= X(X^2 + Y^2)^{-1/2} & (8) \\
 \sin 2\vartheta &= Y(X^2 + Y^2)^{-1/2}
 \end{aligned}$$

and finally to expressions

$$\begin{aligned}
 \cos \vartheta &= [(1 + \operatorname{ccs} 2\vartheta)/2]^{1/2} \\
 \sin \vartheta &= Y/|Y| [(1 - \operatorname{ccs} 2\vartheta)/2]^{1/2} & (9)
 \end{aligned}$$

which were used to construct the programme performing uniform localization. The programme worked iteratively in such a way that all the possible pairs of occupied (or unoccupied) MO's were gradually subjected systematically to transformation. This process was repeated in cycles until the decrease in P_{occ} (or in P_{unocc}) quantity after the cycle including transformation of all the possible pairs of occupied (or unoccupied) MO's was lower than 10^{-4} .

RESULTS AND DISCUSSION

Results of the calculations for the model of dissociative adsorption of the alcohol, the amine and the thiol are shown in Fig. 1. As found earlier with the alcohol as the

example¹², the adsorption of this type does not activate the molecule for dehydration but it does for dehydrogenation (*i.e.* it activates the cleavage of the hydrogen from hydroxyl group and of the hydrogen bonded to the α -carbon to form the oxygen- α -carbon double bond).

According to Fig. 1, this conclusions follow from the weakening of the C_{α} -H bond, which is thus activated most, compared to other C-H bonds in the molecule. This is connected also with the increase in electron density on the H_{α} atom. Also this effect is more pronounced on the H_{α} atom than on other H atoms of the molecule. Deprotonation of the functional groups strenghtens further the C_{α} -X bond in alcohols and amines, which can be interpreted as the first step in formation of the double bond between C_{α} and X atoms.

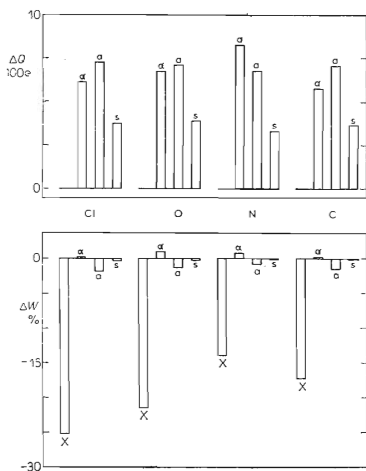


FIG. 2
Changes in charge distribution and relative changes in the strength of selected bonds in modelling molecular adsorption by protonation of $(CH_3)_2CHZ$ molecules ($Z = Cl, OH, NH_2$ and SH). For designation of atoms see the lower part of Fig. 1

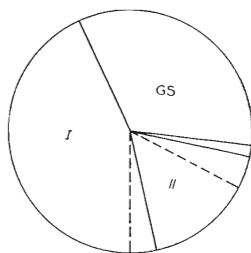


FIG. 3
Results of configuration analysis of the interaction of $(CH_3)_2CHNH_2$ molecule with proton (see Table I). GS ground state; I one-electron transitions; II two-electron transitions; the portion corresponding to charge transfer from the molecule to proton is designated by broken line

Conclusions drawn from the above calculations for the model of dissociative adsorption agree well with the following experimental findings: (a) dissociative adsorption of the molecule is the initial stage of dehydrogenation reaction^{10,11}; (b) alcohols undergo dehydrogenation more easily than amines^{19,20} since they are more activated by adsorption; (c) not well clean-cut activation in the case of thiols can be related obviously to the fact that dehydrogenation of thiols to form the double bond between S and C_α atoms does not take place^{1,2}; (d) in this connection it is worthy of note that the dissociative adsorption of halogenoalkanes is not possible from principal reasons. This provides further, although the indirect evidence for the improbability of the participation of dissociative adsorption in the elimination reaction. The evidence is based on the widely accepted and significant similarity in the course of eliminations of all the reactants under study, and that also as far as the reaction mechanism is concerned^{1,2,8,21}. Provided that the dissociative adsorption does participate in elimination, one is forced to postulate different mechanism for halogenoalkanes compared to other reactants, which on the basis of the known facts does not seem to be justified.

TABLE I

Results of configuration analysis of interaction of (CH₃)₂CHZ molecules (Z = Cl, OH, NH₂ and SH) with proton. Contributions of selected types of electron configurations are given in per cent

Electron configuration	X =			
	Cl	OH	NH ₂	SH
Ground state	35.4	37.8	33.7	29.8
One-electron charge transfers	42.8	40.8	43.2	44.1
One-electron transitions (total)	46.3	45.1	46.7	47.7
Two-electron charge transfers	12.9	11.0	13.9	16.3
Two-electron transitions (total)	17.0	15.6	18.1	20.9
Sum of considered contributions	98.6	98.5	98.4	98.4

The results of calculations for the model of molecular adsorption are represented graphically in Fig. 2. In agreement with earlier calculations performed for alcohols^{4,15} data in the figure confirm that the adsorption of the molecule on the acid centre leads to the elimination of substituent Z (Z = Cl, OH, NH₂ and SH) and of the hydrogen bonded to the β -carbon to form the double bond between C _{α} and C _{β} atoms. This conclusion results especially from the marked weakening of the C _{α} -X bond and the weakening of the C _{β} -H bond, which is accompanied with an increase in the positive charge on the H _{β} atom. From Fig. 2 it becomes further clear that these changes are most distinct for the β -hydrogen in antiperiplanar position with respect to the substituent Z.

The results of calculations for the model of molecular adsorption thus lead to the following conclusions which comport with the following experimental facts: (a) the

TABLE II

Results of configuration analysis of interaction of (CH₃)₂CHZ molecules (Z = Cl, OH, NH₂ and SH) with proton. Performed in terms of uniformly localized MO's. The upper part of the Table relates to one-electron transitions and the lower to two-electron transitions. Only included are configurations with the most significant contributions (in per cent)

Electron configurations ^a	Z =			
	Cl	OH	NH ₂	SH
$\sigma(C_{\alpha}-X) \rightarrow \sigma^*(C_{\alpha}-X)$	1.81	1.75	1.21	1.37
$n \rightarrow \sigma^*(C_{\alpha}-X)$	0.37	0.44	0.24	0.40
$\sigma(C_{\beta}-H) \rightarrow \sigma^*(C_{\alpha}-X)$	0.15	0.11	0.06	0.11
$\sigma(C_{\alpha}-C_{\beta}) \rightarrow \sigma^*(C_{\alpha}-C_{\beta})$	0.15	0.22	0.16	0.12
$\sigma(X-H) \rightarrow \sigma^*(X-H)$	—	0.54	0.35	0.26
$n \rightarrow \sigma^*(X-H)$	—	0.20	0.11	0.42
$\sigma(C_{\alpha}-H) \rightarrow \sigma^*(C_{\alpha}-X)$	2.10	1.89	1.56	1.88
$n \rightarrow H^+$				
$n \rightarrow \sigma^*(C_{\alpha}-X)$	0.28	0.28	0.15	0.33
$n \rightarrow H^+$				
$\sigma(C_{\beta}-H) \rightarrow \sigma^*(C_{\alpha}-X)$	0.18	0.11	0.07	0.15
$n \rightarrow H^+$				
$\sigma(C_{\alpha}-C_{\beta}) \rightarrow \sigma^*(C_{\alpha}-C_{\beta})$	0.17	0.23	0.20	0.16
$n \rightarrow H^+$				
$\sigma(X-H) \rightarrow \sigma^*(X-H)$	—	0.58	0.45	0.34
$n \rightarrow H^+$				

^a Designated electron transition specifies the deviation of a given electron configuration from the ground state.

molecular adsorption of the molecule is a prerequisite of the elimination of $(\text{CH}_3)_2\text{CHZ}$ molecules ($\text{Z} = \text{Cl}, \text{OH}, \text{NH}_2$ and SH) to give olefin^{1,2}; (b) the reaction proceeds with the cleavage of the H_β atom in antiperiplanar position with respect to substituent Z – *i.e.* as the *anti*-elimination^{1,2}; (c) calculated degree of the activation falls down along the series $\text{RCl} > \text{ROH} > \text{RSH} > \text{RNH}_2$ ($\text{R} = (\text{CH}_3)_2\text{CH}-$), this being in good agreement with the reactivities determined experimentally^{1,21-23}.

In Tables I and II and Figs 3 and 4 are presented the results of configuration analysis of the studied molecules interacting with proton, since – as found by CNDO/2 calculations performed – protonation is the suitable model for the initial stage of the elimination reaction. Table I summarizes general results. These are for the amine as the example illustrated more distinctly in Fig. 3. It is seen that the most significant part (45–48%) of the wave function of interacting molecules is given by one electron transitions within the framework of MO's of isolated molecules. About one third (30–38%) is due to the participation of the ground state and the smallest one (15 to 21%) can be ascribed to two-electron transitions. At the same time, the charge transfer from the molecule to proton is dominant component of one- and two-electron transitions. Three- and higher-electron transitions contribute by only c. 1.5 per cent.

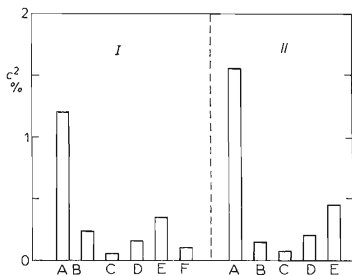


FIG. 4

Results of configuration analysis of the interaction of $(\text{CH}_3)_2\text{CHNH}_2$ molecule with proton (see Table II). Performed in terms of uniformly localized MO's. I one-electron transitions ($\sigma \rightarrow \sigma^*$); II two-electron transitions ($\sigma \rightarrow \sigma^*$ and $n \rightarrow \text{H}^+$)

	A	B	C	D	E	F
σ^*	$\text{C}_\alpha-\text{N}$	n	$\text{C}_\beta-\text{H}$	$\text{C}_\alpha-\text{C}_\beta$	$\text{N}-\text{H}$	n
σ	$\text{C}_\alpha-\text{N}$	$\text{C}_\alpha-\text{N}$	$\text{C}_\alpha-\text{H}$	$\text{C}_\alpha-\text{C}_\beta$	$\text{N}-\text{H}$	$\text{N}-\text{H}$

Table II shows the most important partial contributions of one-electron transitions (without charge transfers presented in Table I). Again, data are illustrated more distinctly for the amine as the example in Fig. 4. Canonical MO's obtained by CNDO/2 calculation were transformed into uniformly localized MO's (see Methods) before performing the configuration analysis. This allowed to discuss electron transfers in terms of the localized chemical bond. As follows from Table II and Fig. 4, the weakening of the C_{α} -X bond (Fig. 2) results from the relatively strong internal excitations from the bonding C_{α} -X MO to antibonding MO of the same bond. The above mentioned weakening of this bond during interaction with proton is to the lesser extent due to electron transfer into the antibonding C_{α} -X MO, both from the nonbonding MO on hetero atom X (free electron pair) and from the bonding C_{β} -H MO, this bond being antiperiplanar with respect to the C_{α} -X bond. As found by a deeper theoretical analysis²⁴, the latter electron transfer is made possible by „through space” and “through bond” interaction with participation of atom orbitals involved in C_{α} -X and C_{β} -H bonds. The obvious consequence of these effect is experimentally observed preference of the *anti*-elimination.

The fact that data presented in Tables I and II change only little with the type of substituent documents that the general character of electron redistribution caused in the molecule by adsorption is preserved in the whole series of reactants studied. This fact can be considered as the main reason for the observed similarity in the behaviour of halogenoalkanes, alcohols, amines and thiols in the elimination taking place in the surface of polar catalysts^{1,2}.

In conclusion, despite of the simplicity of the models used, the calculations performed made it possible to classify and interpret successfully a series of experimental facts concerning heterogeneously catalyzed eliminations and contributed thus to the deeper knowledge of the regularities controlling these processes.

LIST OF SYMBOLS

c	expansion coefficient of linear combination
n	nonbonding MO (free electron pair)
$P_{i,A-B}$	extent of localization of i -th MO in the region of the bond between atoms A and B
ΔQ	absolute change in charge
$S_{\mu\nu}$	AO overlap
ΔW	relative change in Wiberg bond index (in %)
φ_i	molecular orbital (MO)
χ_{μ}	atomic orbital (AO)
Ψ	manyelectron wave function approximated by Slater determinant
Ψ_0	manyelectron function belonging to the ground state
$\Psi_{i \rightarrow j, k \rightarrow l}$	manyelectron wave function belonging to inter- and intramolecular excited states
σ	bonding MO
σ^*	antibonding MO
\mathcal{J}	parameter defining the unitary transformation of MO

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