SIMPLE THEORETICAL MODELS FOR ELIMINATION REACTIONS ON POLAR CATALYSTS; GENERALIZATION OF REACTIVITIES IN SERIES OF CHLOROALKANES, ALCOHOLS, AMINES AND THIOLS

Jiří Sedláček

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol

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CNDO/2 calculations have been made for simple models of adsorption of chloroalkane, alcohol, amine and thiol molecules on the surface of polar catalysts. The calculated values of selected quantum chemical quantities describing the properties of C_α—X and C_β—H_A bonds were correlated with reported experimental reactivities. Very good correlations with experimental data were obtained for quantum chemical quantities relating to the C_α—X bond. The results of calculations are discussed in relation to the reaction mechanism and the type of surface catalytic centres participating in the reaction.

There exists a number of works which deal with heterogeneously catalysed elimination reactions of compounds of the type R–Z (R = alkyl, Z = halogen, OH, NH_2, SH and other groups) proceeding on the surface of polar catalysts (oxides, aluminosilicates and salts) to produce simple molecules H–Z (hydrogen halide, water, ammonia, hydrogen sulphide, *etc.*) and olefin molecules[1,2]. The remarkable amount of experimental material is available on the elimination decomposition of halogenoalkanes[3] and particularly alcohols[4]. Although the study of dehydrohalogenation[5], deamination[6], dehydrosulphidation[7,8] and especially dehydration[9–14] is the subject of continuous interest, regularities controlling these reactions have not yet been satisfactorily explained.

Besides experimental works, also theoretical studies have been reported. These attempted at quantum chemical analysis of the interaction of alcohol molecule with catalyst surface[15–18]. With the use of computer-constructed models also geometrical conditions of this interaction have been investigated[19,20]. Similarly, also the effect of the structure of reactant on the rate of elimination has been studied by quantum chemical methods[21,22].

Results of experimental studies speak for the considerable mutual similarity in the behaviour of given reactants in the course of heterogeneously catalyzed elimination[1,2,5,7,8]. The following features represent common characteristics of elimination: *a*) the participation of a pair of acid and base centres in the reaction and — closely related to it — the formation of similar adsorption structures; *b*) an analogous dependence of the timing of the cleavage of key bonds C_α–X and C_β–H, *i.e.* the dependence of the type of elimination mechanism (E1, E2 or E1cB) on acid–base properties of a given catalyst, on the type of reactant and on temperature; *c*) marked stereoselectivity of synchronous E2 elimination which proceeds, as a rule, as the *anti*-elimination; *d*) the composition of primary reaction products, among which *cis*-2-olefins prevail significantly over thermodynamically more stable *trans*-2-olefins.

Theoretical study explained these phenomena as the result of the specific character of the

electronic and geometrical interaction of the reactant with active centres on the catalyst surface. Quantum chemical calculations showed that the first step of the elimination reaction is most likely the molecular adsorption of reactant on acid surface centres[15-17,23], followed by the elimination itself to give olefin, the latter process being assisted by basic surface centre[16,18]. Quantum chemical calculations revealed also the reason for the energetically favoured *anti*-elimination[17,24] and for the similar behaviour of chloroalkanes, alcohols, amines and thiols in this reaction[23]. Modelling of the geometrical conditions for two-centre adsorption[19,20] confirmed and further specified the original (to the great extent intuitive) explanation[25] of the preference of *cis*-isomerisation of 2-olefins based on the steric hinderance in formation of *trans*-isomers.

In the present work, which extends our quantum chemical study of common features of the behaviour of chloro-, hydroxy-, amino- and mercaptopropane[23], we made an attempt to interpret the experimental reactivity differences in the series of chloroalkanes[26,27], alcohols[28-30], amines[31,32] and thiols[33] on the basis of quantum chemical calculations made by the well-tried CNDO/2 method with the use of the already tested adsorption model[23].

MODEL AND CALCULATIONS

Calculations for R–Z molecules (R = alkyl, Z = Cl, OH, NH_2 and SH) and their protonated forms $R–ZH^+$ (models of molecular adsorption on acid catalytic centre) were performed by semi-empirical quantum chemical CNDO/2 method without considering *d*-orbitals[34]. Molecules were constructed with the use of standard bond lengths[35] (Cl–H 128 pm; Cl–C 178 pm; S–H 134·4 pm; S–C 180·8 pm), tetrahedral angles and staggered conformations. Tetrahedral arrangement of bonds and free electron pairs was adopted for hetero atoms. Within the framework of these rules for the construction of model systems, there exist (particularly for bulkier molecules) different conformations of molecules which differ one from other by their energetical suitability. The calculations were therefore made for several possible conformations of a given system. The results corresponding to the conformation which was found to be the most enegetically stable were used to interpret experiments.

In accordance with the results of previous work[23] and earlier studies[15-18,22], the molecular adsorption on acid surface centres was modelled by protonation of reactant molecule, *i.e.* by protonation of its hetero atom. The degree of activation of the molecule was estimated from the value of selected quantum chemical quantities. These were the charge on the hetero atom X and that on the H_A atom (H_A designates the hydrogen bonded to the β-carbon in such a way that $C_\beta–X$ and $C_\beta–H_A$ bonds are mutually antiperiplanar) and the strengths of $C_\alpha–X$ and $C_\alpha–H_A$ bonds taken as the value of Wiberg bond index[36].

RESULTS AND DISCUSSION

Quantum chemical calculations by CNDO/2 methods were performed for a series of reactants, the experimental elimination reactivity of which was reported in literature (chloroalkanes[26,27], alcohols[28-30], amines[31,32], thiols[33]). As shown in Table I. the adsorption of molecule on the acid catalytic centre (modelled by proton) leads to the activation for elimination, in agreement with previous calculations[15-18,23]. This finding comports well with the concept deduced from the summarization

of reported experimental works[1-4]. According to this concept, the initial stage of the elimination reaction is molecular adsorption of the reactant on the acid catalytic centre which is the sufficiently accessible electron acceptor of suitable strength and position. Of the species occuring on the surface of polar catalysts, the role of such a proton acceptor is usually ascribed to the hydrogen of surface hydroxyl or to metal cation[1,2,4].

In further step of the reaction, the adsorbed molecule interacts with the basic catalytic centre. If by this way the hydrogen bonded to the β-carbon is attacked, the elimination is taking place to give olefin molecule and adsorbed H–Z molecule, as depicted in Scheme 1. Performed calculations show, however, that besides the

SCHEME 1

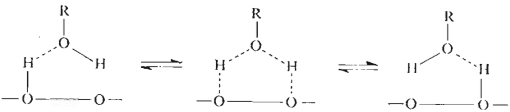
above mentioned hydrogen, there are also other hydrogen atoms in the adsorbed molecule which due to their high positive charge can be attacked. These are the part of substituents —OH, —NH_2 or —SH, as documented in Table I. As also the X–H bond is markedly weakened during the adsorption (Table I), the attack of the so activated hydrogen atom by base can result in its total abstraction from the molecule. The character of the structure formed depends on the type of the acid centre on which

TABLE I

Relative changes in the strength of some bonds (ΔW, in %) and charges on selected H atoms (Q, in 10^{-2} e) in protonated molecules of the type $(CH_3)_2CH.ZH^+$

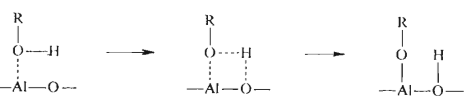
Quantity	Z			
	Cl	OH	NH_2	SH
$\Delta W(X—H)$	—	— 7·5	— 4·1	— 2·7
$\Delta W(C_\alpha—X)$	—25·2	—21·4	—13·5	—17·2
$\Delta W(C_\beta—H_A)$	— 1·9	— 1·3	— 0·8	— 1·5
$Q(H_Z)$	—	30	22	16
$Q(H_A)$	9	8	7	8

the reactant molecule is adsorbed. This is illustrated in Schemes 2 and 3 for the alcohol on alumina.



SCHEME 2

If the acid catalytic centre is hydroxyl group, we deal here only with the exchange of atoms between surface hydroxyl and the hydroxyl of the alcohol molecule, as evident from Scheme 2. The product has the structure equivalent to the starting one, *i.e.* to the adsorbed alcohol molecule. Another situation occurs in the case depicted in Scheme 3. The adsorption on aluminum cation leads to dissociation of alcohol



SCHEME 3

molecule *via* splitting-off hydrogen, forming thus the relatively stable surface alkoxide. The support for the presumption that processes depicted in Schemes 2 and 3 can take place in real systems can be seen both in the H–D exchange between reactant and catalyst surface observed in the adsorption of $(CH_3)_2CHOD$ on alumina and other oxides[37] and further in the proved existence of surface alkoxides reported in studies using IR spectroscopy[4]. The considerations about the suitability of one or another type of acid centre for the studied reaction can be summarized as follows: *a*) The hydrogen of surface hydroxyl is suitable catalytic centre; in molecular adsorption the situation on this centre is not probably complicated by disturbing side processes. *b*) The surface metal cation is in principle also suitable catalytic centre; in this case, however, the successful completion of the elimination depends upon whether the elimination is not outrun by the dissociation of reactant molecule. As shown by experiments[38,39] and calculations[23], the dissociative adsorption initiates other reactions, such as *e.g.* dehydrogenation of reactant molecule to form the $C_\alpha{=}X$ bond. The effectiveness of metal cation as the elimination catalytic centre depends in general on reaction conditions and on the properties of reactants and catalyst.

The main goal of this work is quantum chemical interpretation of reported dependences of elimination reactivities on the structure of reactants. Experimental

data used in this study were obtained under different conditions as well as on different catalysts, *i.e.* oxides[28,31,32], aluminosilicates[29,33] and salts[26,27,30]. Furthermore, the works just mentioned do not contain more detailed information about the type of catalytic centres participating in the reaction. It is therefore possible that *e.g.* in dehydration of alcohols on γ-alumina[28] the active centres differ from those participating in dehydrohalogenation of chloroalkanes on alkali metal chlorides[26] or on $BaSO_4$ (ref.[27]). Notwithstanding, for quantum chemical modelling the adsorption of chloroalkanes, alcohols, amines and thiols we used always the interaction with proton, irrespective of the chemical composition of the catalyst. The reliability of this approximation depends on two presumptions: *a*) On a given catalyst, the type of catalytically active centre taking part in the reaction does not change on going from one member of the group of structurally similar reactants to another one; *b*) the relative reactivity within the group of structurally similar substances does not depend on the type of catalytically active centre participating in the reaction.

TABLE II

Calculated relative change in the strength of the C_α–X bond (in per cent) in the molecule of reactant R–Z obtained by modelling adsorption on surface acid centre by protonation

R	Z			
	Cl	OH	NH_2	SH
Ethyl	−21·30	−19·50	−12·43	−13·78
Propyl	−21·81	−19·43	−12·46	−14·18
Isopropyl	−25·18	−21·43	−13·48	−17·24
Butyl	−22·05	−19·54	−12·56	−14·34
Sec-butyl	−25·18	−21·29	−13·88	−17·64
Isobutyl	—	−19·65	−12·45	—
Tert-butyl	−28·27	−22·89	−14·74	—
Pentyl	−22·19	−19·62	—	—
Isopentyl	—	−19·57	—	—
2-Methyl-1-butyl	—	−19·75	—	—
Neopentyl	—	−20·36	—	—
2-Pentyl	—	−21·37	—	—
3-Pentyl	—	−21·24	—	—
2-Methyl-2-butyl	—	−21·46	—	—
Tert-pentyl	—	−22·68	—	—
Hexyl	−22·25	−19·65	—	—
Cyclohexyl	—	—	−13·84	—

That the above mentioned presumptions are reasonable is confirmed by the fact that reported reactivities expressed as the logarithms of rate constants correlate well with Taft constants[27,29,30,33]. This indicates that the relative reactivities are above all the function of structure. From this it follows that also in constructing the quantum chemical models one should center particularly on the correct picture of the structure of reactants. The choice of the concrete type of surface electron acceptor centre selected for modelling the adsorption ought to be of secondary importance.

For purposes of correlation with experimental data we have chosen different quantum chemical quantities describing the properties of C_α–X and C_β–H bonds, both for the free and the adsorbed reactant molecule[23]. As Figs 1–4 show, very good linear correlations with experimental reactivities for chloroalkanes, alcohols, amines and thiols yield changes in the strength of the C–X bond caused by adsorption.

TABLE III

Coefficients of linear correlations of reported experimental elimination reactivities (log k, log r) with calculated values of selected quantum chemical quantities

Reference	X	$-\Delta W(C_\alpha\text{–X})$	$-\Delta W(C_\beta\text{–}H_A)$	$Q(X)$
26[a]	Cl	0·97	−0·65	0·96
26[b]	Cl	0·94	−0·76	0·94
26[c]	Cl	0·90	−0·89	0·88
26[d]	Cl	0·87	−0·97	0·88
26[e]	Cl	0·78	−0·27	0·76
27[f]	Cl	0·93	−0·76	0·92
27[g]	Cl	0·92	−0·85	0·87
28	O	0·72	−0·83	0·95
29	O	0·97	−0·49	0·98
30[h,i]	O	0·97	−0·70	0·98
30[h,j]	O	0·96	−0·71	0·98
30[h,k]	O	0·95	−0·71	0·97
30[l,m]	O	0·91	−0·53	0·92
30[l,n]	O	0·96	−0·51	0·95
31	N	0·75	0·22	0·59
32[o]	N	1·00	−0·30	0·94
32[p]	N	0·96	−0·14	0·91
33[q]	S	1·00	−0·86	1·00
33[r]	S	1·00	−0·85	0·99
33[s]	S	0·98	−0·89	0·95

[a] NaCl; [b] RbCl; [c] KCl; [d] AgCl; [e] LiCl; [f] 493 K; [g] 553 K; [h] Ca-deficit hydroxyapatite; [i] 503 K; [j] 553 K; [k] 623 J; [l] stoichiometric hydroxyapatite; [m] 553 K; [n] 663 K; [o] 555 J; [p] 590 K; [q] 473 K; [r] 523 K; [s] 573 K.

The values of this quantity, which can be regarded as the measure of the activation induced by interaction with the catalyst, are presented in Table II for all the reactants studied. The values of the coefficients of linear correlations of the reactivities with the weakening of the C_α–X bond caused by adsorption for all the sets of experimental data used are summarized in Table III. The coefficients obtained (Table III) also document that the attempts at correlating the reactivities with the weakening of C_β–H_A bonds have not been successful. Similarly unsuccessful were also correlations performed for the total strength of the C_β–H_A bond and for the charge on the H_A atom, both in the free and in the adsorbed molecule. In these cases, the frequently obtained negative values of the coefficients indicate opposite trends in experimental and theoretical quantities in the series of reactants. The positive coefficients found have as a rule only low absolute values.

Quite opposite situation has been encountered in the case of the C_α–X bond.

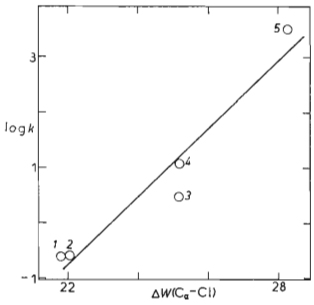


FIG. 1

Calculated relative C_α–Cl bond weakening (in per cent) caused in chloroalkane molecule by modelling adsorption, correlated with logarithm of rate constant of dehydrohalogenation catalyzed by NaCl (for conditions see ref.[26]). *1* Propyl, *2* butyl, *3* sec-butyl, *4* isopropyl, *5* tert-butyl chloride

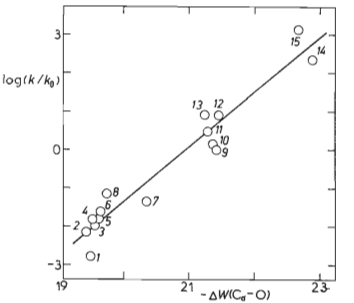


FIG. 2

Calculated relative C_α–O bond weakening (in per cent) caused in alcohol molecule by modelling adsorption, correlated with logarithm of relative rate constant of dehydration catalyzed by Ca-deficit hydroxyapatite at 503 K (for conditions see ref.[30]). *1* Ethyl, *2* propyl, *3* isobutyl, *4* butyl, *5* pentyl, *6* isobutyl, *7* neopentyl, *8* 2-methyl-1-butyl, *9* isopropyl, *10* 2-pentyl, *11* sec-butyl, *12* 3-methyl-2-butyl, *13* 3-pentyl, *14* tert-butyl, *15* tert-pentyl alcohol

In addition to the above mentioned excellent correlation of the reactivity with the weakening of this bond, documented for selected sets of data in Figs 1–4, comparably good linear correlations were obtained also with other theoretical quantities relating to this bond. These were the total strength of the C_α–X bond in adsorbed and free molecule and even the charge on the hetero atom X in the free molecule, which situation is exemplified in Fig. 5. That, in this respect, the alcohols are not exception is documented by high values of the coefficients of linear correlations of the reactivity with the charge on hetero atom in the molecules of chloroalkanes, amines and thiols which are presented in Table III. Calculated charges on the hetero atom of free molecule of all the reactants are presented in Table IV.

These findings allow to conclude that in all the cases studied (*i.e.* dehydrochlorination on alkali metal chlorides[26] and on $BaSO_4$ (ref.[27]), dehydration on alumina[28], silica–alumina doped with NaOH (ref.[29]) or on hydroxyapatite[30], deamination on alumina[31,32], dehydrosulphidation on silica–alumina[33]) the cleavage of the C_α–X bond and not that of the C_β–H_A bond is involved in the rate determining step of the reaction. This means that in all the cases studied the cleavage of the C_α–X

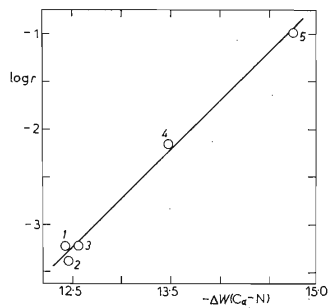


FIG. 3

Calculated relative C_α–N bond weakening (in per cent) caused in amine molecule by modelling adsorption, correlated with logarithm of rate of deamination catalysed by alumina at 555 K (for conditions see ref.[32]). *1* Ethyl, *2* propyl, *3* butyl, *4* isopropyl, *5* tert-butyl amine

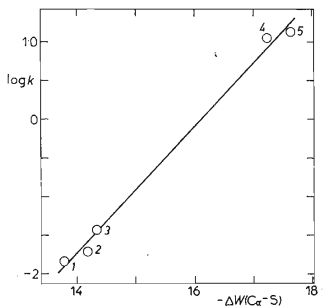


FIG. 4

Calculated relative C_α–S bond weakening (in per cent) caused in thiol molecule by modelling adsorption, correlated with logarithm of rate constant of dehydrosulphidation catalyzed by silica-alumina at 473 K (for conditions see ref.[33]). *1* Ethyl-, *2* propyl-, *3* butyl-, *4* isopropyl-, *5* sec-butylthiol

bond preceds to the greater or lesser extent the cleavage of the C_β–H_A bond. This corresponds to the elimination mechanism lying in the region demarcated by E2 mechanism (synchronous cleavage of both bonds) on one side and by E1 mechanism

TABLE IV

Calculated charge on hetero atom in the free molecule of reactant R–Z (in 10^{-2} e)

R	Z			
	Cl	OH	NH_2	SH
Ethyl	−15·27	−25·51	−20·81	− 9·18
Propyl	−15·37	−25·58	−21·10	− 9·15
Isopropyl	−17·39	−26·58	−21·63	−10·77
Butyl	−15·49	−25·63	−21·12	− 9·18
Sec-butyl	−17·47	−26·63	−21·52	−10·73
Isobutyl	—	−25·67	−21·17	—
Tert-butyl	−19·17	−27·46	−21·94	—
Pentyl	−15·57	−25·65	—	—
Isopentyl	—	−25·61	—	—
2-Methyl-1-butyl	—	−25·71	—	—
Neopentyl	—	−25·96	—	—
2-Pentyl	—	−26·67	—	—
3-Pentyl	—	−26·91	—	—
3-Methyl-2-butyl	—	−26·73	—	—
Tert-pentyl	—	−27·53	—	—
Hexyl	−15·60	−25·66	—	—
Cyclohexyl	—	—	−21·38	—

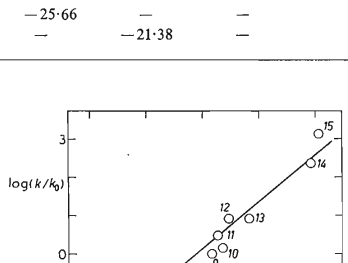


FIG. 5

Calculated charge on atom O in the free molecule of alcohol correlated with logarithm of relative rate constant of dehydration catalyzed by Ca-deficit hydroxyapatite at 503 K (for conditions see ref.[30]). For designation of points see Fig. 2

(formation of carbonium ion) on the other side[1]. This finding is in excellent agreement with conclusions reported in the works from which the above mentioned experimental data were taken[27,29-33].

Let us turn now to the correlation of reactivities with the calculated degree of the C_β–H_A bond activation. Table III shows that nearly all the correlations are characterized by the negative coefficient, the absolute value of which is relatively high. From this finding it follows that on basic catalysts, for which E1cB elimination mechanism, characterized by the cleavage of the C_β–H_A bond in the rate determining step of the reaction, is typical, the very opposite trend in reactivities of a given series of reactants should be observed. Such a phenomenon has been reported for dehydration of secondary alcohols on various oxide catalysts[40]. In this case, the reactivities of alcohols on strongly acidic SiO_2 increased with increasing size of alkyls, while on rather basic alumina doped with NaOH the reactivities decreased in the same series of reactants. This fact was attributed by the authors to the change of E1 elimination mechanism operating on acid catalysts[1] to E1cB mechanism which is typical for base catalysts[1]. This change concerns the type of the bond cleaved in the rate determining step – *i.e.* the C_α–X bond on acid catalysts and the C_β–H_A bond on base catalysts.

The fact that the experimental reactivities correlate well also with the quantities relating to the free reactant molecules, such as the total strength of the C_α–X bond and the charge on the hetero atom X (Table III) allows to conclude that the reactivity in E1 eliminations can be quite reliably estimated already from static properties of given molecules. For observed dependences of the reactivity on theoretical quantities one can find easily the rational physical interpretation: *a*) The ease of the elimination depends on the strength of the C_α–X bond in the molecule of reactant. If the bond is less strong, it is easier to cleave it completely. It holds also that the less strong this bond, the easier the destabilization by adsorption. *b*) The elimination reactivity is connected also with the magnitude of the negative charge on hetero atom. It obviously holds that the greater the negative charge on the hetero atom in the free molecule, the easier the initiated transfer of electron (necessary for carbonium ion formation).

The results show that consistent quantum chemical interpretation of a broad set of experimental data taken from different sources is possible. We succeeded in finding theoretical quantitaties, the values of which, obtained by quantum chemical calculation, correlate very well with the reactivities determined by different authors for different reactants and catalysts From this the following conclusions can be drawn: *a*) The semiempirical quantum chemical method used (CNDO/2) confirmed its ability to describe correctly the behaviour of all the studied reactants in heterogeneously catalysed elimination. *b*) Modelling of the molecular adsorption on acid catalytic centre by interaction with proton reflects precisely the dependence of the reactivity on the structure of reactant, in spite of its great simplicity. *c*) Calculations

further proved that in all the reactant–catalyst systems studied[26-33], the rate determining step is the cleavage of the C_α–X bond, *i.e.* that the reaction proceeds by the mechanism closely resembling E1 elimination mechanism involving carbonium ion formation. *d*) Obtained correlations allow, with the use of calculations, to predict the behaviour of other, experimentally still not studied reactants in the course of elimination reactions on given catalysts, and that at least on semiquantitative level.

Quantum chemical calculations can therefore provide the reliable and on experiment independent information about the course of even such a complicated process as a heterogeneously catalyzed chemical reaction. Therefore, calculations make it possible to classify and interpret the known experimental facts and to evaluate from another aspects the validity of hypotheses proposed on the basis of experiments.

LIST OF SYMBOLS

H_Z	hydrogen atom of substituent Z
H_A	hydrogen atom bonded to the β-carbon such that the C_α–X and C_β–H_A bonds are mutually antiperiplanar
Q(A)	charge on atom A
ΔW(A–B)	relative change in the A–B bond strength (Wiberg bond index[36]) caused by modelling the adsorption (%)
X	hetero atom Cl, O, N or S
Z	substituent Cl, OH, NH_2 or SH

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