

SIMPLE THEORETICAL MODELS OF ELIMINATION REACTIONS ON POLAR CATALYSTS; DEHYDRATION REACTIVITY OF SECONDARY ALCOHOLS ON ACIDIC AND BASIC CATALYSTS

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CNDO/2 calculations for simple models of adsorption and dehydration reactions of secondary aliphatic and aromatic alcohols on polar catalysts are presented. The models involve selected stages of elimination mechanisms of various types (E1, E2 and E1cB elimination). Calculated quantum chemical quantities were correlated with reported experimental data. It is shown that reactivities for the series of substituted phenylethanols correlate very well with the ease of carbonium ion formation. In the case of aliphatic alcohols, calculated quantities correlate generally with the reactivities on SiO_2 and are in anticorrelation with the reactivities on $\text{Al}_2\text{O}_3\cdot\text{NaOH}$.

There is a great number of works dealing with dehydration of alcohols on polar catalysts^{1,2}. Recently, the mechanism of this reaction has been studied with the aid of quantum chemical calculations³⁻⁵. Quantum chemistry proved to be useful also in interpreting theoretically relative reactivities observed for elimination reactions of various types on different polar catalysts⁶⁻¹⁰.

Experiments show that both acidic and basic surface centres play an important role in this reaction. The mechanism of heterogeneously catalysed elimination is obviously very similar to that of homogeneously catalysed reaction^{1,2}. The ease with which the key $\text{C}_\alpha\text{-O}$ and $\text{C}_\beta\text{-H}$ bonds are cleaved is affected by the structure of reactant, by the acid-base properties of catalyst and likely also by temperature. Therefore, it is not surprising that a wide spectrum of mechanisms have been proposed, starting from E1 elimination (taking place *via* carbonium ion) going through E2 elimination up to E1cB elimination² (proceeding *via* carbanion).

In dehydration of alcohols¹¹ and ethers¹² catalysed by oxides, the reactivity in a given series of reactants was found to decrease or increase, depending on acid-base properties of the catalyst. It was further established that the slope of Taft correlations of reactivities of selected secondary alcohols ($(\text{CH}_3)_2\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{R}$; $\text{R} = \text{CH}_3, \text{C}_3\text{H}_7, \text{CH}(\text{CH}_3)_2, \text{CH}(\text{C}_2\text{H}_5)_2$) dehydrated on $\text{SiO}_2, \text{ZrO}_2, \text{TiO}_2$, and Al_2O_3 doped with NaOH relate closely to the sensitivity of catalysts to pyridine poisoning, to the heat of adsorption of water or diethyl ether, and also to the slopes of Taft correlations of specific adsorption capacities of ethers in the series: diethyl, dipropyl, and dibutyl ether¹¹. These findings led to the assumption that dehydration on $\text{Al}_2\text{O}_3\cdot\text{NaOH}$ proceeds by E1cB or E2 mechanism and that in the series of catalysts, on going from $\text{Al}_2\text{O}_3\cdot\text{NaOH}$ to SiO_2 , the E1 character of the activated complex increases gradually, being predominant mechanism on SiO_2 . Kinetic isotope effect measurements for dehydration of deuterated 2-propanols on the same catalysts provided strong support for this hypothesis¹³.

However, the study of dehydration of aromatic alcohols of the type $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{R}'$ ($\text{R}' = \text{H}, p\text{-CH}_3, p\text{-F}, m\text{-F}, m\text{-OCH}_3$) on the same series of catalysts revealed parallel trends

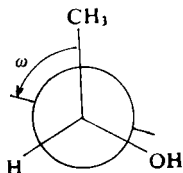
in reactivities in the form of Hammett correlations, which speaks for the prevailing E1 mechanism also on rather basic catalysts¹⁴. The observed shift to E1 mechanism for aromatic alcohols has been ascribed to the significant stabilization of carbonium ion resulting from interaction of the unoccupied p_z orbital of C^+ atom with the conjugated π -electron system of aromatic ring.

In the present work we report on quantum chemical interpretation of the reactivities of series of aliphatic alcohols of the type $(CH_3)_2CH.CH(OH).R$ ($R = CH_3, C_3H_7, CH(CH_3)_2, CH(C_2H_5)_2$; ref.¹¹) and aromatic alcohols of the type $CH_3.CH(OH).C_6H_4.R'$ ($R' = H, p-CH_3, p-F, m-F, m-OCH_3$; ref.¹⁴) on two catalysts of different acid-base properties (SiO_2) and NaOH-doped Al_2O_3).

MODELS AND CALCULATIONS

Quantum chemical calculations were made by semiempirical CNDO/2 method¹⁵ for free molecules of the alcohols under study^{11,14} ($CH_3CH(OH).C_6H_4.R'$; $R' = H, p-CH_3, p-F, m-F, m-OCH_3$; $(CH_3)_2CH.CH(OH).R$, $R = CH_3, C_3H_7, CH(CH_3)_2$, and $CH(C_2H_5)_2$) and for structures I–VI that model characteristic stages of adsorption or surface reaction as E1 or E1cB elimination. In the case of aliphatic alcohols, the calculations were also made for structures VII–XI that model E2 elimination.

Molecules of alcohols and structures I–IX were constructed using standard bond lengths¹⁶, tetrahedral bond angles and staggered conformations. The sp^3 hybridization on oxygen atom was considered both for bonding and free electron pairs and the sp^2 hybridization on C^+ atom was taken for σ bonds in carbonium ions. In the case of substituted phenylethanol, sp^2 hybrid orbitals were located in the plane of aromatic ring so that unoccupied p_z orbital of C^+ atom be capable of interaction with the conjugated π -electron system. For the structures other than carbonium ions, the conformation with minimal energy was adopted, *i.e.* that for conformation angle $\omega = 75^\circ$ (see Scheme 1 and Fig. 1).



SCHEME 1

Adsorption bonds to surface acidic (modelled by H^+) and basic (modelled by OH^-) catalytic centres were modelled by hydrogen bonding with the length of 160 pm and are depicted in structures I, III, IV, and VI by dotted line. In structures VII–IX, the $C_\alpha-O$ and $C_\beta-H$ bonds that are lengthened by 20 pm compared to standard lengths are depicted by broken lines, the neighbouring hydrogen bonds (dotted) being shorter by 20 pm. In these structures, bond lengthening and shortening is designated by $+\Delta$ and $-\Delta$ respectively.

Quantitative description of the activation induced in molecules of alcohols by model interactions is based on the following quantum chemical quantities: W – the strength of $C_\alpha-O$ and $C_\beta-H_A$ bond (Wiberg bond index¹⁶; H_A is hydrogen atom bonded to the β carbon so that $C_\alpha-O$ and $C_\beta-H_A$ bonds be mutually antiperiplanar), Q charge on atom O and atom H_A , E the total

energy of the system. We used both the absolute values of these quantities and their changes induced by model interactions. At the same time, charge and energy changes are absolute: $\Delta Q = Q - Q_0$ and $\Delta E = E - E_0$, while bond strength change is relative and is related to the initial state and expressed on per cent: $\Delta W = 100(W - W_0)/W_0$. The activation of $C_\beta-H_A$ bond, *i.e.* the bond antiperiplanar to $C_\alpha-O$ bond, was studied based on the fact that dehydration proceeds as a rule as *anti*-elimination^{1,2} and that — as confirmed by calculations — it is the antiperiplanar hydrogen which is most significantly activated by adsorption on acidic surface centre^{8,9}.

RESULTS AND DISCUSSION

Coefficients of correlations of experimental data with quantum chemical quantities are given in Tables I and II for all the models of interaction considered. Table I shows the results of calculations on the dehydration of aliphatic secondary alcohols on two catalysts differing in their acid-base properties¹¹, *i.e.* on acidic SiO_2 and on basic Al_2O_3 doped with NaOH.

Quantum chemical calculations reported earlier for the set including primary, secondary, and tertiary alcohols^{8,9} indicated that in this series of alcohols, the ease of $C_\beta-H_A$ bond cleavage decreases with increasing ease of $C_\alpha-O$ bond cleavage and *vice versa*. This phenomenon has been related to the observed opposite trends in the reactivities of alcohols. On acidic catalysts that prefer $E1$ mechanism, the rate determining step involves carbonium formation and thus the cleavage of the $C_\alpha-O$ bond, whereas on basic catalysts that prefer $ElcB$ mechanism, the rate determining step is carbanion formation and involves thus the cleavage of the $C_\beta-H_A$ bond.

The above assumption has been, however, based on calculations^{8,9} made for the series of alcohols different from that for which experimental data were available. Furthermore, also the structures on which these calculations were based, modelled only molecular adsorption of alcohols on surface acidic centre. For that reason, in this

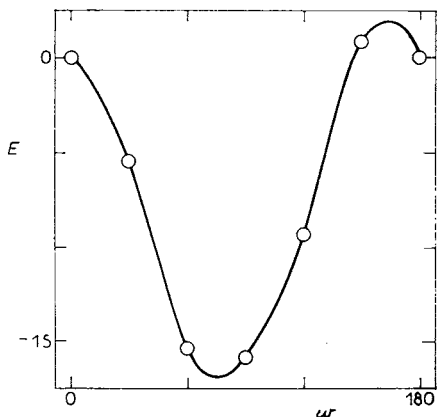


FIG. 1
Dependence of total energy of 1-phenylethanol on its conformation (for definition of dihedral angle ω see Scheme 1)

TABLE I

Coefficients of the correlation of rate constants for dehydration of aliphatic alcohols of the type $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{OH})\text{R}$ ($\text{R} = \text{CH}_3, \text{C}_3\text{H}_7, \text{CH}(\text{CH}_3)_2, \text{CH}(\text{C}_2\text{H}_5)_2$) on acidic (SiO_2) or basic ($\text{Al}_2\text{O}_3 \cdot \text{NaOH}$) catalyst¹¹ with quantum chemical quantities calculated for the models of selected stages of the reaction (signs of quantities were chosen so that increase in quantities parallels an increase in the reactivity of molecule)

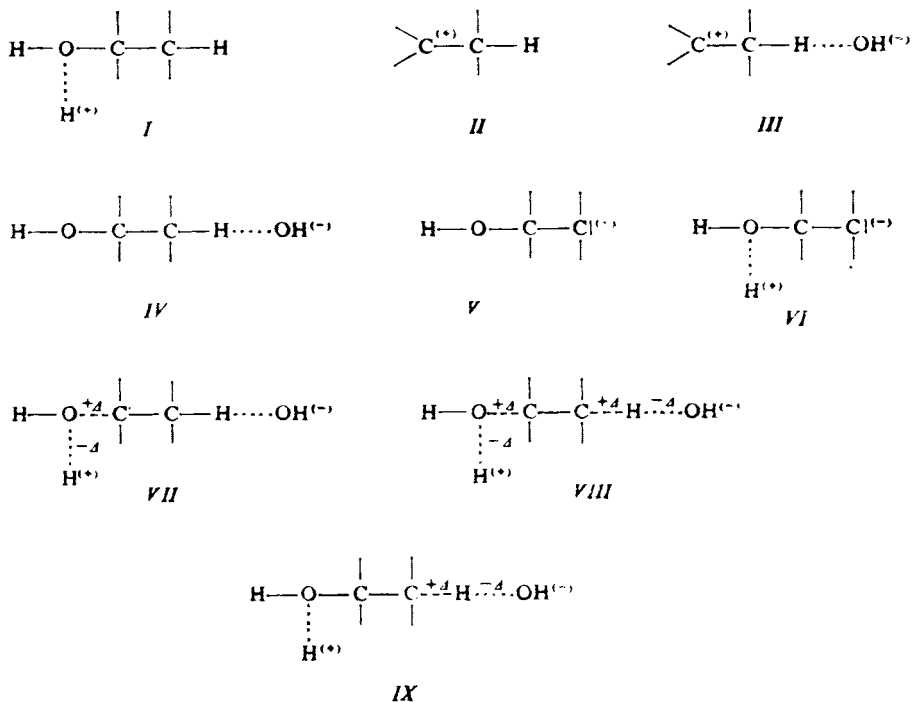
Catalyst	Model structure	Correlated quantity																			
		$-\Delta E$	$-Q(\text{O})$	$-\Delta Q(\text{O})$	$Q(\text{H}_A)$	$\Delta Q(\text{H}_A)$	$-W(\text{C}_\alpha-\text{O})$	$-\Delta W(\text{C}_\alpha-\text{O})$	$-W(\text{C}_\beta-\text{H}_A)$	$-\Delta W(\text{C}_\beta-\text{H}_A)$											
SiO_2	free molecule				0.80																
	I		0.97		0.81	-0.84	-0.97														
	II	0.90	0.86	0.81		-1.00	-0.98														
	III	0.86				0.91	0.90														
	IV	0.93	0.76	-1.00	-0.92	-0.89															
	V	0.99	0.93	-0.97																	
	VI	0.98	0.91	0.81																	
	VII	0.97																			
	VIII	0.99																			
IX	0.93																				
$\text{Al}_2\text{O}_3 \cdot \text{NaOH}$	free molecule				-0.75																
	I		-0.81	-0.81	-0.78	0.74	0.88														
	II	-0.74				0.83	0.84														
	III	-0.61				-0.73	-0.57														
	IV	-0.79	-0.68	0.88	0.75	0.76															
	V	-0.83	-0.93	0.81																	
	VI	-0.92	-0.88	-0.82																	
	VII	-0.86																			
	VIII	-0.88																			
IX	-0.88																				

TABLE II

Coefficients of the correlation of rate constants for dehydration of aromatic alcohols of the type $\text{CH}_3\text{.CH(OH).C}_6\text{H}_4\text{.R}'$ ($\text{R}' = \text{H, } p\text{-CH}_3, p\text{-F, } m\text{-F, } m\text{-OCH}_3$) on basic catalyst¹⁴ ($\text{Al}_2\text{O}_3\text{.NaOH}$) with quantum chemical quantities calculated for the models of selected stages of the reaction (signs of quantities were chosen so that an increase in quantities parallels an increase in the reactivity of molecule)

Model structure	Correlated quantity										
	$-\Delta E$	$-Q(\text{O})$	$-\Delta Q(\text{O})$	$Q(\text{H}_A)$	$\Delta Q(\text{H}_A)$	$-W(\text{C}_z-\text{O})$	$-\Delta W(\text{C}_z-\text{O})$	$-W(\text{C}_\beta-\text{H}_A)$	$-\Delta W(\text{C}_\beta-\text{H}_A)$		
Free molecule	—	0.90	—	-0.90	—	0.81	—	0.00	—	—	—
I	0.61	-0.23	-0.86	-0.88	-0.56	0.71	0.60	-0.80	-0.80	-0.80	-0.80
II	0.96	—	—	-0.98	-0.95	—	—	-0.98	-0.98	-0.98	-0.99
III	0.97	—	—	0.92	0.93	—	—	-0.98	-0.98	-0.98	-0.98
IV'	0.72	0.88	-0.61	-0.81	0.95	0.81	0.10	-0.68	-0.68	-0.67	-0.67
V	-0.64	0.77	-0.96	—	—	0.82	0.21	—	—	—	—
VI	-0.06	-0.44	-0.97	—	—	0.62	0.02	—	—	—	—

work the calculations have been performed for the alcohols for which phenomenon just discussed was observed, and the set of structures modelling adsorption or surface reaction was significantly extended. Structures *I–III* are models of E1 mechanism while structures *IV–VI* model E1cB mechanism. Structures *I* and *IV* model the adsorption of molecule on acidic and basic surface centre, resp. Structures *II* and *V* approximate the activated complex by carbonium ion and carbanion, respectively. The activated complex is obviously modelled more precisely by structures *III* and *VII* that take into account also adsorption bond to surface acidic or basic centre.



The values of correlation coefficients in Table I demonstrate that the results of calculations performed here cannot be interpreted in such a consistent way as data in our previous work⁹. The important difference is *e.g.* the finding that in the series of aliphatic alcohols, the rate of dehydration on the acidic catalyst correlates with the charge on oxygen atom in the free alcohol molecule, while the strength of $\text{C}_\alpha\text{-O}$ bond is in anticorrelation, *i.e.* the correlation coefficient is close to -1 . The same holds also for structure *I* that differs from the model used earlier⁹ only by the length of adsorption bond.

The measure of $\text{C}_\beta\text{-H}_\alpha$ bond activation, *i.e.* the charge on atom H_α and its change

as well as the strength of $C_{\beta}-H_A$ bond and its change in structure *I* correlate with the reactivities obtained for the acidic catalyst. This result has simple physical meaning and can be directly used to interpret the observed phenomenon: in structure *I* that models the early stage of the reaction, there is correlation of reactivities with charge on oxygen, which indicates E1 mechanism of elimination, while on the basic catalyst, the reactivities correlate with charge on periplanar hydrogen, which indicates E1cB elimination. The validity of this conclusion is weakened by inconsistent behaviour of $C_{\alpha}-O$ bond, as to its strength, and also by the fact that the stage of the reaction modelled by structure *I* is far from the activated complex for E1cB elimination.

As follows from Table I, as to its strength, the behaviour of $C_{\alpha}-O$ bond is untypical for all the structures considered. In order to explain the above mentioned phenomenon, one has to state that quantities that characterized the properties of $C_{\alpha}-O$ bond in structures *I-III* (models of E1 elimination) correlate with reactivities on the acidic catalyst and do not correlate with reactivities on the basic catalyst. In addition, the quantities that characterize the properties of $C_{\beta}-H_{\alpha}$ bond in structures *IV-VI* (models of E1cB mechanism) should correlate with reactivities on the basic catalyst and do not correlate with reactivities on the acidic catalyst. The inspection of Table I shows that this is not generally the case. This leads us to conclude that charges and strengths of bonds calculated for the structures that model distinct E1 or E1cB elimination do not make it possible to explain the above fact.

Table I presents data that characterize the correlation of reactivities with the quantity which is related much closer to the rate constant. This quantity is the change in the total energy induced by model interaction. In a suitable model, this quantity should be proportional to the activation energy and should thus correlate well with logarithm of the rate constant (provided that the reaction entropy is constant or at least proportional to enthalpy, which is frequently the case). Relevant data from Table I show that increasing size of the molecule enhances its stability toward all the model interactions. As a consequence, in all the model structures, the total energy correlates with reactivities on the acidic catalyst while those for the basic catalyst are in anticorrelation. This is unsatisfactory result, too.

Structures *I-VI* model clean-cut E1 or E1cB elimination, the real mechanism being more likely synchronous, *i.e.* of E2 type more or less shifted to E1 or E1cB mechanism. For that reason, the above calculations were extended to structures *VII-IX* that model an ideal synchronous E2 elimination (structure *VIII*) as well as E2 elimination shifted somewhat to E1 (structure *VII*) or E1cB (structure *IX*) mechanism. As documented by data in Table I, neither these calculations allowed to get qualitatively new answer.

Therefore, one has to look for the reason why interpretation of experimental data based on quantum chemical calculations is not unambiguous. This is obviously due to several factors:

a) Very simple models used in the present work cannot be naturally applied generally. It seems likely that these models are not able to account for the details needed to describe correctly the behaviour of the system studied. It is worthy of note that the more detailed inspection of correlations reported in previous work⁹ reveals that these correlations hold for sets of data involving primary, secondary and tertiary alcohols. As to the correlations for individual types of alcohols, only data for primary alcohols can be correlated as such. Secondary alcohols do not give satisfactory correlations. Based on this fact, the failure of quantum chemical calculations to interpret experimental data, presented in this work, appears thus to be less surprising.

b) It cannot be excluded that experimental data reflect also other effects that only the change in the reactivity caused by electronic factor. It seems likely that also *e.g.* geometrical factor can play a role here, *i.e.* the steric interaction of alcohol molecules with the catalyst surface. Nevertheless, quantum chemical calculations discussed above describe only electronic factor.

c) Last but not least, the presumed characteristic features of the activated complex, on which the models used were constructed, do not correspond to the reality and must be therefore revised. Some indications concerning this problem can be found in recent works^{18,19}.

The other calculations presented in this work have been made with the aim to interpret trends in reactivities observed for aromatic secondary alcohols on the same series of acidic and basic catalysts¹⁴. The results of these calculations are summarized in Table II. With all the aromatic secondary alcohols and on all the catalysts, there exist parallel trends of dehydration reactivity determined experimentally, their

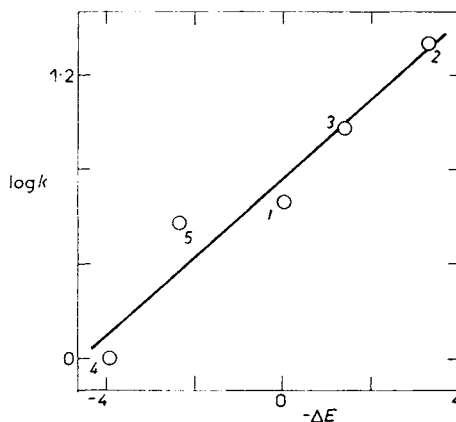


FIG. 2

Logarithm of rate constant of dehydration of the alcohols¹⁴ $\text{CH}_3\text{-CH(OH)-C}_6\text{H}_4\text{-R}'$ on NaOH-doped Al_2O_3 correlated with total energy decrease, the characteristic stage of E1 elimination being modelled by structure III ($n = 0.97$); R': 1 H, 2 *p*- CH_3 , 3 *p*-F, 4 *m*-F, 5 *m*- OCH_3

slopes indicating the occurrence of E1 elimination also on basic catalyst¹⁴. The observed shift to E1 mechanism was ascribed to the stabilizing effect of π -electron system of aromatic ring in the stage of carbonium ion. This stabilization is made possible by inclusion of the unoccupied p_z orbital of C^+ atom to the conjugated π -electron system.

By contrast to the values given in Table I, data presented in Table II allow more consistent interpretation of observed phenomenon to be made. The important fact is that the strength of C_x-O bond in all the structures considered correlates more or less with experimental reactivities, while the strength of $C_\beta-H_A$ bond does not correlate with reactivities or it is in anticorrelation with them. As to the charges on oxygen atom and on periplanar hydrogen, even in the case of aromatic secondary alcohols the results of calculations cannot be interpreted unambiguously. The most significant in Table II are the coefficients of correlations of reactivities with the decrease in the total energy, especially for structures III and VI that model closely the activated complex of E1 and E1cB elimination respectively. Fig. 2 documents very good correlation of reactivities with the energetical stability of the model of adsorbed carbonium ion (structure III), which provides direct evidence for the correctness of the hypothesis formulated in previous work¹⁴. Dehydration reactivities of secondary alcohols can be thus interpreted satisfactorily by quantum chemical calculations.

In conclusion, the attempt at quantum chemical interpretation of dehydration reactivities of secondary aliphatic alcohols on catalysts differing in their acid-base properties, described in the present work, has shown that the simple models of interaction of alcohol molecules with surface centers used here are not always capable of describing the situation. One cannot exclude, however, that discrepancy in conclusions drawn from calculations and experimental data arises from commonly accepted concept about probable course of the reaction, *i.e.* from ideas on which the models used in this work have been based. Although in the case of aromatic secondary alcohols quantum chemical calculations were applied with success to interpret experimental data, it becomes clear that in further research in this field, the more precise, even though more sophisticated, models of the interaction of reactant molecules with the catalyst surface need to be constructed.

LIST OF SYMBOLS

E	the total energy of a given system [KJ/mol]
k	experimental rate constant of the reaction [mol/h kg _{cat}]
n	correlation coefficient [-]
$Q(A)$	the charge on atom A [e]
$W(A-B)$	the strength of bond between atoms A and B (Wiberg bond index ¹⁷) [-]
ΔE	absolute change in total energy of a given system [kJ/mol]
$\Delta Q(A)$	absolute change in the charge on atom A [e]

- $\Delta W(A-B)$ relative change in the strength of bond between atoms A and B (with respect to the free molecule) [%]
 ω dihedral angle determining the conformation of molecule of phenylethanols (Scheme 1) [deg]

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