

QUANTUM CHEMICAL MODEL OF DEHYDROGENATION OF SECONDARY ALCOHOLS ON OXIDES

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Using the CNDO/2 method, models for dehydrogenation of secondary alcohols on oxides of some metals have been calculated. The relative changes of bond strength and of atom charges in 2-propanol on interaction with atoms of Be, Mg, Al, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Ni were satisfactorily correlated with relative activities of these oxides published in the literature. Similar agreement was obtained for the series 2-propanol, 2-butanol, 3-methyl-2-butanol and 3,3-dimethyl-2-butanol on Cr₂O₃.

It is a well known experimental fact that a number of oxides is able to catalyze dehydration and/or dehydrogenation of alcohols^{1,2}. The surface of the oxides is covered by acidic and basic active centres of both Brønsted and Lewis types. Because molecules of the alcohols may behave as acids or bases we can expect the occurrence of several types of adsorption; this has been confirmed by IR spectra of surface complexes³⁻⁵. It was found that the centre of the adsorption activity of the alcohol molecule is the OH group: the alcohol can be adsorbed a) by means of hydrogen bond between the hydroxyl group of the alcohol and lattice oxygen, b) by formation of surface alcoholate, c) by means of hydrogen bond between a surface hydroxyl group and oxygen of the alcohol.

Chuvylkin, Zhidomirov and Kazanskii⁶⁻⁸ have shown on the basis of quantum-chemical calculations for ethanol that the interaction of the OH group of the alcohol with an electron acceptor (H⁺ in their model) causes changes which would eventually result in dehydration whereas the interaction with an electron donor (H⁻ in their model) leads to dehydrogenation. Sedláček and Kraus⁹ and Nondek and Sedláček¹⁰ have arrived at identical conclusions using 2-propanol and similar models. On the basis of a very simplified model, *i.e.* an isolated alcoholate ion, they have assumed that surface alcoholate ions are intermediates in the dehydrogenation of alcohols¹⁰.

In quantum-chemical studies of adsorption and catalytic phenomena the key problem is the construction of a reasonable model of the solid surface. In general, the larger is the model, the better are the results^{11,12}. However, technical difficulties restrict the size of the model appreciably. Some papers have shown that satisfactory explanation of some experimental observations can be obtained with one-atomic model of the solid phase^{13,14}, especially if only trends in series of catalysts should be compared.

The aim of the present paper has been to confirm previous results obtained with very simple models¹⁰ using now the one-atom model of the catalysts. The calculations included a series of catalysts in interaction with 2-propanol and a series of secondary alcohols in interaction with one chromium atom.

METHODS AND RESULTS

The calculations were made using a program for the CNDO/2 method¹⁵ which has been modified and enlarged for systems containing transition metals of the 4. period¹⁶; orbital exponents after Gouterman¹⁷ (Table I) have been used. As the energy criterion for self-consistence the value of $4.36 \cdot 10^{-22}$ J (10^{-4} u.a.) was chosen. The calculation were of two kinds: *a*) 2-Propanolates of the type $\text{CH}_3\text{CHOMCH}_3$ where $\text{M} = \text{Be, Mg, Al, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu}$. *b*) Chromium alcoholates RCHO CrCH_3 , where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{iC}_3\text{H}_7, \text{tC}_4\text{H}_9$. Besides that the parent molecule of each alcohol has been calculated.

In construction of the model, typical bond lengths¹⁸, tetrahedral bond angles and staggered conformations have been applied. The length of the metal–oxygen bond (Table I) was estimated from Pauling's ionic radii¹⁹. The sp^3 hybridization was assumed for oxygen. The geometry of the models was selected on the basis of preliminary calculations of the system $\text{CH}_3\text{CHOAlCH}_3$ for different values of the dihedral angle μ (Fig. 1); all final calculations were made for the conformation with $\mu = 60^\circ$ which yields maximal negative charge on H_α (Fig. 2). The number of electrons was such as to give zero charge on the whole model. The occupation schemes of electron levels corresponded to the ground states. For calculation the computer of the type BESM (Computer Centre of the Academy of Sciences of USSR, Novosibirsk) was used.

For the discussion, the following quantities describing the interaction adsorbate-catalyst were selected:

a) Change of charge on atom A (10^{-2} e)

$$Q_A = Q_A(\text{R}'\text{OM}) - Q_A(\text{R}'\text{OH}). \quad (1)$$

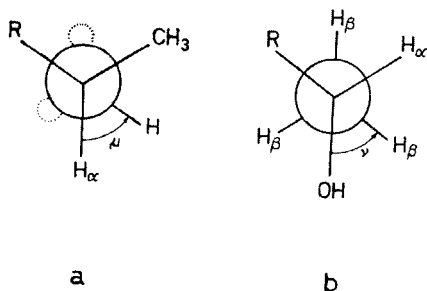


FIG. 1

Newman's Projection along the $\text{C}_\alpha\text{—O}$ bond, (a), along the $\text{C}_\alpha\text{—C}_\beta$ bond (b)

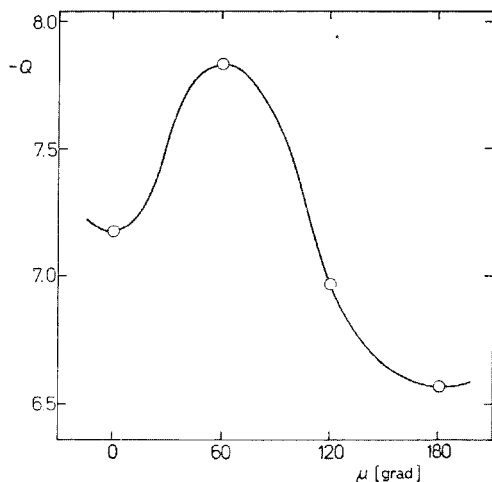


FIG. 2

Charge on H_α in Dependence on Dihedral Angle in $\text{CH}_3\text{CHOAlCH}_3$

b) Index of bond strength change between atoms A and B (%)

$$I_{AB} = 100 [W_{AB}(R'OM) - W_{AB}(R'OH)]/W_{AB}(R'OH) \quad (2)$$

where Q_A is the charge on atom A calculated from electron density and the core and $W_{AB} = \sum_{ij} p_{ij}^2$ ($i \in A; j \in B$) is the Wiberg's bond index²⁰ calculated from elements of density matrix. Preliminary calculation are shown on Fig. 2. The results for 2-propanol and the series of catalysts are given in Table I and on Fig. 3. Table III and Fig. 4 summarize the results for the series of alcohols on chromium oxide. Besides that Table III and Fig. 4 together with Table II allow comparison of the quality of the dehydrogenation model by Nondek and Sedláček¹⁰ with the present model.

DISCUSSION

The adsorption of alcohols on oxide catalysts is modelled here by exchanging the hydrogen atom in the hydroxyl group for a metal atom. Table II allows comparison of calculations made for scandium and iron oxides with those for isolated alcoholate

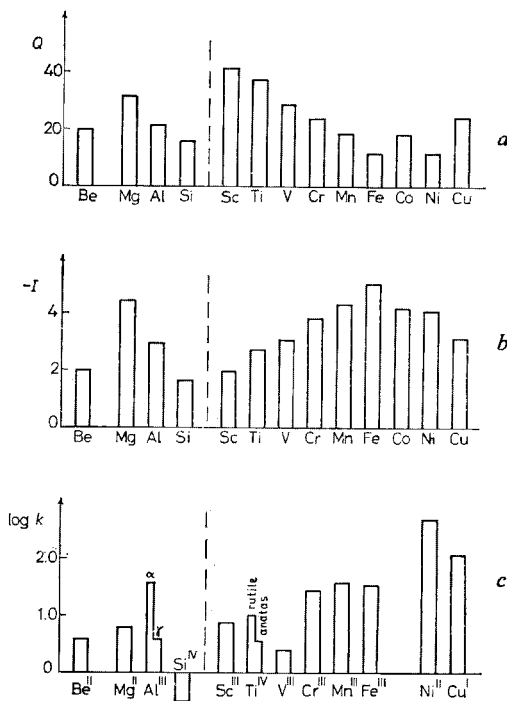


FIG. 3

Comparison of Selected Quantities Characterizing Different Metal Oxides

a Charge on metal atom, b weakening of the $C_{\alpha}-H_{\alpha}$ bond $I_{C_{\alpha}-H_{\alpha}}$, c experimental relative reactivities for dehydrogenation of 2-propanol².

TABLE I
Some Quantities Characterizing the Dehydrogenation of 2-Propanol on Different Catalysts

M	Q_M	$I_{C\alpha-H\alpha}$	$\log k^a$	l_{M-O}^b , nm	ξ^c
Be(II)	19.93	-1.99	0.59	17.1	—
Mg(II)	31.15	-4.43	0.79	20.5	—
Al(III)	21.59	-2.91	1.56 ^d 0.57 ^e	19.0	—
Si(IV)	15.93	-1.62	0.50	18.1	—
Sc(III)	41.17	-1.95	0.87	22.1	1.24
Ti(IV)	37.20	-2.70	0.55 ^f 1.01 ^g	20.8	1.27
V(III)	28.64	-3.07	0.40	20.6	1.30
Cr(III)	23.93	-3.83	1.44	20.4	1.33
Mn(III)	18.72	-4.29	1.56	20.2	1.36
Fe(III)	11.69	-4.99	1.52	20.0	1.37
Co(II)	18.37	-4.17	—	21.2	1.423
Ni(II)	11.61	-4.07	2.67	20.9	1.473
Cu(I)	23.93	-3.13	2.11	23.6	1.482

^a Relative rate constant found experimentally²; ^b length of bond metal-oxygen; ^c orbital exponents according to Gouterman¹³; ^d α -Al₂O₃; ^e γ -Al₂O₃; ^f anatase; ^g rutile.

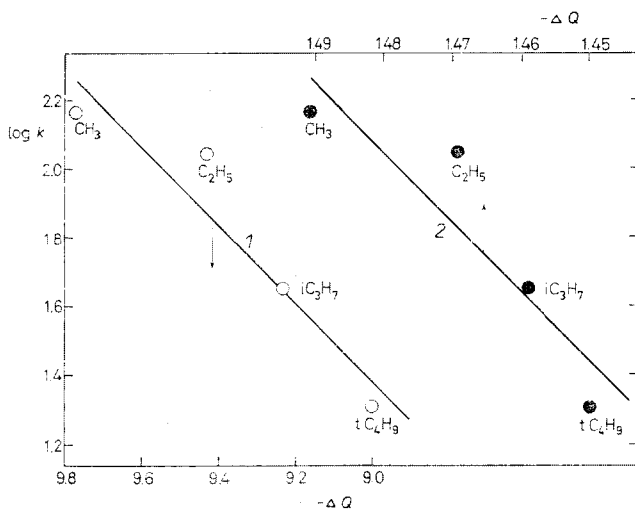


FIG. 4

Correlation of the Logarithm of Rate Constant of the Dehydrogenation¹⁰ and Change of Charge on H_α Atom for Model¹⁰ RCHO(-)CH₃ (1) and for Model RHO CrCH₃ (2)

ion¹⁰. The trend is the same in all cases and this confirms qualitative conclusions presented in the preceding paper¹⁰. The modelled type of adsorption changes the parent alcohol molecule in the direction to dehydrogenation, by weakening the $C_\alpha-H_\alpha$ bond and by increasing the negative charge on H_α . Experiments have shown that the rate determining step is the splitting of H_α .

Fig. 3 compares calculated and experimental relative reactivities of 2-propanol, taken from the literature² and expressed as logarithmi of rate constants. The reactivities correlate satisfactorily with weakening of the $C_\alpha-H_\alpha$ bond as given by the index of the change of bond strength I_{AB} . In spite of some local discrepancies general agreement between experiment and calculation can be observed. The observed deviations may have two causes: a) The influence of type and parameters of the crystal lattice of the adsorbents could not be respected in our simple model. b) The experimental rate constants are a product of two quantities^{21,22}, an intensive one and an extensive one. Only the intensive quantity, *i.e.* the true rate constant for one

TABLE II

Atom Charge and Index of the Change of Bond Strength for Different Models of Adsorption of 2-Propanol

For the definition of the dihedral angle see Fig. 1b.

Atom charge	R'OH	R'O ⁽⁻⁾ ^a	R'OSc	R'OFc
O	-26.58	-66.46	-42.34	-34.15
C_α	17.67	13.87	16.96	19.97
H_α	-3.15	-12.92	-6.93	-3.48
C_β	-3.87	-1.74	-3.12	-0.59
H_β (60°)	0.32	-4.48	-1.32	3.60
H_β (180°)	0.88	-7.19	-0.57	1.65
H_β (300°)	1.29	-3.82	0.45	2.64

Index of change of bond strength	R'O ⁽⁻⁾ ^a	R'OSc	R'OFc
$C_\alpha-O$	2.84	2.19	-4.00
$C_\alpha-H_\alpha$	-4.04	-1.95	-4.99
$C_\alpha-C_\beta$	-3.09	-1.87	-3.76
$C_\beta-H_\beta$ (60°)	-0.46	-3.31	-13.53
$C_\beta-H_\beta$ (180°)	-0.97	-0.16	-0.59
$C_\beta-H_\beta$ (300°)	-0.36	-0.18	-0.61

^a Isolated alcoholate ion as model of adsorption¹⁰.

TABLE III
Change of Charge on H_{α} for Different Models of Adsorption of Alcohols $RCHOHCH_3$

R	$R'O^{(-)}$ see ¹⁰	$R'OCr$	k (see ¹⁰) mol/l. kg
CH_3	-9.77	-1.4909	145.6
C_2H_5	-9.43	-1.4693	110.9
<i>i</i> - C_3H_7	-9.23	-1.4589	44.6
<i>i</i> - C_4H_9	-9.00	-1.4500	20.3

active centre, can be expected to correlate well with the results of theoretical treatment, whereas the extensive component of the rate constant, *i.e.* the concentration of active sites per unit surface area, may differ appreciably from one catalyst to another.

It should be noted that, according to our calculations, the dehydrogenation activity is not proportional to the donating ability of the metals although the interaction of the alcohol with an electron donor as the necessary condition for dehydrogenation, stated previously^{6-8,10}, has been confirmed. With non-transition metals the decrease of positive charge on metal atom parallels the decrease of the extent of $C_{\alpha}-H_{\alpha}$ bond weakening, whereas for transition metals the bond weakening increases. This may be explained in such a way that an over-all transfer of electrons is only a result of their exchange on which changes in molecular orbital structure are dependent. *E.g.* the large decrease of electron density on Sc atom (-0.4117 e) is composed from the following changes: -0.7205 e in the 4s orbital, +0.2853 e in the 4p orbitals and +0.0235 e in 3d orbitals. In comparison, the relatively small decrease on Fe atom (-0.1169 e) is caused by large exchange of electrons: -1.0630 e in the 4s orbital, +0.8781 e in 4p orbitals and +0.0680 e in 3d orbitals. These data show also that the interaction involves mainly 4s and 4p orbitals.

The results concerning the homologous series of alcohols on chromium oxide are given in Table III which summarizes also data obtained with the simpler model¹⁰ and the experimental data¹⁰. Fig. 4 demonstrates no improvement of the correlation between calculated and experimental values by substituting the more realistic model for the simple one. It can be therefore concluded that both models yield a satisfactory picture of the rearrangement of the electrons resulting from interaction with an electron donating centre which is in agreement with the assumed mechanism of dehydrogenation^{10,23}.

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