

## EFFECT OF STRUCTURE ON CATALYTIC DEHYDRATION OF ALCOHOLS AS MODELLED BY QUANTUM-CHEMICAL CALCULATIONS

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Quantum-chemical calculations of a series of secondary alcohols  $R-CHOH-CH_3$  and their protonated forms  $R-CHOH_2^+-CH_3$  ( $R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9$ ) have revealed increased activation of the  $C_\alpha-O$  bond and decreased activation of the  $C_\beta-H$  bond with increasing size of the group  $R$  due to protonation. This finding is in agreement with previous experimental observations of structure effect on rate in dehydration of similar series of alcohols on oxides exhibiting different surface acidity.

Kinetics of the catalytic dehydration of secondary alcohols of the structure  $R-CHOH-C_3H_7$  ( $R = \text{alkyl}$ ) on various oxides was studied in this Laboratory and the rate data were correlated by the Taft equation<sup>1</sup>. The slope of the linear relationship of  $\log k$  vs  $\sigma^*$ , i.e. the parameter  $\rho^*$ , changed its values from positive to negative ones with increased acid strength of the catalyst surface. This finding has been interpreted as a gradual transition from an E2-like (concerted) mechanism of elimination to an E1-like mechanism with increasing acidity. This hypothesis was then supported by a study of deuterium isotope effects using the same series of catalysts<sup>2</sup>.

The purpose of this paper was to bring further evidence by quantum-chemical modelling of changes caused within the alcohol molecule of different structure by adsorption leading to dehydration. On the basis of our previous experience with similar calculations concerning the dehydration of 2-propanol<sup>3</sup>, the proton added to the hydroxyl group was chosen as a simple model of the active centre of the catalyst. The same CNDO/2 programme and parametrization of studied molecules were used as in the preceding paper<sup>3</sup>.

### RESULTS

The calculations concerned alcohols  $R-CHOH-CH_3$  and protonated alcohols of the structure  $R-CHOH_2^+-CH_3$ , where  $R = CH_3, C_2H_5, i-C_3H_7$  and  $t-C_4H_9$  (Fig. 1). The pertinent results of the calculations are summarized in Table I. The changes of the bond strength, of the charge on  $H_\beta$  (in  $CH_3$ ) and of the total energy caused

TABLE I

Results of CNDO/2 Quantum-Chemical Calculations of the Alcohols R—CHOH—CH<sub>3</sub> and of Its Protonated Forms

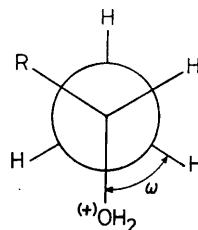
Bond ( $\omega$ ) <sup>a</sup>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	i-C <sub>3</sub> H <sub>7</sub>	t-C <sub>4</sub> H <sub>9</sub>
Change in bond strength <sup>b</sup> , %				
O—H	-7.52	-7.38	-7.25	-7.19
C <sub>α</sub> —O	-21.43	-21.28	-21.93	-22.03
C <sub>α</sub> —H	0.96	0.93	0.89	0.88
C <sub>α</sub> —C <sub>β</sub>	-0.02	0.01	-0.01	0.02
C <sub>β</sub> —H (60°)	-0.17	-0.13	-0.13	-0.13
C <sub>β</sub> —H (180°)	-1.30	-1.27	-1.21	-1.20
C <sub>β</sub> —H (300°)	-0.23	-0.22	-0.21	-0.22
Change of charge on H <sub>β</sub> (180°) <sup>b</sup> , e				
—	0.0711	0.0693	0.0665	0.0655
Relative change in total energy of the species <sup>b</sup> , kcal mol <sup>-1</sup>				
—	0	-2.12	-4.31	-4.84

<sup>a</sup> Dihedral angle, for definition see Fig. 1; <sup>b</sup> caused by protonation.

by protonation of the parent alcohol vary systematically in the series of alcohols. Two different trends are observed. With increasing number of carbon atoms in the group R the weakening of the C<sub>α</sub>—O bond also increases. In contrast, the weakening of the C<sub>β</sub>—H bond decreases in the same direction, as well as the charge on H<sub>β</sub>.

It can be concluded that the protonation of the parent alcohol results in increased activation of the C<sub>α</sub>—O bond and decreased activation of the C<sub>β</sub>—H bond in the series of alcohols from R = CH<sub>3</sub> to R = t-C<sub>4</sub>H<sub>9</sub>. This is in agreement with the assumed mechanism of dehydration on oxide catalysts<sup>1</sup>. The E2-like mechanism involves the

FIG. 1

Newman Projection of the Protonized Alcohol Molecule R—CHOH<sub>2</sub><sup>(+)</sup>—CH<sub>3</sub> and Definition of the Dihedral Angle  $\omega$ 

rupture of the  $C_\beta$ —H bond in the rate determining step<sup>2,4</sup> and therefore a decrease in the rate with increasing size of the group R may be expected on the basis of our calculations. This has been experimentally observed<sup>1</sup> on non-acidic catalysts (*e.g.* alkalinized  $Al_2O_3$ ) for which the E2-like mechanism was proposed (*cf.* also<sup>5</sup>). On the contrary in the E1 mechanism, the rupture of the  $C_\alpha$ —O bond is more important for the rate. In accord with our calculations, the rate in the series increases with increasing size of the group R if the dehydration precedes on acidic catalysts (like  $SiO_2$ ) where the E1-like mechanism was assumed.

The data in Table I allow some other conclusions. As with 2-propanol<sup>3</sup>, all other alcohols show maximal activation of the  $C_\beta$ —H bond if it stands in antiperiplanar position relative to the  $C_\alpha$ —O bond. This arrangement corresponds to *trans*-elimination which is preferred on most oxide catalysts.

The change of total energy of the molecule caused by protonation may be taken as measure of the basicity of the alcohols. Table I shows a decrease of this quantity with increasing number of carbon atoms in the group R. This indication of decreasing basicity in the series from  $R = CH_3$  to  $R = t-C_4H_9$  agrees well with spectral measurement of basicities of gaseous alcohols<sup>6</sup>.

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