

POSSIBLE ROLE OF NONCLASSICAL IONS IN ACID CATALYSED DEHYDRATION OF ETHANOL

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On the basis of CNDO/2 calculations, the geometrical changes accompanying the activation of the ethanol molecule in the acid catalysed dehydration have been analysed. The activation of the ethanol molecule *via* protonation of its hydroxyl group manifests itself above all in the lengthening of the C—O bond. Further elongation of this bond leads to the formation of nonclassical structure, in extreme case to the nonclassical ion which is more stable than the classical one. The above reaction mechanism is confronted with the known facts and provides acceptable unifying explanation of *e.g.* the stereoselectivity anomalies and the isotope effect of β -deuterated alcohols as well as other experimental and theoretical data.

Some time ago, Sedláček¹ studied theoretically the role of the geometrical factor in elimination reactions of alcohols on alumina. His assumptions can be generally summarized as follows. The molecule of the alcohol is adsorbed on two surface active sites; the acid adsorption site is represented by the proton of the surface hydroxyl group and the basic site by the surface oxygen ion. The above assumptions² explain well the anti-elimination mechanism found experimentally³⁻⁵.

On the other hand, there is a number of studies which indicate the participation of the alcohol bonded to Lewis acid sites in elimination reactions⁶. Sedláček¹⁰ has also analysed the geometrical conditions for this type of adsorption and has found that they are much less favourable than the adsorption on Brønsted sites. The reason is a restricted possibility of the alcohol bonded to aluminium ion to interact simultaneously with the basic surface site *via* the antiperiplanar hydrogen atom on the β -carbon atom. This discrepancy between theoretical prediction and experimental results has initiated our attempt at revising the elimination mechanism.

THEORETICAL

Having in mind the result of Sedláček¹⁰, the first step of such a revision consists in obvious necessity to disregard the requirement of uninterrupted two centre adsorption, since in the case of the alcohol bonded to aluminium ion such an interaction is unfeasible. Having admitted the possibility of single centre adsorption, further

progress of our considerations is possible by taking into account the principle of the microscopic reversibility. This principle requires the dehydration to proceed by the same mechanism as the reverse addition of water to the C=C double bond with the formation of the π -complex¹¹. One can thus expect the elimination to end at the same structure that represents nonclassical form of the ethyl cation. The intermediacy of nonclassical ions in dehydration reactions was already reported in the literature^{12,13}.

In order to support our qualitative considerations theoretically, we have performed semiquantitative, but nevertheless sufficiently detailed study of geometrical changes accompanying the activation of the ethanol molecule in acid catalysed dehydration. In modelling this reaction, we have accepted the following simplifying assumptions: a) The acid site activating the ethanol molecule is simply a proton (see Fig. 1). b) In the course of the reaction no other interactions between the molecule and the surface are considered. c) The role of the reaction coordinate plays the C—O bond length.

The first assumption was dictated by computational reasons, and despite of the fact that the replacement of the Lewis acid site by the Brønsted one may be rather crude, we believe that it does not affect the qualitative validity of our conclusions¹⁴. The second assumption reflects the restriction arising from the results of the study by Sedláček¹⁰ concerning the geometrical impossibility of the interaction of the β hydrogen atom with the surface. It should be, however, realized that the impossibility of the two-centre adsorption modifies only the first step of the reaction. After the nonclassical ion has been formed, the interaction with the surface basic site enters again into play, to ensure the elimination of the proton from the nonclassical ion. We assume that this step has no special geometrical restriction with respect to the arrangement of surface atoms.

The model accepted for the calculations is depicted in Fig. 1. The C—O bond was placed on the Z axis and the positions of both atoms for several selected values of interatomic distances were fixed. Positions of all the remaining atoms have been optimised. In a subsequent series of calculations, the geometries of isolated $C_2H_5^+$ ions have also been optimised for both classical and nonclassical forms. The initial geometries were determined using the following data¹: bond lengths C—C 154 pm, C—H 109 pm, O—H 96 pm, C—O 138 pm, tetrahedral bond angles.

RESULTS AND DISCUSSION

In the first phase of calculations, the geometry of the free ethanol molecule was optimized. In the next step, the changes due to protonation on oxygen have been studied. In agreement with the expectation, the protonation was found to affect above all the C—O bond length (elongation by about 4 pm). In order to model the dehydration reaction, the C—O bond length was then gradually increased while optimizing the geometry of the rest of the molecule. Because of the crudeness of our calculations,

not taking into account the possible secondary interactions of the reacting ethanol molecule with the surface, we have not paid attention to quantitative energetic aspects of the classical *vs* nonclassical ion isomerism, since they may be very sensitive to the perfection of the model chosen. We have concentrated our attention only to qualitative discussion of geometrical changes accompanying the reaction. These geometrical changes, taking place during the lengthening of the C—O bond are schematically depicted in Figs 2–4 and can be described in the following way: a) The proton in the antiperiplanar position moves in the original H—C—C plane to the axis perpendicular to the C—C bond; b) the remaining C—H bonds of the CH₂CH₂ fragment display the tendency to planarisation.

The most important conclusion arising from these results is that C—O bond cleavage does not lead to simple weakening of the C_β—H bond but above all to the change in the C—C—H angle, supporting thus the hypothesis about the participation of nonclassical ion in the acid catalysed dehydration, which is also the more stable than the classical ion¹⁵. Despite of the simplicity of the model, the possibility of participation of nonclassical structures in the mechanism of the acid catalysed dehydration seems thus to be supported by our calculations. The only unresolved problem is then the fate of the nonclassical structure on the surface, particularly the proton transfer from it to the surface basic site. As the complexity of the problems still prevents the appropriate theoretical description to be made, we attempt only at qualitative discussion of this last step of the reaction. When analysing the possible steric situation on the surface we propose this last step to proceed *via* formation of the intermediary hypothetical complex depicted in Fig. 5. The transfer of proton

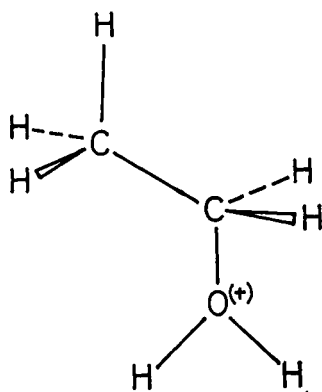


FIG. 1

Scheme of the ethanol molecule activated by protonation on oxygen atom

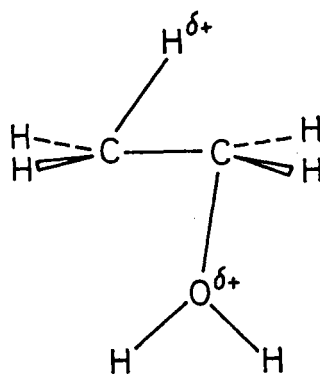


FIG. 2

Scheme of the activated ethanol molecule after lengthening of its C—O bond by 200 pm

to the surface basic site requires the substituents on both carbon atoms to come near to the surface (Fig. 5). The condition of the minimum steric hindrance in this step requires to prefer such surface structures in which the bulkier substituents are mutually *cis*-oriented and hold not too close to the surface. The preference of *cis*- over *trans*-alkenes in reactions of substituted ethanols have been observed experimentally^{16,17}. Further experimental result which speaks strongly for nonclassical ion mechanism has been provided by Kochloeff and coworkers¹⁸ who studied the reactivity of *cis*- and *trans*-cyclohexanols. The observed preference of *cis* over *trans* reactivity is clearly related to the presence of antiperiplanar hydrogen which is present only in the *cis* and not in *trans* isomer. The importance of antiperiplanar arrangement has been theoretically analysed by Sedláček¹. As the conformational rigidity of some alkylcyclohexanols excludes the possibility of two-centre adsorption, the observed *cis* over *trans* reactivity can be explained by the above proposed one centre adsorption model in which the ethanol molecule is activated by the interaction with alu-

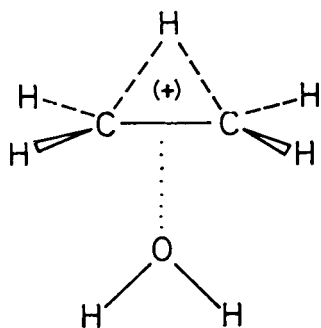


FIG. 3

Scheme of the nonclassical ethyl cation interacting with water molecule — the limit stage of the molecule from Fig. 2

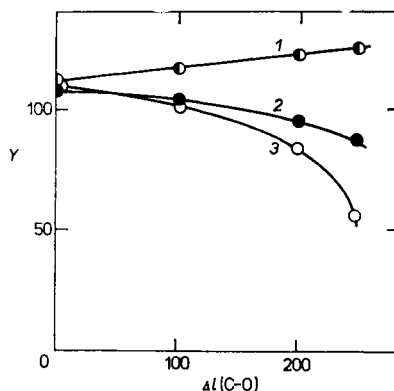
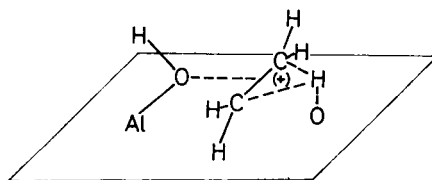


FIG. 4

Dependence of the $\text{C}_\beta\text{-H}$ bond length (pm) — curve 1; the C-C-O bond angle ($^\circ$) — curve 2; the $\text{C-H-H}_{\text{anti}}$ bond angle ($^\circ$) — curve 3; on C-O bond lengthening (pm)

FIG. 5

Simplified scheme of two-centre interaction of the ethanol molecule with alumina surface in the elimination reaction



minium atoms acting as a Lewis acid type site. The importance of acidic active sites was demonstrated in the study by Jiráto \acute{v} a and Beránek²⁰ and also in theoretical study by Sedláček²¹ who reported the excellent correlation of the reactivity of alcohols with the extent of the weakening of the C—O bond in the alcohol due to protonation. It is worth mentioning that similar correlation with the extent of the weakening of the C $_{\beta}$ —H bond is unsatisfactory. This finding can be rationalised by our results since we have found that the C—O bond cleavage does not lead to simple weakening of the C $_{\beta}$ —H bond but above all to the change in the H—C—C bond angle. This angular movement of the antiperiplanar hydrogen can also cause the isotope effect in dehydration of deuterated alcohols observed by Knözinger and Kochloeff^{22,23}.

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