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ROLE OF IONIZED STATES OF WATER MOLECULES IN THE REACTION OF HYDROLYSIS OF SACCHAROSE ON SILICA SURFACES

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An ion-pair model has been proposed explaining the origin of acidic sites at the silica surface–aqueous solution interface. The results of quantum chemical simulation testify the idea on principal role of ion-pair state of water molecules in the hydrolysis of saccharose adsorbed on silica surface.

INTRODUCTION

The theoretical treatment of adsorption processes on solid oxide surfaces becomes considerably complicated when the influence of the liquid medium should be taken into account. This necessity arises every time when a detailed simulation is needed to shed light on the sorption mechanism and the rate-limiting stages.

Usually, the experimental data available reveal a substantial role of the solvent in sorption phenomena [1, 2]. Water is by far the most important and frequently used solvent. As a rule, the solvent is portrayed as an ensemble of neutral molecules. However, as water and other solvent molecules have dipole moments they can indeed get coordinated to reaction sites.

Recently a lot of reports appeared that use advanced quantum chemical techniques to study the role of the solvent [3, 4]. These studies reveal the coexistence of clusters of the solvent in the state of molecules and ion-pairs (Fig. 1).

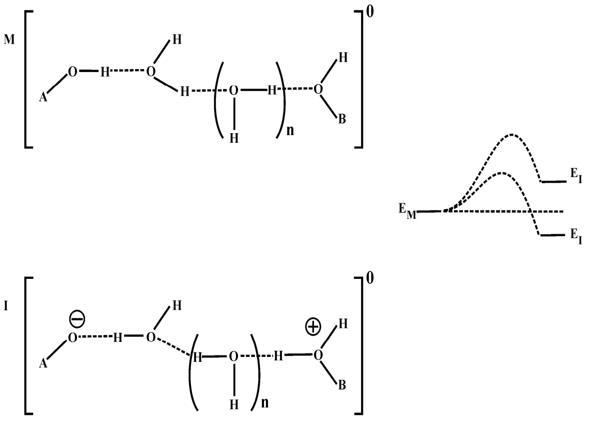

Fig. 1. Energy levels. Molecular state *vs* ion-pair state

Systems containing only molecules are called "molecular state" systems. Other systems can also exist that though being electrically neutral as a whole, have ions together with neutral molecules. These are the "ion-pair" systems. Ions appear as a result of proton transfer between molecules. Provided surface acid-base sites are strong enough, the energy level of the ion-pair state can be lower than that of the molecular state.

The most interesting problem in aqueous systems with ion pairs is to find a minimum number of water molecules needed to produce stable isolated ion pairs (H_3O^+ and OH^-). There is no definite answer to this question because the results of quantum chemical calculations depend on both the accuracy of the method and the basis set used. No experimental data are available for verifying such calculations.

A similar situation could be found in other systems containing water and ionic substances. A general conclusion for the systems is that only a few molecules, from 5 to 10, are enough to produce the transition from molecular associates to isolated ion-pairs. A cluster of 8 water molecules is an example of the existence of isolated ion pairs (Fig. 2) [5]. All oxygen atoms are located in the cube vertexes. We can see that in this cluster both molecular water and ion-pair states can coexist with a transition temperature of 259 K. Similar results about the state (ion-pairs or molecular) of hydrated complexes of some acids, bases, and salts can be found elsewhere [6–9].

RESULTS AND DISCUSSION

The presence of hydroxyl groups on oxide surfaces (including silica) and their possible

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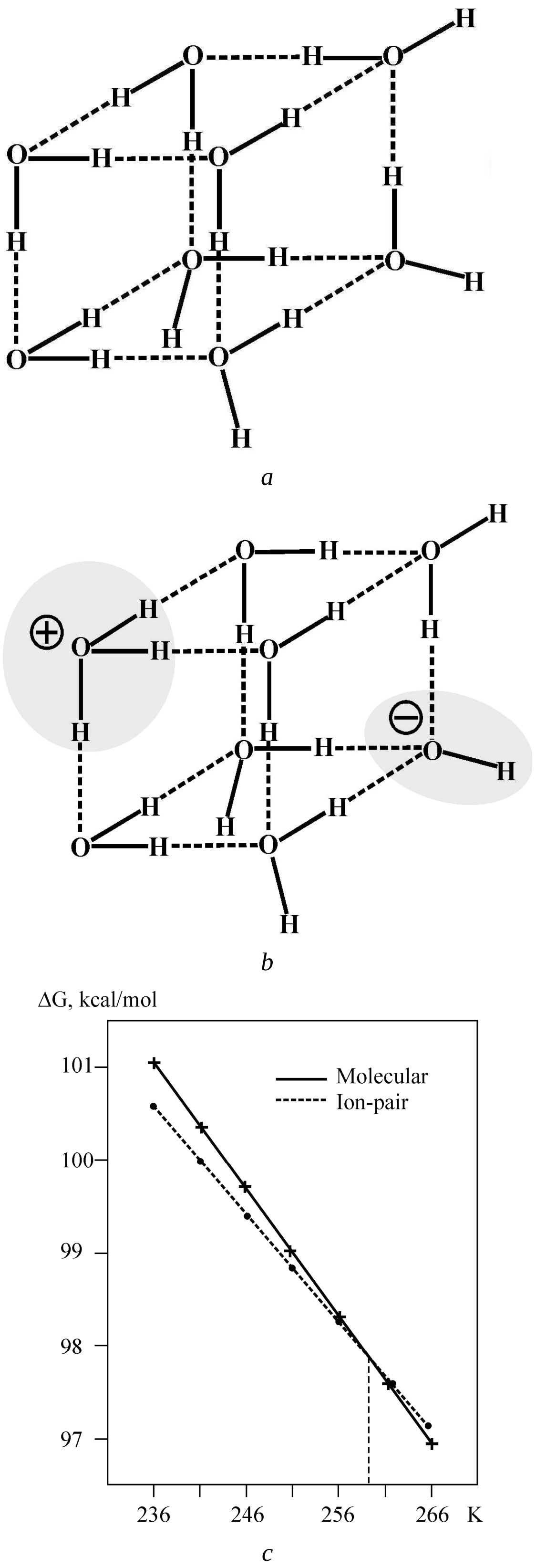

a

b

c

Fig. 2. Isomeric forms of the $(H_2O)_8$ cluster [6] (*a*, *b*) and equilibrium (*c*) of isomeric forms of the $(H_2O)_8$ cluster (phase transition at 259 K)

hydration in clusters pose the question on the possible formation of ion-pairs within the surface layer and their possible role in chemical transformation of adsorbed species.

Let us analyze an example of such a transformation, namely the hydrolysis of saccharose catalyzed by acid silanol groups, by means of quantum chemistry. A general scheme of the process should be as follows:

$$\underset{\substack{\textbf{Sacch}\\\textbf{(saccharose)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\substack{\textbf{SiO}_2\\\textbf{surface}}]{\textbf{T, K}} \underset{\substack{\textbf{Glc}\\\textbf{(glucose)}}}{C_6H_{12}O_6} + \underset{\substack{\textbf{Fru}\\\textbf{(fructose)}}}{C_6H_{12}O_6}$$

Calculations were carried out using the density functional theory method. All initial geometry optimizations and zero point vibrational energy corrections were performed by the B3LYP/ 6-31G**method [10] widely used for studying similar systems with hydrogen bonding and proton transfer. Silica surface was simulated with an adamantane-like structure of $(SiO_2)_9{\cdot}8H_2O$ (A) [11].

Equilibrium structures and total energies of reagents and products were calculated in both the gas phase (vacuum) and an aqueous environment. For the latter the effect of the solvent was taken into account using the continuous self-consistent reaction field theory (SCRF). The results in Fig. 3 show two effects: (i) the solvent noticeably decreases the sum of the total energies of the initial species (Sacch and water); (ii) the presence of an aqueous environment results in a reversal of the sign of the energy change of the reaction, that now becomes more feasible.

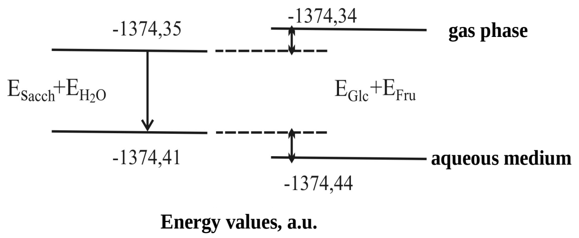

Fig. 3. Energies of saccharose hydrolysis in gas phase and in aqueous medium

The second part of the research was devoted to studies of the structure and formation energy of the adsorption complexes of glucose adsorbed on a dehydrated silica surface. Despite the presence of weak acidic silanol groups on silica, no point was found on the potential energy surface of the system

(A+Sacch) related to a proton transfer from a silanol group to a Saccharose molecule. This result can be explained by a high value of the energy for deprotonation of the silanol group, 1129.3 kJ/mol as theoretically calculated (or 1400±25 kJ/mol as experimentally determined [12]).

Complicate physicochemical processes at the water/silica interface are known to define the structure and properties of water adsorption complexes. It was shown in some theoretical works that in an aqueous shell near silica surface the existence is possible of ion pairs along with polymolecular adsorption complexes of individual water molecules. The structure of the former is built of H_3O^+ ions and superficial $\equiv SiO^-$ groups which in water are separated by a few water molecules. (Fig. 4) According to the results of the calculations, in such structures the Si–O bond is substantially shorter (1.56 Å) than the Si–OH one (1.66 Å). The length of the shortest hydrogen (O···HOH) bond is of 1.75 Å. A characteristic of the ionized states is that the energy of isolation of protons from the water molecules separating the charged centers is far lower (975.8 kJ/mol as calculated) than that of isolated silanol groups (1129.3 kJ/mol). This proves that intermediate water molecules have an enhanced acidity as compared to isolated silanol groups.

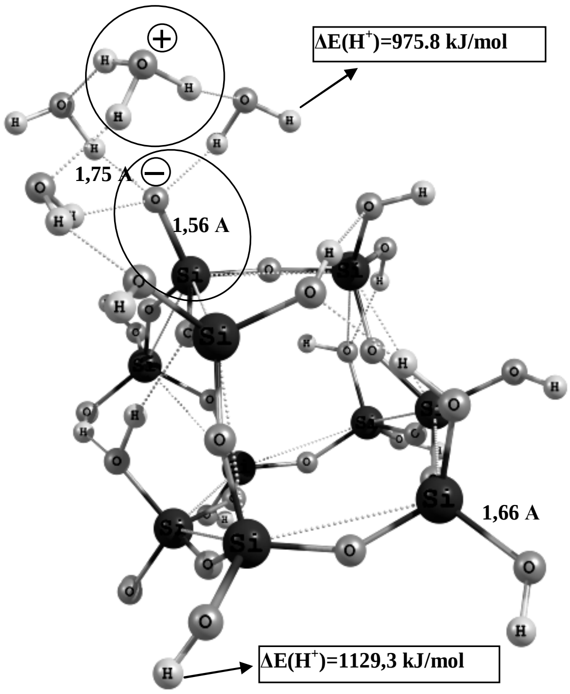

Fig. 4. Structure of a water cluster around isolated silanol group in ion-pair state

The reaction of disaccharide hydrolysis itself can be considered monomolecular. It consists in the breaking up of a glycoside bond of the protonated molecule that results into the formation of a monosaccharide molecule and a carbenium ion. Interaction of the latter with water molecules within the reaction zone produces another monosaccharide molecule and the recovery of the silanol groups.

The calculated formation energy of the adsorption complex of saccharose on hydrated silica surface is of 50.9 kJ/mol. In the case of a dehydrated surface the deprotonation energy is lower (41.0 kJ/mol).

Calculations show a synchronous elongation of the bonds of the glycoside oxygen atom and the carbon atom of the glucose residue. Therefore the hydrolysis should occur by a simultaneous transfer of two protons, as it occurs in most processes of ion-pair formation. Thus, formed fructose molecule would be kept near silica surface by hydrogen bonding (Fig. 5).

The results of computations on the total energy of adsorption complex as a function of the O–H bond length of one of the intermediate water molecules are shown in the Fig. 6.

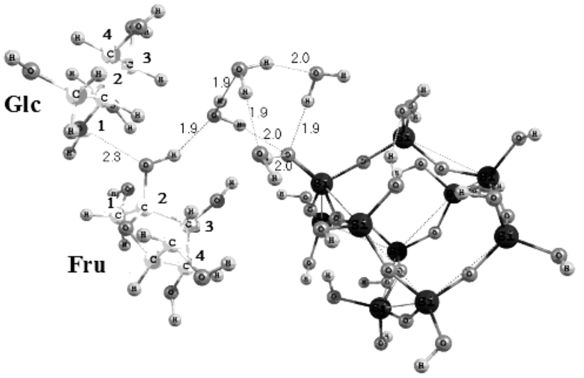

Fig. 5. Proton transfer from the ionized hydrated complex formed around silanol group to the adsorbed saccharose molecule

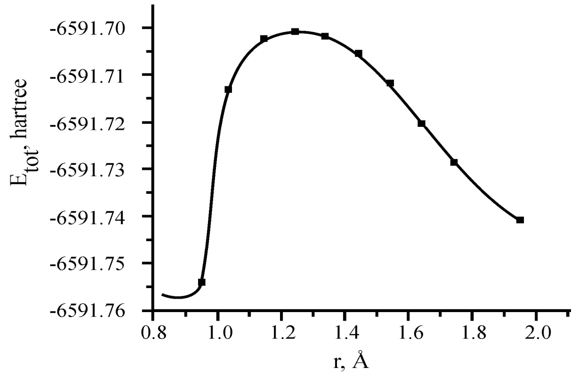

Fig. 6. Dependence of the total energy of the adsorption complex on the O-H bond length of one of the intermediate water molecules

The activation energy of the reaction of saccharose hydrolysis on hydrated silica is rather high (178 kJ/mol) and therefore it is only feasible at relatively high temperatures.

CONCLUSIONS

When adsorbed over silica surface, water gains acidic properties and acts as a catalyst for saccharose hydrolysis.

The application of the idea of ionized states to the hydrated layer of silica surfaces enables simulating a complex set of physical and chemical processes occurring on solid surfaces. These phenomena cannot be simulated using ordinary theoretical techniques that considering only neutral water molecules.

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Роль іонізованих станів молекул води в гідролізі сахарози на поверхні кремнезему

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Запропоновано модель іонних пар, яка пояснює виникнення кислотних центрів на межі поділу фаз поверхня кремнезему – вода. За допомогою квантово-хімічного моделювання було показано, що дисоційована вода відіграє істотну роль в гідролізі сахарози, адсорбованої на поверхні кремнезему.

Роль ионизированных состояний молекул воды в гидролизе сахарозы на поверхности кремнезема

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Предложена модель ионных пар, объясняющая возникновение кислотных центров на поверхности раздела фаз кремнезем – вода. С помощью квантово-химического моделирования было показано, что диссоциированная вода играет существенную роль в гидролизе сахарозы, адсорбированной на поверхности кремнезема.