

Investigation of the Mechanism of Acidic Hydrolysis of Cellulose

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Abstract: The mechanism of an acidic hydrolysis of cellulose is investigated by means of the PM3 molecular-orbital method. The investigation is performed on a sample consisting of 8 monomeric glucose units. The activation energies for the reactions of attacks of hydronium ions on glycosidic bonds in different positions are determined. It is found, on the basis of these energies, that hydrolysis is not favoured in any of the examined positions, i.e. an attack of hydronium ion on all etheric hydrogens is possible with similar probability. This is in agreement with experimental data.

Key words: cellulose, hydrolysis, monosaccharides, glycosidic bonds

Introduction

There are two major types of hydrolysis of cellulose: chemical hydrolysis where dilute and concentrated acids are used, and enzymatic hydrolysis. The factors that make significant influence upon both types of hydrolysis are: characteristics of cellulose material, concentrations of reactants, temperature and reaction time. Some of these factors influence directly the mass and energy transfers, whereas some of them exercise influence upon kinetics (Torget et al., 2000).

Fig. 1. shows that the hydrolysis of cellulose begins with the reaction of acidic proton and oxygen that bonds two glucose units, forming the corresponding conjugated acid. Then, a cleavage of the C-O bond occurs, and a cyclic carbocation is formed. In the next step, after a rapid addition of water, a sugar molecule is formed, and a proton is released (Fengel and Wegener 1998). It is worth pointing out that the formation of the intermediate carbocation is faster at the ends than in the middle of the polysaccharide chain. In accordance

The mechanism of the acidic hydrolysis of cellulose has not been investigated by means of semiempirical methods. The objective of the present work is to fill this gap. The investigations are carried out on a sample consisting of 8 monomeric units.

Materials and Methods

All calculations are carried out with the Spartan'02 program package. The "conformer distribution" function is used to find the minimum energy conformation (Wavefunction, Inc.) The geometry optimization is undertaken at the restricted Hartree-Fock PM3 level. This allows treatment of the system at the quantum-chemical level, and thus provides the opportunity to describe the electronic structures of reactants, intermediates and transition states. The effects of solvent are not considered in this work.

Results and Discussion

Conformational search and optimization of the cellulose fragment with 8 glucose units is carried out. The most stable conformation is shown in Fig. 2.

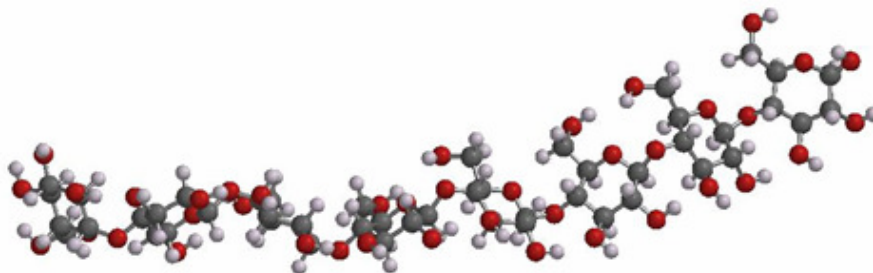


Fig. 2. Optimized structure of a cellulose fragment

The HOMO-LUMO analysis shows that the HOMO orbital is mainly located on the terminal molecule of glucose (Fig. 3.). Therefore, it is justified to expect that this glucose unit will participate in electrophilic reactions. The NBO (Natural Bond Orbital) charge analysis of the investigated fragment reveals that the negative charge is mostly located on oxygen atoms, particularly on the ether oxygen. It is worth pointing out that the molecules of cellulose are stabilized with hydrogen bonds formed among hydroxyl groups. Only ether oxygen is not involved in these bonds. Since the hydroxyl groups are protected, it is reasonable to expect that the ether oxygen will be the most favorable site for an electrophilic attack of hydronium ion.

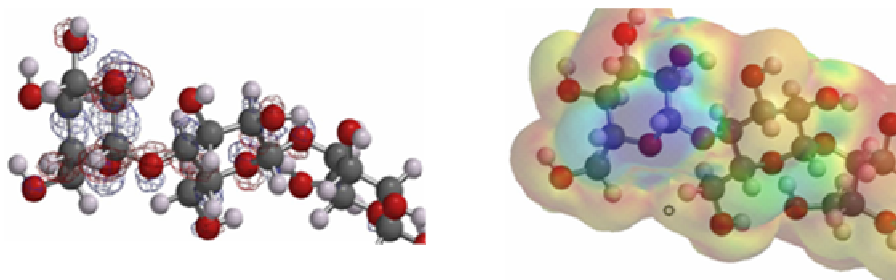


Fig. 3. The HOMO of the investigated fragment (left), and the absolute value of the HOMO mapped on the electron density surface (right).

It is assumed that the hydrolysis reaction starts with an attack of hydronium ion on the oxygen of glucosidic bonds. An attack of hydronium ion on ether oxygen in the positions 1, 2, 3 and 4 is simulated, as illustrated in Fig. 4.

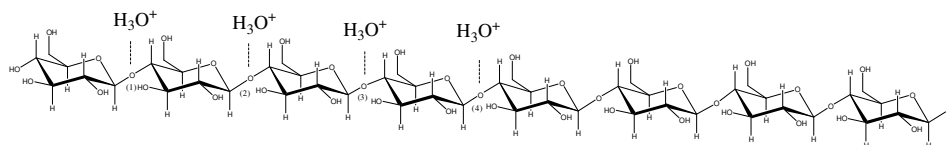
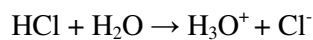


Fig. 4. An attack of hydronium ion on cellulose molecule in positions 1, 2, 3 and 4.

The obtained results for heat of formation of reactants, transition states and products are shown in Fig. 5. It is clear that the activation energy values are mutually very similar, and amount to approximately 21 kcal/mol.

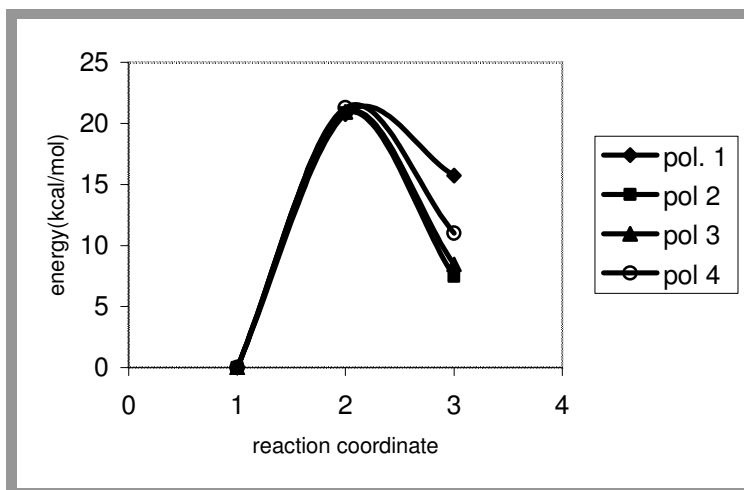


Fig. 5. Variation of heat of formation during the reaction in the positions 1, 2, 3, 4 and 5.

The geometry of the transition state for the reaction in the position 1 is presented in Fig. 6.

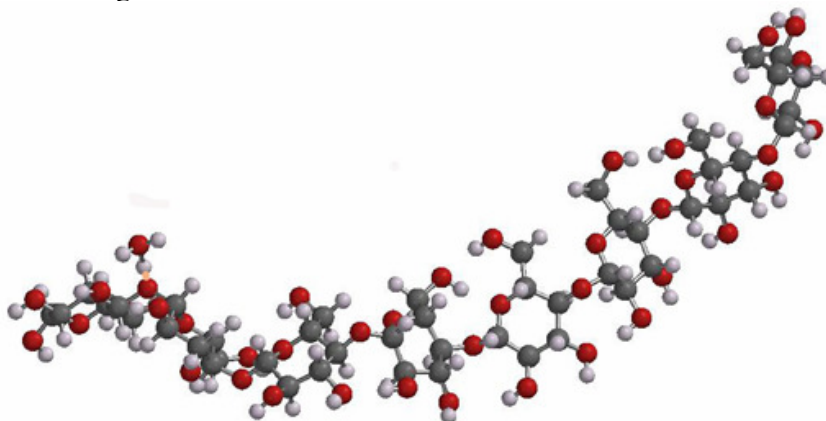


Fig. 6. Transition state for an attack of hydronium ion in the position 1.

The length of the new formed O-H bond in the transition state amounts to 1,128 Å, whereas the length of the O-H bond that is being broken equals to 1.237 Å. In both cases the O-H distances are longer than those in ordinary O-H bonds (0.956 Å). In the transition state the etheric C-O bonds are also elongated (1.477 and 1.459 Å). The corresponding bond lengths in the initial fragment amounted to 1.4 and 1.431 Å, respectively.

In the next step, a water molecule is abstracted, and a relatively stable intermediate (i.e. protonated cellulose fragment) is formed. As shown in Fig. 5., all intermediates are less stable than the reactants. An analysis of the geometries of these intermediates reveals that the above mentioned C-O bonds are additionally elongated (1.518 and 1.449 Å), whereas the length of the new-formed O-H bond is very close to the length of an ordinary O-H bond, and amounts to 0.972 Å. These structural changes are responsible for the stabilization of these intermediates.

An NBO analysis of the cellulose fragment obtained in the reaction in the position 1 shows that the positive charge is located on the C atom bonded to the etheric oxygen, whereas the corresponding C atom in the glucose part is almost neutral. For this reason it is reasonable to expect that the final step of the reaction, i.e. an attack of a nucleophile, will take place on the positive carbon of the cellulose fragment. This step of the reaction is under intense scrutiny.

Conclusion

The obtained values of activation energies for hydrolysis of cellulose in these 4 positions show that the acidic hydrolysis of cellulose is not significantly favoured in any position. This confirms an assumption that on acidic hydrolysis the glycosidic bonds are attacked and broken randomly. In this way numerous

smaller molecules are formed: glucose, cellobiose, and other oligosaccharides. With the further progress of the reaction the quantity of released glucose is increased.

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ISPITIVANJE MEHANIZMA KISELE HIDROLIZE CELULOZE

- originalni naučni rad -

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Rezime

Ispitivan je mehanizam kiselinske hidrolize celuloze na uzorku sa 8 monomernih glukoznih jedinica, pomoću PM3 semiempirijske molekularno-orbitalne metode. Na osnovu dobijenih energija aktivacije za reakcije napada hidronijum jona na glikozidne veze u različitim položajima, nadjeno je da hidroliza nije favorizovana u bilo kom od ispitivanih položaja, odnosno da je moguć napad hidronijum jona na sve etarske kiseonike sa sličnom verovatnoćom, što je u skladu sa eksperimentalno dobijenim podacima.