Roles of hydroxyls in the noncatalytic and catalyzed formation of levoglucosan from glucose

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ABSTRACT

Hydroxyl groups in the simple cyclic sugar β-D-glucose are key to its formation of bicyclic levoglucosan, whether by unimolecular reaction or by catalysis through external hydroxyls or acid molecules. Computational-quantum chemistry calculations of transition states are conducted with substitutions of NH_2 and CH_3 for OH, which reveal the role of lone pairs on the oxygen; with explicit water molecules or implicit water-solvation models, which show the mixed impact of hydrogen bonding; and with Brønsted acid molecules, which relate acid strength to decreased enthalpy of activation.

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1. Introduction

Levoglucosan (1,6-anhydro-β-D-glucopyranose) is one of the most important products in cellulose pyrolysis [1–4], so its formation and pyrolysis paths have been the subject of great interest. It does not appear to pyrolyze before it vaporizes, and its normal boiling point is approximately 550 K [5]. Takahashi et al. [2] experimentally studied high-selectivity glucose decomposition to levoglucosan using high-temperature water, but their empirical modeling proved unsuccessful. Recent research has proposed that concerted reactions form levoglucosan from glucose, cellobiose, and cellulose [6,7], where Seshadri and Westmoreland [6] proposed a pseudopericyclic pathway for the formation of glucose to levoglucosan.

Hydrogen bonding between alcohol groups in glucose and in cellulose plays an important role in the yield of levoglucosan, as do the anions and cations of inorganic salts [8]. Lakshmanan and Hoelscher [9] pyrolyzed starch in a gas stream of helium, nitrogen, and steam and found that use of steam increased the levoglucosan yield. They also found that pretreatment of starch with acetic acid increased the yield of levoglucosan. Inorganic salts and acids promote char formation in cellulose pyrolysis through dehydration reactions [10,11]. Zhou et al. showed experimentally that addition

of excess sulfuric acid promotes dehydration and causes levoglucosan to dehydrate further to levoglucosenone during pyrolysis of wood [12]. They suggested that ash content in wood causes lower catalytic dehydration activity of sulfuric acid at low concentrations. In cellulose pyrolysis, the concentration of organic acid and water provides a delicate balance between depolymerization of cellulose by hydration, dehydration of the products formed due to acid catalyst, and char and carbon formation [10,13].

In this work, the noncatalytic and catalytic chemistry involved in the formation of levoglucosan is analyzed using quantum-chemistry calculations. First, the importance of the OH groups involved in the levoglucosan formation is studied. Further, the influence of water as solvent and catalyst is studied. For this purpose, implicit (CPCM solvation model) and explicit-implicit water molecules are used in the quantum-chemistry calculations. Finally, influence of nonsolvated inorganic acids such as HF, HCl, and H_2SO_4 on the formation of levoglucosan is studied.

2. Computational method

Quantum-chemistry calculations were performed using the Gaussian 09 software package [14]. Structure-optimization calculations were performed at CBS-QB3 [15] or UB3LYP/aug-cc-pvdz level of theory. Transition-state structures were also calculated and verified using intrinsic reaction coordinate (IRC) calculations. Implicit solvation effects were simulated with the CPCM solvation model [16,17]. The electron localization function (ELF), a measure of local excess kinetic energy due to Pauli repulsion introduced by Becke

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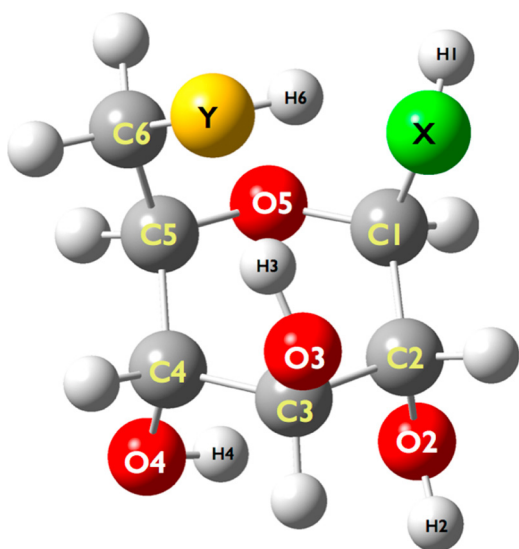[1] Eastman Chemical Company, Kingsport, TN 37662.

Fig. 1. Structure of inverted-chair β-D-glucose substituted for OHs with X and YH at carbon 1 and 6.

		YH				
		OH	NH_2	CH_3	Comparable bond	BDE, kcal/mol
XH	OH	45.1	62.7	84.1	H_3CO—H	104.6 ± 0.8
	NH_2	43.8	60.8	97.8	H_3CNH—H	101.6 ± 2.0
	CH_3	71.0	87.2	109.6	H_3CCH_2—H	100.5 ± 0.3

and Edgecombe [18], was used as a tool to understand the chemistry of levoglucosan formation at a deeper level [19]. DGrid software was used to calculate the ELF [20], and ParaView was used for its visualization [21].

This approach is often described as making "gas-phase" calculations, but the reactions do not necessarily have to happen in the gas phase. Rather, the molecules are independent of interactions with other molecules or, alternatively, the approach can be used to examine specific interactions with other molecules carefully, such as the molecular basis for solvent effects.

3. Results

The molecule conformation and numbering used for the parametric analysis of levoglucosan formation is shown in Fig. 1. Based on the structure of inverted-chair β-D-glucose used in our previous work [6], this structure uses XH for the OH at carbon 1 and YH for the OH at carbon 6. Computationally, various substitutions are made for Y and X to study the combined effects of hydrogen bonding (decreasing from OH to NH_2 to CH_3), lone pairs (changing from 2 to 1 to 0), and XH/YH bond strengths. In this work, "glucose" refers to inverted-chair β-D-glucose unless stated otherwise.

3.1. Effect of substituting OH groups at 1 and 6 in glucose

Noncatalytic unimolecular formation of levoglucosan from glucose is examined by varying the group on carbon 1 (XH) and on carbon 6 (YH) by varying the groups among OH, CH_3, and NH_2, as shown in Fig. 2. These substitutions help in understanding the effects of hydrogen bonding, lone-pair electrons, and size of the substituents on the unimolecular enthalpy of activation. All the calculations in this section are performed using CBS-QB3 level of theory.
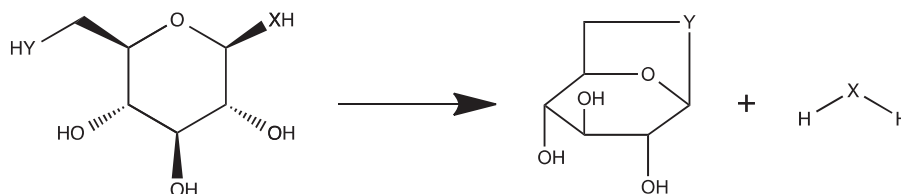
Computed unimolecular transition states are shown in Fig. 3, arranged such that XH (the topmost heavy atom) defines the rows (OH, NH_2, CH_3, top to bottom) and YH the columns (same order). In the (XH, YH)=(OH, OH) transition state shown in Fig. 3a, XH is observed to be detaching from C1 as it attaches to the hydrogen leaving from YH. At the same time, C1 is attaching to Y, forming the levoglucosan ring and completing the four-atom, four-bond cycle of bonding changes. For all the cases where both XH and YH are OH or NH_2 (Figs. 3a, b, c, d, e, and g), the same four-centered transition-state structure is observed. In the other structures (Fig 3f and i), no levoglucosan-like second ring is formed although an H is transferred to XH. The transition-state structures in Fig 3f and i and the imaginary frequency indicate that the hydrogen atom from YH is abstracted by XH. Optimization of the end point from IRC calculations confirmed that the product is not a bicyclic ring but a monocyclic singlet species.

Enthalpies of activation at 298 K are compared in Table 1 for the various substitutions. The increase in enthalpy of activation is higher when YH is NH_2 or CH_3 than when XH is substituted. This effect may be due to steric hindrance and lower lone-pair interaction. In glucose, the hydrogen bonding between H3 and O—H6 (Y—H6) contributes to reduction in activation energy of levoglucosan formation. As the number of lone pairs in YH decreases, the interaction with H3 causes a larger increase in activation energy. This effect does not occur with the substitutions in XH. Based on the structures of the transition states, the effect of hydrogen bonding between the H in OH at carbon 3 with nitrogen is very strong for structure e compared to structure b. This difference seems to be the main reason for the reduction in activation energy.

The substitution of methyl leads to a pure bond-breaking and bond-making interaction rather than lone-pair-driven interaction. Computed bond dissociation energies of methanol, methylamine, and ethane [22,23] are also shown in Table 1. For glucose conversion to levoglucosan, enthalpy of activation is less than half the value of the bond dissociation energy of an O—H bond in methanol. When both the alcohol groups were substituted with methyl groups, the enthalpy of activation is close to the bond dissociation energy of C—H bond in ethane. Moreover, strain in the transition-state structures for XH=CH_3 and YH=CH_3 (Fig. 3, lower right corner) causes the enthalpy of activation to be more than the bond dissociation energy of the methyl C—H bond.

ELF is used to distinguish between the pericyclic and pseudopericyclic nature of a transition state in concerted electrocyclic reactions. When the electrons are localized, ELF = 1, and ELF = 0.5 in the case of a delocalized homogeneous electron gas [24]. For pseudopericyclic reactions, there is participation of non-bonding

Fig. 2. The oxygen atoms at position 1 and 6 of glucose are replaced by X and Y, respectively.