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Abella, Lorene

Applied Quantum Physics and Nuclear Engineering, Faculty of Engineering, Kyushu University

Nanbu, Shinkoh

Computing and Communications Center, Kyushu University : Associate Professor

Fukuda, Kenji

Institute of Environmental Systems, Faculty of Engineering, Kyushu University : Professor

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A Theoretical Study on Levoglucosan Pyrolysis Reactions Yielding Aldehydes and a Ketone in Biomass

by

Lorene ABELLA^{*}, Shinkoh NANBU^{**} and Kenji FUKUDA^{***}

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Abstract

Cellulose composes most of domestic, industrial, and agricultural wastes, forest products and indigenous plant materials valued as biomass resources. The immensity of these materials should be a driving force to efficiently exhaust them as energy sources and, in effect, offset environmental impact of wastes. This study focuses on the pyrolysis reactions of cellulose as a main component in biomass through thermal degradation of levoglucosan – an intermediate crucial to the formation of char and other products. Theoretical calculations involving DFT and MP2 methods were employed to investigate molecular and activation energies as well as verify proposed reaction mechanisms in cellulose pyrolysis. The differences between the calculated proposed structures are illustrated.

Keywords: biomass, cellulose, levoglucosan, density functional theory (DFT), 2nd order Møller-Plesset (MP2) theory

1. Introduction

Cellulose, which is an abundant component in plants and wood, comes in various forms and a large fraction comes from domestic and industrial wastes. With the volume of wastes accumulating every day, these sources would best be recycled as biomass sources, which can be combusted to produce heat, fuel gases, and charcoal that may be stored as a reserve fuel, or converted to alcohols as an alternative fuel source to fossil fuels. At present, most countries are seriously considering biomass for energy. China, for example, is one of the major biomass consumers in the world exceeding 200% more than the quantities utilized by other countries in 2002. Brazil produces charcoal from eucalyptus and ethanol from sugarcane and bagasse. The US uses forest products and residues for energy¹⁾. These are just a few of a myriad of examples of biomass utilization for energy. On the fuel procurement and waste management points of view, biomass sources are

* Graduate Student, Applied Quantum Physics and Nuclear Engineering

** Associate Professor, Computing and Communications Center

*** Professor, Institute of Environmental Systems

relatively at zero cost²⁾ and their carbon-neutral properties offset environmental impact since most of these are recovered from waste. In Japan, the potential energy equivalent of municipal wastes for 2005 and 2010 is statistically estimated to be 2~3% of its primary energy consumption³⁾.

The main purpose of this paper is to show that effective biomass burning for alternative energy production boils down to efficient pyrolysis of cellulose. It is widely accepted that cellulose degradation through pyrolysis proceeds in two separate paths: (1) depolymerization, which is responsible for levoglucosan (1,4- β -D-glucopyranose) production and (2) dehydration that accounts for char formation⁴⁾. Anhydrosugars constitute more than 40%^{5, 6)} of the depolymerization products in path (1), which is mainly levoglucosan that further breaks down into other smaller and volatile substances⁷⁾. Polymerization of levoglucosan is deemed crucial not only in the formation of char in that its inhibition may preclude the production of the latter and limiting it eventually leads to the formation of the same⁸⁾ but also other pyrolysis products that are essential chemicals. Identical pyrolysis products of both levoglucosan and cellulose were obtained; of these are formic acid, hydroxyacetaldehyde, 2, 3-butanedione, CO, CO₂, acetaldehyde, and so on to name a few^{9, 10)}. A clear understanding of the reactions of levoglucosan degradation is therefore essential to elucidate the reaction mechanism of cellulose pyrolysis. Four reaction mechanisms of the thermal degradation of levoglucosan for the formation of smaller molecules that are mostly composed of aldehydes and a ketone were proposed by Pouwels et al¹¹⁾, and in this paper ab initio and quantum molecular calculations and were performed to confirm these reactions, however, only the first mechanism (see Fig.1) is discussed in this paper.

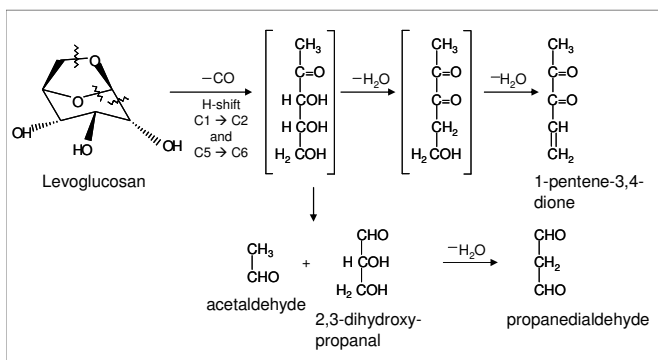


Fig. 1 One of the proposed mechanisms on the thermal decomposition of levoglucosan by Pouwels et al⁷⁾.

2. Methods

Levoglucosan decomposition via dehydration, release of carbon monoxide, and ketone and aldehyde formation are theoretically verified according to the first mechanisms proposed by Pouwels et al.¹¹⁾ Theoretical chemical calculations are effective in numerically simulating chemical reactions and structures that are otherwise unobtainable through direct experimentations¹²⁾. The theoretical methods adhere to the fundamental physical laws that involve accurate orbital approximations of molecular structures consistent with actual experimental observations. Geometry optimizations and transition state (TS) structures calculations were carried out by employing the Becke-3-Lee, Yang, and Parr (B3LYP) level density functional theory¹³⁻¹⁵⁾ and the second-order Møller-Plesset (MP2) perturbation theory with Dunning's correlation consistent, polarized valence, double zeta (cc-pVDZ) basis set¹⁶⁾. Harmonic vibrational frequencies were obtained at each level

of theory to characterize the stationary points at local minima or first-order saddle points, make zero-point vibration energy (ZPE) corrections, and generate force constant data needed in the intrinsic reaction coordinate (IRC) calculations¹⁷⁾ for the reaction channels with a saddle point. The IRC method was used to track minimum energy paths from TS to the corresponding local minima. Basis set superposition errors (BSSE) were also corrected through counterpoise correction. All calculations were performed using the Gaussian 03 software package¹⁸⁾. For a thorough description of the above methods, refer to [19–21]. A brief introduction is discussed in our previous work²²⁾ with a focus merely onto the breakdown of levoglucosan into smaller components.

3. Results and Discussion

The optimized geometries of all stationary points are shown in **Fig.2** according to their order of formation and decomposition in the proposed reaction mechanism. The bond angles and bond lengths of optimized product species and some of the important reaction sites are listed in **Table 1**. The relative energies and corrected barrier heights integrated with ZPE corrections of all species at MP2 and B3LYP levels are shown in **Fig. 3**. The maximum activation energy achieved for both levels without the introduction of ZPE corrections is about 7% higher than the ones introduced with ZPE corrections. Single point calculations were also performed to evaluate effects on the results as the quality of basis sets is improved; augmented cc-pvdz and cc-pvtz were used. A uniform decrease in the molecular energies of each species was observed, however, nothing conclusive can be made on the activation and complex energies. Formation of the first intermediate and the ketone are exothermic while the rest are endothermic, and these are discussed in each of the reaction steps in the succeeding sections.

3.1 CO removal step

Figures 2a and **3a** show the molecular structures and energetics of the CO removal step. Opening of the pyranose ring in levoglucosan due to the cleavage of C₁-O₇ and O₈-C₆ resulted to a C₁-O₈ double bond formation and consequently, forming a cyclic C₆-O₇-C₅ bond. In MP2, this cyclic bond shifted to partial double bonds between C₅-O₇ and C₅-C₆, with H19 breaking away from C₅ as it approaches C₆ during transition (TS1). In B3LYP, however, none of these partial double bonds were formed, but instead, a pseudo linear C₁-O₈=H₁₂ bond was found at TS. Culmination of the carbon monoxide release reduced the molecule to the first intermediate— a five-member carbon chain, 3,4,5-trihydroxy-2- pentanone (I₁) with O₇ rotating right-handedly at ~100° from the its original orientation. The barrier height in B3LYP is 3 times greater than in MP2. This over-approximation may be attributed to the long-range interaction energy obtained by the dynamical correlation which is not thoroughly considered in the DFT method¹⁹⁾, hence, only the optimized structures in MP2 are illustrated. In ref. [22] and [23] as cited in [24], cellulose and levoglucosan are known to have similar enthalpies of formation, which suggests that the dissociation of both to other substances will occur in a relatively similar fashion, and can be supported by the presence of similar condensation products²⁵⁾ from separate thermal decomposition processes of both substances. Thus, the reaction should proceed easily at an activation energy of 26.96 kcal·mol⁻¹ (in MP2) since this is small compared to that of microcrystalline cellulose calculated at ~45 kcal mol⁻¹²⁶⁾ and some wood species whose activation energies are as high as ~109.9 kcal·mol⁻¹²⁷⁾.

3.2 Dehydration step and Ketone Formation

Breakdown of the aforementioned intermediate led to simultaneous bond cleavages in C₃-C₄,

O₈-H₁₄ from C₂, and deprotonation of O₉ in favor of the leaving OH to produce water resulted to a partial double bond formation between O₉-C₃ and C₃-C₂ during TS2; see **Fig.2b**. The main molecule divides into two separate structures during the transitory separation between C₃ and C₄. From the B3LYP calculation, C₃-C₄ bond does not break during TS nor a partial double bond formed between C₃-C₂, however, O₉=C₃ weakens after being transformed to a partial double bond. Water was released after H₁₆ bonded with O₈-H₁₄ thus forming the second intermediate where a C₃-O₉-C₂ cyclic bond was formed. This differs from the proposed structure where O₉ is doubly bonded to C₃. Further dehydration took place prior to the formation of the final product. Cleaving

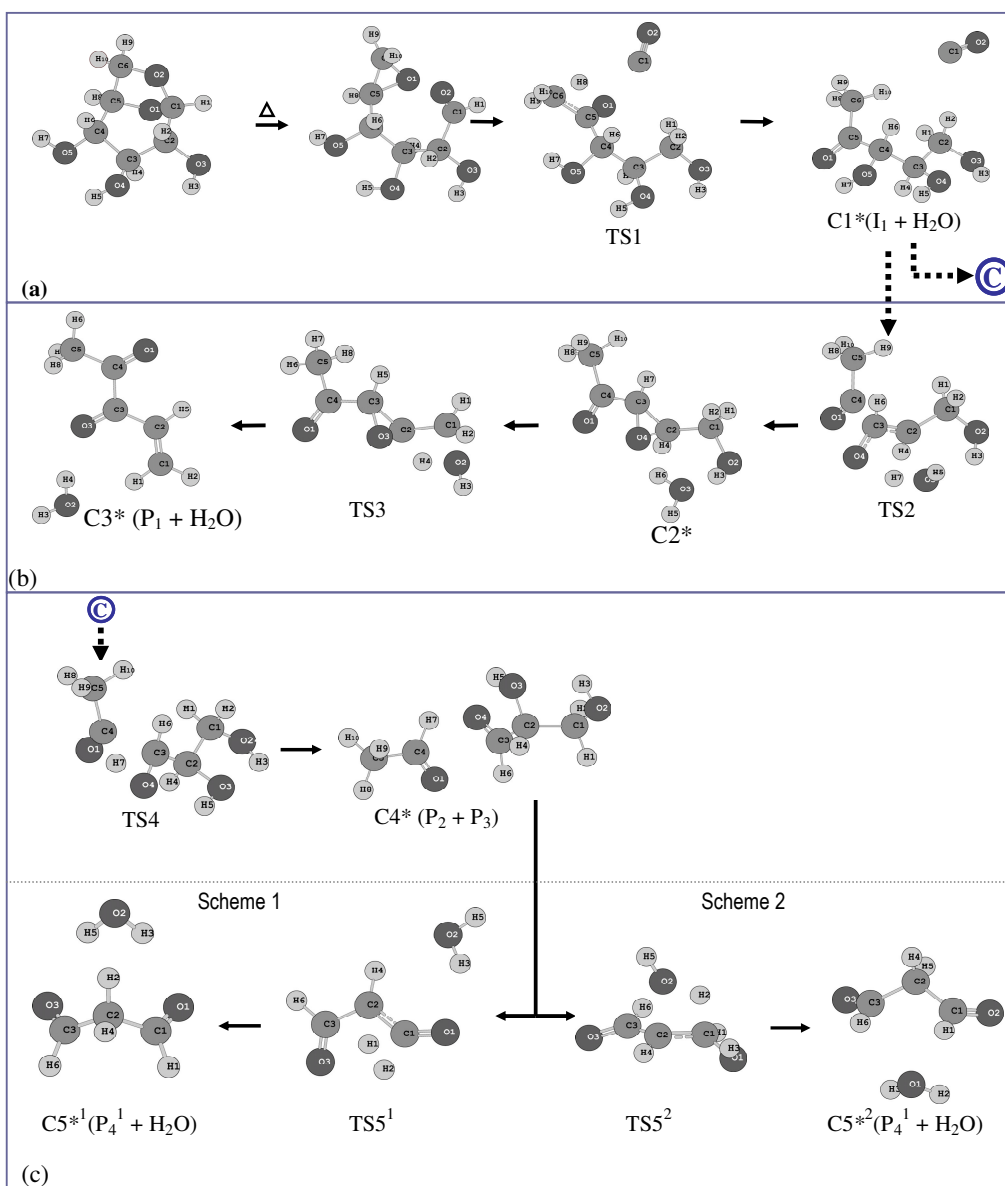


Fig. 2 Optimized geometries and reaction mechanism of levoglucosan in the MP2 level. (a) CO elimination, (b) Dehydration, and (c) Aldehyde formation.

Table 1 Selected bond lengths (in angstroms) and angles (in degrees) of active sites in the transition, complex, and optimized product structures.

Complexes, TS, and Products	Atom Numbers	Bond Lengths and Angles		Complexes, TS, and Products	Atom Numbers	Bond Lengths and Angles		Complexes, TS, and Products	Atom Numbers	Bond Lengths and Angles		
		B3LYP	MP2			B3LYP	MP2			B3LYP	MP2	
Levoglucosan	C1-C2	1.5457	1.5385	Path 1: C3*	C1-C4	2.9268	2.9335	1-pentene-3,4-dione	C1=C2	1.3401	1.3506	
	C1-O8	1.4315	1.4346		C1-O5	1.2077	1.2175		C2-C3	1.4845	1.4900	
	C1-O8-C6	106.8681	106.5015		C3-O6	1.2077	1.2175		C3-C4	1.5487	1.5428	
	C3-C4-C5	109.2310	109.0597		C1-C2-C3	113.7650	113.1129		C4-C5	1.5067	1.5094	
C6-O8 cleavage	C1-O8	1.2110	1.2221	Path 2: TS3	C1-O4	1.2356	1.219		C3=O7	1.2203	1.2294	
	C6-O8	4.8921	3.0902		C2-O5	3.1537	3.2342		C4=O6	1.2153	1.2256	
	C6-O7	1.4326	1.4432		C3-O6	1.2230	1.2296		C1-C2-C3	120.6989	120.0001	
	C5-O7-C6	61.9493	61.5662		C1-C2-C3	119.0760	118.449		C3-C4-C5	116.1143	115.8130	
TS1	C1-O8	1.1709	1.1467	Path 2: C3*	C1-O4	1.2111	1.2188		C1-C2-C3-C4	180.0000	-179.9963	
	C1-H12	1.0930	-		C2-O5	3.3477	3.4527		6-C2-C3-O7	-179.9788	-179.9940	
	C2-H12	1.7625	1.0989	C3-O6	1.2055	1.2188	acetaldehyde	C1-C2	1.5067	1.5097		
	C5-C6	1.4720	1.4293	C1-C2-C3	112.7904	108.4022		C1=O3	1.2083	1.2183		
	C5-O7	1.4405	1.2936	TS4	C2-C3	1.4673	1.4342	C1-H4	1.1239	1.2145		
	C6-O7	1.4376	-		C3-C4	1.6132	1.7970	O3-C1-C2	124.8189	124.5996		
	O7-C5-C6	59.1331	109.2190		C3-O9	1.2887	1.3035	C2-C1-O3-H4	180.0000	180.0000		
C1*	C1-O8	1.1338	1.1460		C4-O6	1.1985	1.2046	2,3-dihydroxypropanal	C1-C2	1.5417	1.5349	
	C5-O7	1.2202	1.2279	C3-H15	1.1665	1.1164	C2-C3		1.5104	1.5131		
	TS2	C1-C2	1.5223	1.5194	C4*	C2-C3	1.4850		1.4849	C3=O6	1.2133	1.2228
		C2-C3	1.5323	1.5312		C2-O9	1.4366		1.4394	C1-O4	1.4088	1.4110
		C3-O9	1.3544	1.3558		C3-O9	1.4337		1.4377	C2-O5	1.4108	1.4136
C4-C5		1.5067	1.5098	C1-O7		1.4070	1.4094	C1-C2-C3	111.5478	110.8859		
C4-O6		1.1955	1.2056	C3-H15		1.0975	1.0983	C1-C2-C3-O6	-116.6375	-114.3603		
C2*	C1-C2-C3	114.8078	115.5404	TS5	C2-O9-C3	62.3112	62.1419	propanedialdehyde	C1-C2	1.5189	1.5193	
	C1-C2	1.5416	1.5348		C3-O8	1.4314	1.4307		C2-C3	1.5189	1.5193	
	C2-C3	1.5097	1.5144	C1-O7	1.7883	1.7447	C1=O4		1.2060	1.2169		
	C3-O9	1.2165	1.2233	C2-O8-C3	61.9825	61.6987	C3=O5		1.2060	1.2169		
	C4-C5	1.5045	1.5077	C5*	C1-C2	1.3431	1.3522		C1-H6	1.1224	1.1209	
C4-O6	1.2109	1.2205	C2-C3		1.4780	1.4853	C2-O7	1.0984	1.0998			
C1-C2-C3	111.5225	111.0711	C3-O8		1.2253	1.2319	C1-C2-C3	113.1136	111.8547			
Path 1: TS3	C1-O4	1.3970	1.4042		C4-O6	1.2148	1.2253	C1-C2-C3-O4	-130.2777	-126.7239		
	C2-O5	1.9986	1.9187		C1-C2-C3	121.9504	120.9830	water	O-H	0.9685	0.9649	
	C3-O6	1.2129	1.2227	C2-C3-C4-C5	179.5063	179.7284	H-O=H		102.7508	101.8938		
	C1-C2-C3	121.4828	120.1297	O8-C3-C4-O6	179.4583	179.7068	Carbon monoxide	C-O	1.1347	1.1472		

off of the hydroxyl bond from C_1 did not have any effect on the cyclic bond; at TS3 in MP2, the hydrogen approached O_7 of this hydroxyl group. Water was formed exothermically unlike the endothermic requirement of the first dehydration step. A full left-handed rotation of C_3 - C_4 - C_5 produced the stable *trans*-isomer of a planar 1-pentene-3, 4-dione (P_1) molecule. There was no mention of whether the molecule existed as a *cis*- or *trans*-isomer in the proposed mechanism. B3LYP results showed no double bond in C_1 - C_2 during TS. Dry α -cellulose has a heating value of $4177.693\text{kcal}\cdot\text{kg}^{-1}$ ²⁸⁾ and $\sim 4242\text{kcal}\cdot\text{Nm}^{-3}$ ²⁹⁾ or approximately $95\text{kcal}\cdot\text{mol}^{-1}$. Comparing the barrier heights in **Fig. 3b** and **3c**, TS2 has a much lower energy requirement and may proceed

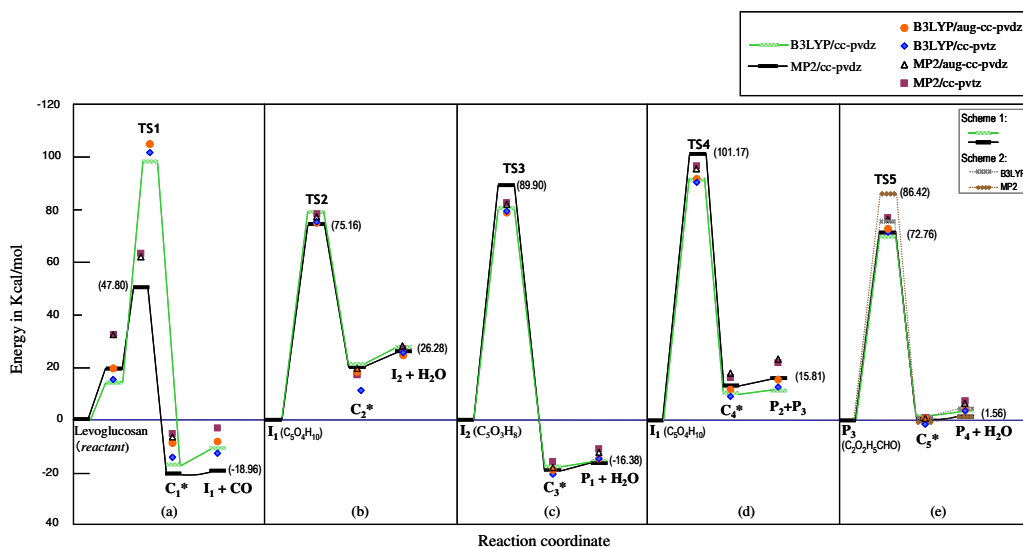


Fig. 3 Potential energy diagram of the thermal decomposition of levoglucosan where C_i^* , I_i , and P_i are the product complexes, intermediates, and products in the reactions. All values are BSSE and ZPE corrected.

spontaneously after heat treatment, TS3 however, is close to the above limits and may proceed slowly and forms products in rather small quantities. This is consistent to the mass spectrometry (MS) data given by Pouwels et al.

3.3 Aldehyde Formation

Acetaldehyde and 2,3-dihydroxypropanal are also formed after cleavage of the C_3 - C_4 bond in the first intermediate (**Fig. 2c**). A simultaneous hydrogen transfer occurs from the larger to the smaller molecule, i.e., to C_4^* , during TS4, which is highest (**Fig. 3d**) among all reactions in this proposed path. 2,3-Dihydroxypropanal is dehydrated to form propanedialdehyde and there are two possible ways by which this is achieved. The first mechanism is the cleavage of the hydroxyl group of the α -carbon and simultaneous deprotonation of the hydroxyl group in the β -carbon to bond with the leaving OH due to steric effects. The second mechanism differs in that the one leaving is the hydroxyl group of the β -carbon followed by migration of the one bonded to the α -carbon to replace it. One of the two remaining H atoms on the terminal carbon delocalizes to bond with the β -carbon. However, with a relatively consistently large difference of 15kcal/mol in MP2 and 5kcal/mol in B3LYP for the TS energy (**Fig. 3e**), only the first condition is likely to occur. Though the activation energy, TS5, for the dehydration of 2,3-dihydroxypropanal to produce propanedialdehyde is quite low, the preceding reaction, although just mildly endothermic, requires too high an energy that propounds less probability for such reaction to occur in this particular step.

Basing on the calculation results, the transition energies are too high for the reactions to proceed and since such are slightly endothermic this particular path may not be ideal for heat production.

4. Conclusion

The present results corroborate the proposed reaction mechanisms. In addition to these, we found some notable differences from our results: (1) dehydration of 2,3-dihydroxypropanal to form propanedialdehyde formation is only possible via α -carbon release, however, due to a very high activation energy of acetaldehyde and 2,3-dihydroxypropanal formation, such reaction might not be the appropriate pathway for production of these aldehydes; (2) the first dehydrated intermediate, I₁, possesses a cyclic C-C-O bond; and (3) 1-pentene-3, 4-dione exists as a more stable *trans*-isomer, which is not considered in the proposed mechanism. However, the high activation energies suggest that the reactions in this present mechanism are unlikely to occur, and that the species obtained from the experimental observations of our reference paper must have undergone through another separate mechanism. Moreover, since the overall reaction in the mechanism presented here is slightly endothermic, this path is not suitable on the viewpoint of biomass as a heat source. A complete and thorough evaluation of the rest of the proposed mechanisms will be presented in a separate paper with an aim to find pathways of lower energy requirements and thus can be deemed ideal for energy production and evolution of other valuable chemicals; further calculations are in progress.

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