LETTER

# Pyrolysis of D-Glucose to Acrolein

Chong Shen, Igor Ying Zhang, Gang Fu, Xin Xu*

*State Key Laboratory for Physical Chemistry of Solid Surfaces; Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005*

Despite of its great importance, the detailed molecular mechanism for carbohydrate pyrolysis remains poorly understood. We perform a density functional study with a newly developed XYG3 functional on the processes for D-glucose pyrolysis to acrolein. The most feasible reaction pathway starts from an isomerization from D-glucose to D-fructose, which then undergoes a cyclic Grob fragmentation, followed by a concerted electrocyclic dehydration to yield acrolein. This mechanism can account for the known experimental results.

**Key words:** D-glucose, Pyrolysis, Acrolein, Reaction mechanism, Density functional theory, XYG3

Carbohydrate pyrolysis is of great importance in the use of biomass [1, 2]. This process is also intensively involved in food industry and tobacco industry [2, 3]. D-glucose is an important representative of carbohydrates. Formations of simple aldehydes, such as formaldehyde, acetaldehyde, and acrolein, are correlated to D-glucose pyrolysis [4−6]. Simple aldehydes are not only widely used industrial chemicals, but also classified as carcinogens. Hence understanding of the chemistry of D-glucose pyrolysis is vitally important.

Despite of this importance, much of the detailed mechanism of carbohydrate pyrolysis is still little-known [4−9]. Such a gap has been partially filled by a recent systematical experimental work of Paine et al. [4−6], who investigated the flash pyrolysis of D-glucose using variously labeled $^{13}C$ in conjunction with gas chromatography/mass spectroscopy (GC/MS). Possible pyrolysis mechanisms have been suggested, although no theoretical calculations have been carried out to quantify the mechanisms. There are a few related theoretical studies. For instance, Nimols et al. have performed CBS-QB3 [10] calculations to investigate dehydration mechanisms of neutral glycerol [8]. Abella et al. [9] have studied the reaction mechanisms of cellulose pyrolysis and levoglucosan decomposition by using density functional theory (DFT) method (B3LYP [10−12]) as well as the second-order Møller-Plesset (MP2 [10]) perturbation theory.

B3LYP is one of the most widely used theoretical methods, especially in chemistry [10−12]. Despite of its great success, there are now accumulating evidences showing that B3LYP degrades in thermochemistry calculations as the system size increased, and has a ten-

dency to underestimate the reaction barrier heights as well as the nonbonded interactions [13, 14]. Recently, our group has developed a new functional, XYG3 [15], which was shown to significantly surpass B3LYP to overcome these drawbacks. As a specific validation of XYG3 for carbohydrate chemistry, we have firstly compared the B3LYP and XYG3 results with Nimlos CBS-QB3 results [8] on the energetics of glycerol dehydration. As compared to the accurate CBS-QB3 results, the mean absolute deviation (MAD) associated with XYG3/6-311+G(3df,2p) is 9.20 kJ/mol, while the corresponding MAD of B3LYP with the same basis set is 32.19 kJ/mol.

In this work, we present the first theoretical study on the pyrolysis mechanisms from D-glucose to acrolein. Geometry optimizations and frequency calculations were carried out by using B3LYP/6-311G(d,p). The final energies were evaluated by single point calculations using XYG3/6-311+G(3df,2p). Experimentally, it was found that aldehydes were formed at temperature ranges between 600 and 800 K, with 700 K as the most preferable [2]. Hence, in addition to zero-point energy (ZPE) correction, thermo corrections to 700 K were also included. All calculations were performed by using Gaussian 03 suite of program [10].

It was reported that there are 126 possible conformers of glycerol due to the formation of internal hydrogen bonds [8]. D-glucose shall bear more conformational complexity. A detailed characterization of its conformers goes beyond the scope of the present work. To simplify the calculations, we choose the corresponding conformer of the open chain form (**1** in Fig.1) as the initial reactant for each reaction path. The terminal aldehyde carbon is labeled as C1, and all six carbons are labeled sequentially. The possible reaction mechanisms for pyrolysis of D-glucose to acrolein are summarized in Fig.1. Our calculated reaction energetics are depicted in Fig.2, and the optimized transition state structures are shown

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*Author to whom correspondence should be addressed. E-mail: xinxu@xmu.edu.cn
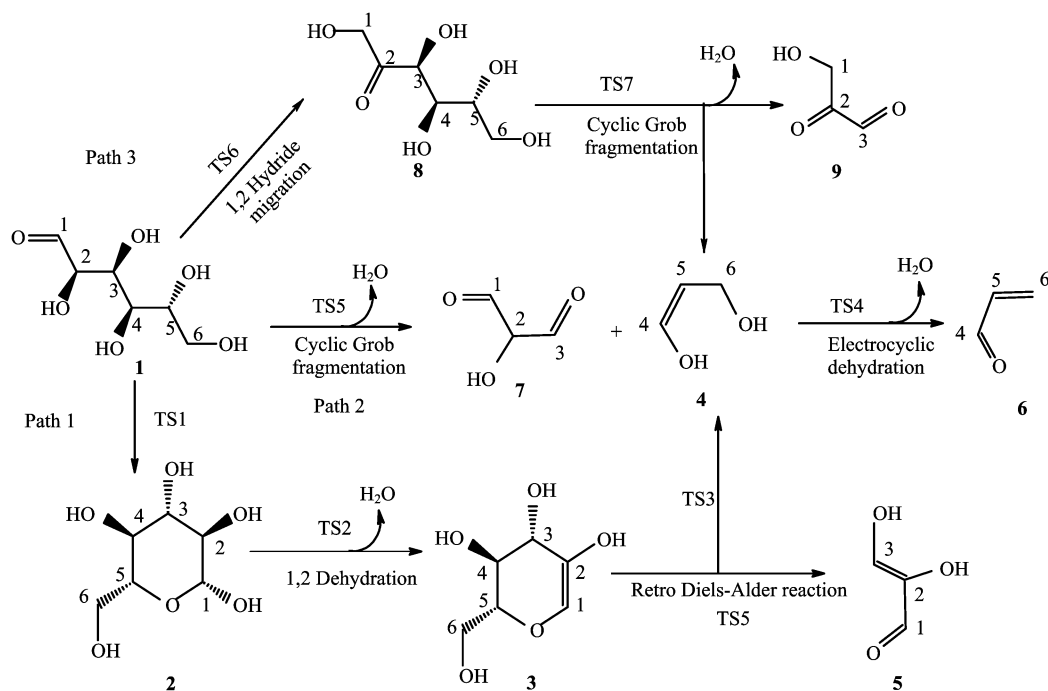
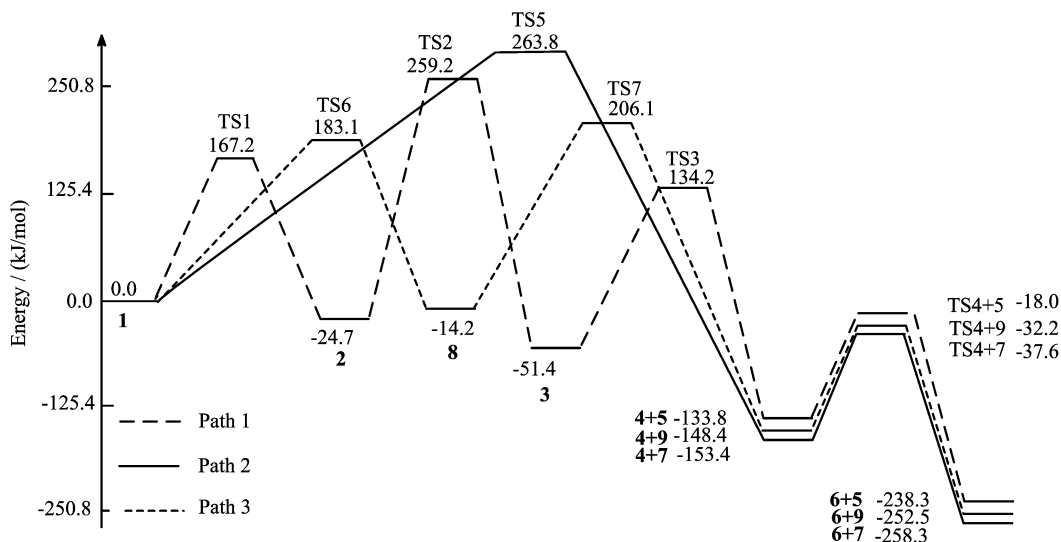FIG. 1 Reaction mechanisms for pyrolysis of D-glucose to acrolein.



FIG. 2 Schematic potential energy curves for pyrolysis of D-glucose to acrolein.

in Fig.3.

It is well known that the carbonyl group in glucose is not free, which may combine with the hydroxyl group at C5 to form a hemiacetal (path 1). **2** is an anomer of six-membered pyranose, which is 24.66 kJ/mol more stable than the open chain form glucose **1**. A barrier of 167.2 kJ/mol (TS1) has to be overcome from **1** to **2**. The step followed is a 1,2-dehydration process, where a hydroxyl group at C1 and a hydrogen at C2 are expelled as a water to generate a cyclic enol **3**. The associated barrier height (TS2) is as high as 283.82 kJ/mol, which represents the rate determining step of path 1. Fragmentation is carried out via a retro-Diels-Alder reaction with the reaction barrier of 186.01 kJ/mol (TS3). Fragment **4** (prop-1-ene-1,3-diol) is the alkene and fragment **5** (2,3-dihydroxyacrylaldehyde) is the corresponding diene in the Diels-Alder reaction. Fragment **4** is made of C4, C5 and C6, which, upon a concerted electrocyclic dehydration with a barrier height of 115.79 kJ/mol (TS4), affords the target product acrolein **6**.

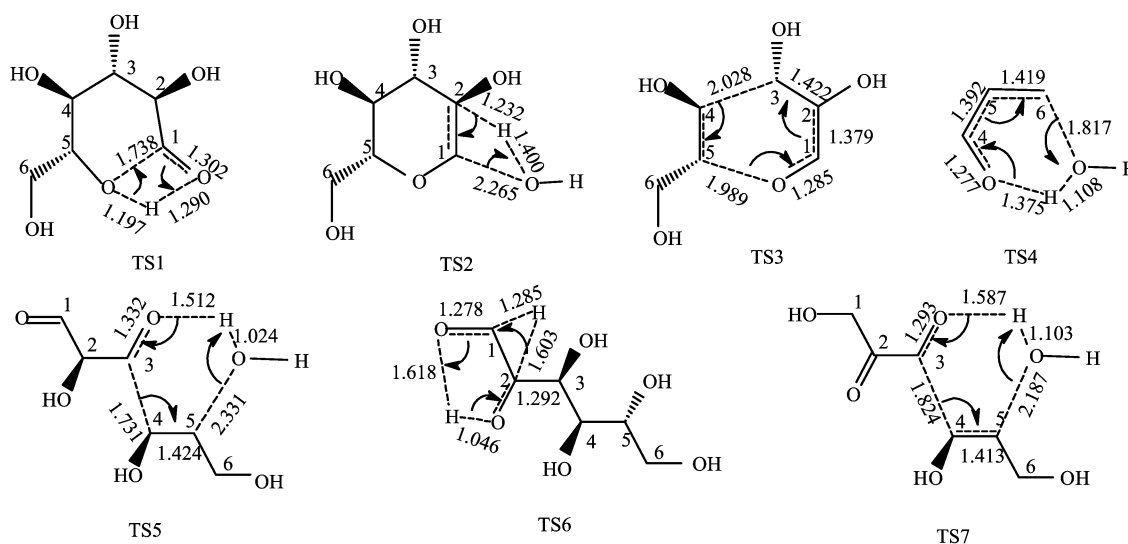Cyclic Grob fragmentation was assumed to be the

FIG. 3 The optimized geometries of the transition states for pyrolysis of D-glucose to acrolein. Bond distances are in Å.

main reaction path leading to carbohydrate degradation [4−6]. We calculate the barrier (263.76 kJ/mol) for such a process from **1** via TS5 (path 2). Here proton in the hydroxyl group at C3 will be transferred to the hydroxyl group at C5, losing the 5-oxygen as water. At the meantime, the C−C bond between C3 and C4 will be cleaved, forming fragments **4** and **7**. Fragment **7** (2-hydroxymalonaldehyde) is a tautomer of fragment **5** in path 1, while fragment **4** will again undergo electrocyclic dehydration, yielding the desired product acrolein **6**.

It is well known that D-glucose can convert to D-fructose by way of enediol intermediate as a consequence of base-catalyzed reaction. Our calculations suggest that, in gas phase pyrolysis, the isomerization of D-glucose to D-fructose can also be realized without going through enolization. As shown in path 3 in Fig.1, a 1,2-hydride migration initiates a one-step process that exchanges the carbonyl and the hydroxyl group between C1 and C2, converting D-glucose **1** to D-fructose **8**. The corresponding transition state (TS6) is displayed in Fig.3, where the hydride at C2 attacks the electro-positive C1, and simultaneously, proton of hydroxyl at C2 is transferred to the terminal aldehyde oxygen. The activation barrier for this step is calculated to be 183.08 kJ/mol. The next step is the cyclic Grob fragmentation of D-fructose **8** via TS7, leading to fragments **4** and **9**. As compared to that via TS5, barrier height via TS7 is less by 43.05 kJ/mol, probably due to structure of more favorable internal hydrogen bondings. Fragment **9** (3-hydroxy-2-oxo propanal) is an isomer of **5** in path 1 and **7** in path 2. We calculate that **9** and **7** are 14.63 and 19.65 kJ/mol, respectively, more stable than **5**. As compared to the other two pathways, path 3 is the most feasible, the barrier from **8** to TS7 is 220.7 kJ/mol.

By means of isotopic ^{13}C labeling and GC/MS, Paine *et al.* have systematically investigated the product distribution from flash pyrolysis of D-glucose [4−6]. As 63% of all the acrolein formed was found to be from C4, C5 and C6, with the aldehyde group derived specially from C4 and the vinyl group derived from C5 and C6, they suggested that the dominant mechanisms should be unimolecular, where there were two competing channels as path 1 and path 2 shown in Fig.1 [4−6]. Paine's unimolecular pathways are, however, not in accordance with earlier experimental conjecture of Stein's, which involved homolytic cleavage of C−C bond between C1 and C2 to form radicals [7]. Stein reported an activation energy (232.40±22.99 kJ/mol) [7], which was criticized by Paine *et al.* as being not consistent with the energy needed for C−C bond homolysis [4−6]. Nevertheless, there were no corresponding calculations reported up to now to quantify Paine's proposals [5]. Our present work fulfills such a purpose, giving strong support to Paine's cyclic unimolecular mechanisms. We show here path 1 and path 2 are indeed competitive. Particularly, the best pathway is identified as path 3 where glucose is first converted to fructose, which then undergoes cyclic Grob fragmentation. Path 3, possessing an effective barrier of 206.07 kJ/mol, also yields acrolein made of C4, C5 and C6, in good agreement with known experimental results.

To summarize, the present work provides the first density functional study with a newly developed XYG3 functional on the pyrolysis reaction pathways from D-glucose to acrolein. It is shown that the most feasible reaction pathway involves an initial isomerization of D-glucose to D-fructose, followed by cyclic Grob fragmentation to propene-1,3-diol, which undergoes a concerted electrocyclic dehydration to yield acrolein. Our proposed mechanism is in good agreement with the ex-

perimental results based on $^{13}C$ isotopic labeling in conjunction with GC/MS characterization.

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