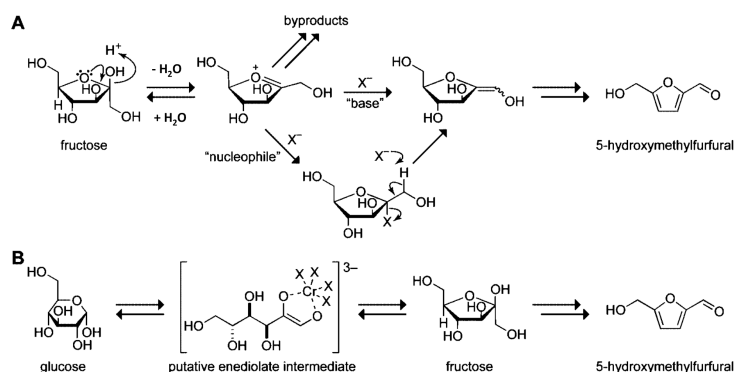


Theoretical Study of Glucose Hydrolysis Mechanisms using RISM-SCF-SEDD

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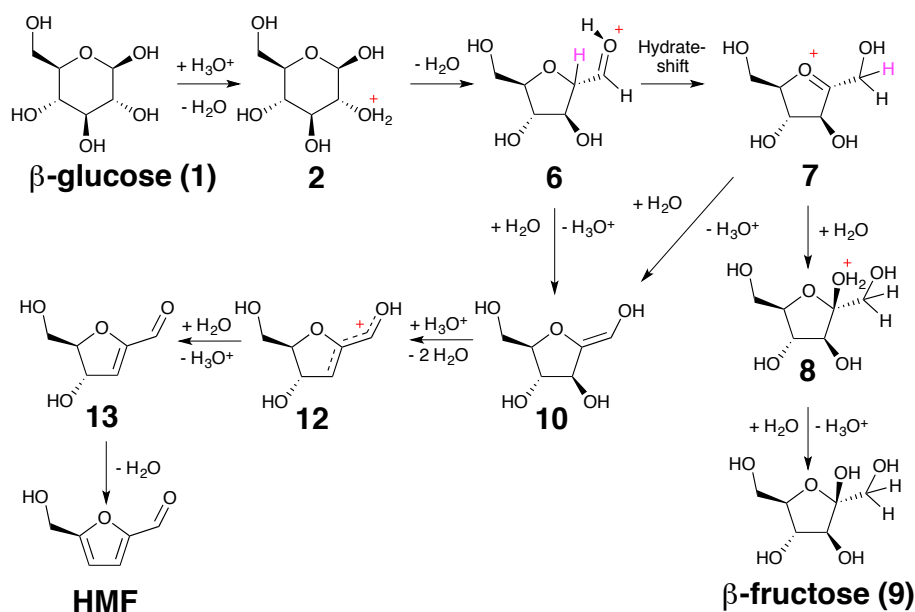
[Introduction] The aim of this study is to investigate the important factors of glucose hydrolysis into 5-hydroxymethylfurfural (HMF), in order to increase and develop the production ways and utilizations of this reaction. Many computational and experimental studies have been conducted to learn about this reaction, but we still lack a detailed understanding about how the chemical reactions proceed.

Previously proposed mechanisms for conversion of glucose into HMF, as given in Scheme 1, suggest that glucose needs to be first transformed into fructose (**B**) whereas fructose directly converts into HMF (**A**) [1]. These mechanisms were suggested on the basis of reactions in alkylimidazolium chloride ionic liquids, such as [BMIM]Cl and [EMIM]Cl. Before modeling the reactions in ionic liquids, however, we decided to first investigate the reaction mechanisms in acidic aqueous environments.



Scheme 1. Previously proposed mechanisms via open ring [1]

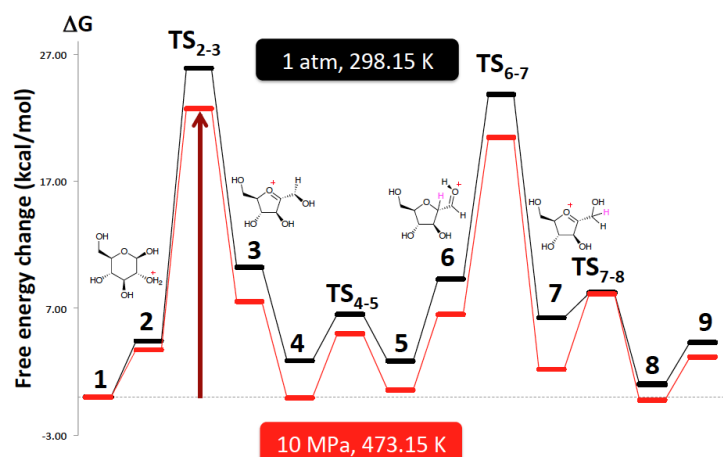
Besides the open ring mechanism, cyclic or closed ring mechanisms have been proposed by experimental and theoretical works [2] as the reaction pathways of glucose isomerization into fructose. In the present work, we consider both cyclic (Scheme 2) and open ring mechanism and further dehydration of fructose into HMF.



Scheme 2. Proposed cyclic mechanisms

[Computational Details] To tackle the complexities of the reaction paths, originating from the solvent effect, we applied RISM-SCF-SEDD [3] as the solvation theory in combination with DFT and coupled-cluster electronic structure methods. RISM-SCF-SEDD method is a combination between statistical mechanics for molecular liquid and molecular orbital (MO) theory. All of the geometries were optimized with RISM-SCF-SEDD-B3LYP/6-31+G(d) level of theory. The energies were evaluated at RISM-SCF-SEDD-CCSD(T)/aug-cc-pVDZ. All calculations were performed by a modified version of the GAMESS program package.

[Results and Discussions] Figure 1 shows the free energy surface of the glucose isomerization into fructose, via cyclic mechanism, at room condition (1 atm, 298.15 K) and experimental condition (10 MPa, 473.15 K). The free energy of activation (TS_{2-3}) for this mechanism are $25.87 \text{ kcal mol}^{-1}$ and $22.70 \text{ kcal mol}^{-1}$, respectively for room and experimental condition.



Free energy diagram for fructose transformation into HMF is shown in Figure 2. There are at least two possible reaction pathways involving different transition states. The free energy of those transition states were very close each other.

Figure 1. Free energy surface of glucose isomerization

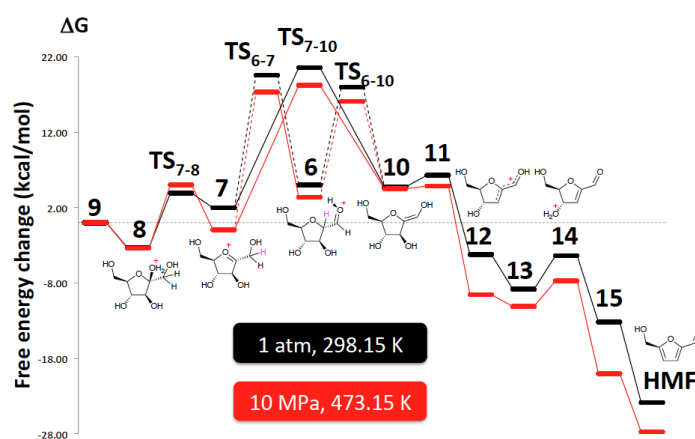


Figure 2. Free energy surface of fructose hydrolysis into HMF

More details will be given in the oral presentation.

[References]

- [1] Binder, J. B., Raines, R. T. *J. Am. Chem. Soc.*, **131**, 1979, 2009.
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