Density Functional Theory Study of Glyceraldehyde Hydrolysis in Supercritical Water.

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Abstract

The glyceraldehyde conversion in terms of dehydration, keto-enol tautomerism, and retro-aldol reaction has been discussed by means of ab initio density functional theory calculation to elucidate the catalytic water molecule influence on the pathways. The optimized structures of reactants, products, and transition state structure on the glyceraldehyde conversion pathways were fully optimized with the B3LYP/AUG-cc-pVDZ level. At first, the retro-aldol reaction through a six-membered ring-like transition state structure reduced the threshold energy, which was preferred pathway in the absence of water. The presence of water on the dehydration and the tautomerism pathways reduces the threshold energies, but dehydration is consistently more favorable than tautomerism and retro-aldol reaction. Water molecule can enhance glucose conversion by directly participating in the transition state by forming ring-like water bridge and lowering the threshold energy. In the future study, the discrete solvation model simulation in terms of the solvation effect will be investigated on the glyceraldehyde conversion in supercritical water by means of quantum mechanics / molecular mechanics (QM/MM) simulation.

Introduction

Glucose, a monomer unit of cellulose, is the most abundant organic compound on the earth. The conversion of glucose in hot compressed water into useful chemical will be an alternative process to petroleum chemistry. In spite of the glucose conversion is recognized as a candidate for suitable sustainable feed stock, it is difficult to control product distribution, and to build reaction network.

Many researchers have attempted to elucidate the mechanism of glucose conversion by means of supercritical water quick heating apparatus that can roughly classified the elementary reactions of glucose into following three reactions: dehydration, keto-enol tautomerism, and retro-aldol reaction. Sasaki et al. [1] have elucidated water density dependence of these elementary reactions. The retro-aldol reaction is preferred at low water density (higher temperature or lower pressure). On the other hand, the high water density experiments point to the dehydration as the major pathway. This difference in the selectivity in the low and the high water density conditions could possibly be explained by water molecule being a homogeneous catalyst for the dehydration pathway or being the inhibitor for the retro-aldol reaction.

A number of ab initio calculations for organic reactions have been reported to elucidate the catalytic role of water molecule. The reduction of activation barrier by means of the presence of water in the transition state complex has been revealed by ab initio calculation of formic acid decomposition performed by Akiya and Savage [2]. They suggested that the water molecules behave homogeneous catalyst for both dehydration and decarboxylation, and the decarboxylation pathway with water molecule is the most favored pathway. Furthermore, Takahashi et al. [3] performed ethanol oxidation into acetaldehyde by means of ab initio calculation to elucidate the catalytic role of water in supercritical conditions. They found that the direct participation of water molecules through a multi-center transition state including an ethanol molecule and two water molecules bridging the oxygen atom of ethanol and the α-hydrogen substantially reduced threshold energy of the oxidation compared to those in the absence of water molecules.

The recent appearance of the water density dependence on the elementary reaction based on well-controlled experiments and the presence of water molecule as catalysts reduce threshold energy on some organic reactions in supercritical water motivated the present study of the effect of water on glyceraldehyde conversion. Glyceraldehyde is a simple carbohydrate compound, which can be converted into pyruvaldehyde by dehydration and glycolaldehyde can be formed from glyceraldehyde by means of retro-aldol reaction [4]. As mentioned above, the both dehydration and retro-aldol reaction may be enhanced those reactions by participating the catalytic water in the transition state. In the present study, we considered three scenarios on glyceraldehyde conversion described in Figure 1. (1) Glyceraldehyde is converted into pyruvaldehyde by means of tautomerism through the formation of acrolein by dehydration. (2) The acrolein can be formed from glyceraldehyde by tautomerism to 1,2,3-propenetriol, followed by dehydration. The path after acrolein is the same as scenario (1). (3) A retro-aldol reaction

from glyceraldehyde gives the formation of formaldehyde and 1,2-ethenediol.   The latter compound could be converted into glycolaldehyde by means of tautomerism.
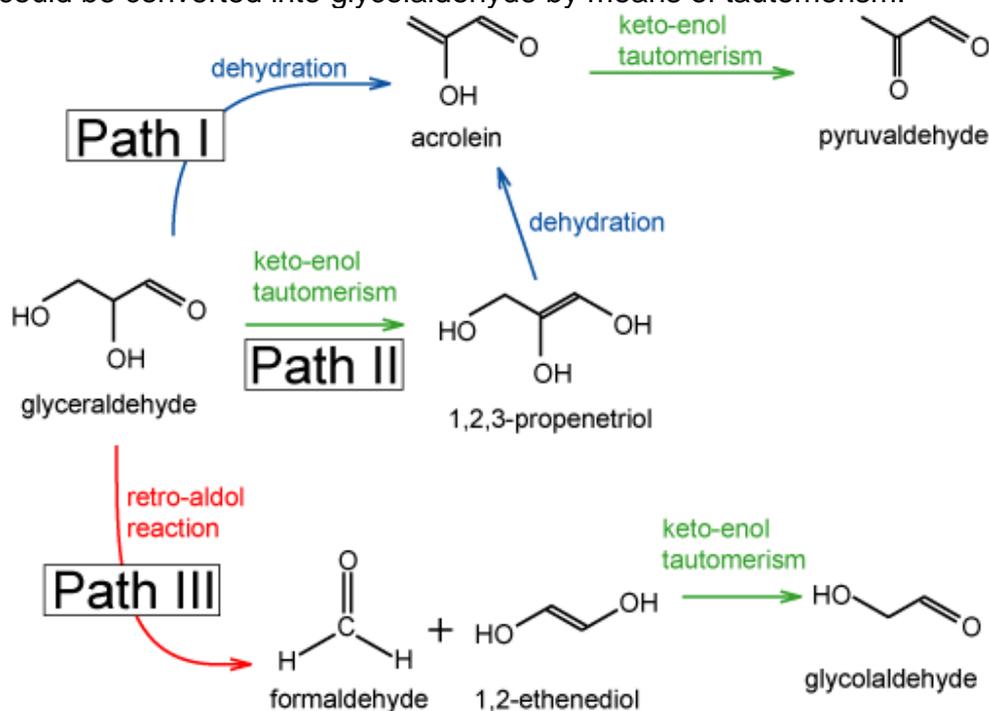

Figure 1.   Reaction network of glyceraldehyde conversion.

Computational Details

Density functional theory calculations were performed with Gaussian 03 Revision C.2 [5]. The equilibrium geometries of reactants and products were optimized with the Berny optimization method.   The synchronous transit-guided quasi-Newton method located the transition state structure according to the optimized structures of reactant and product.   The intrinsic reaction coordinate calculations carried out to confirm that the transition state structures leads to the expected reactant and product molecular structures.   We also performed the frequency calculation to take into account for zero-point correction and thermal energy at 400 °C and 250 atm.   All of the quantum chemical calculations were performed in a medium of zero dielectric constant by means of the B3LYP and the AUG-cc-pVDZ basis set.

Results and Discussion

According to Figure 1, glyceraldehyde can converts three intermediates such as acrolein, 1,2,3-propenetriol, and 1,2-ethenediol with formaldehyde by means of dehydration, keto-enol tautomerism, and retro-aldol reaction, respectively.   We performed the DFT calculations for the reaction of them.   Figure 2, shows optimized transition state structures along the three elementary pathways through glyceraldehyde conversion.
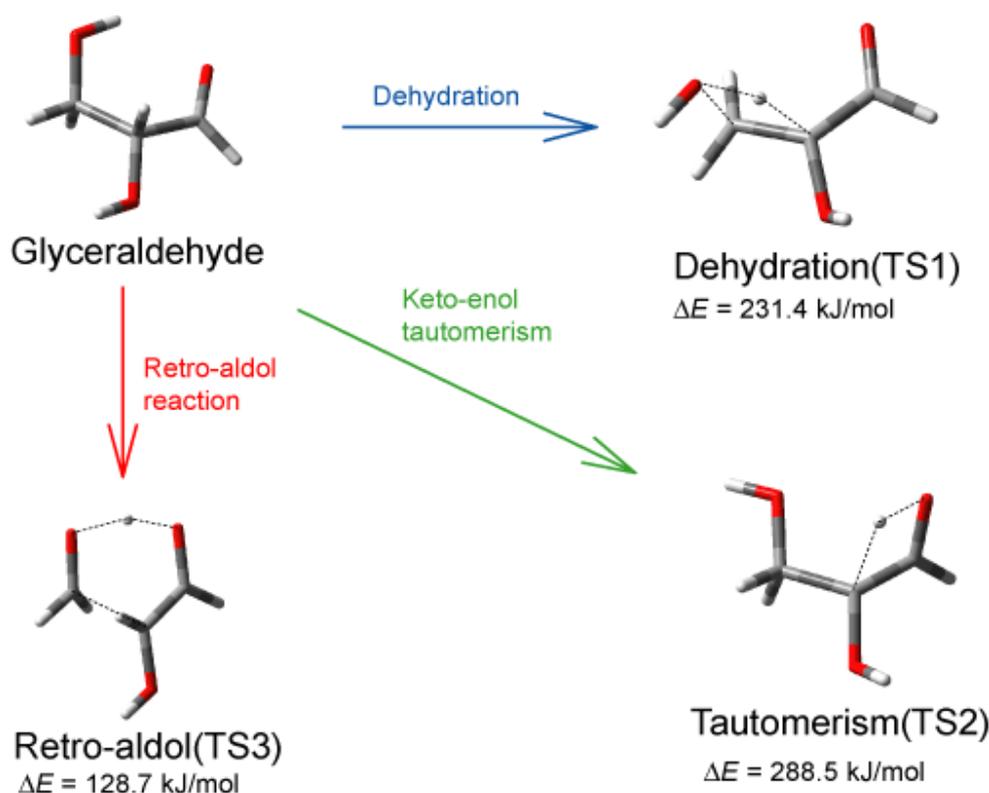
Figure 2. Optimized glyceraldehyde structure and optimized transition state structures of dehydration, tautomerism, and retro-aldol reaction.

Glyceraldehyde dehydration can form acrolein by moving a hydrogen atom from center carbon to side hydroxyl oxygen. During the reaction, the transition state structure forms four-membered ring-like structure (TS1). The threshold energy of dehydration was 231.4 kJ/mol. The mechanism of the glyceraldehyde tautomerism is found to be similar to the dehydration, the transition state have a four-membered ring-like structure by means of a hydrogen translation from central carbon, however, it bounds to carbonyl oxygen (TS2). The threshold energy found to be 288.5 kJ/mol that is by ca. 57.1 kJ/mol higher than that of the dehydration. The retro-aldol reaction, on the other hand, forms intramolecular hydrogen bonding, which transfers hydroxyl hydrogen to carbonyl oxygen. Moreover, a carbon-carbon bond cleavage occurs to form 1,2-ethenediol and formaldehyde. A six-membered ring-like structure involving intramolecular hydrogen bonding relaxes bond angles and drastically reduced threshold energy (TS3). As a result, the threshold energy became 128.7 kJ/mol, it is indicated that the retro-aldol pathway is a main route on the glyceraldehyde conversion in the absence of water.

We also discussed subsequent reactions from acrolein, 1,2,3-propenetriol, and 1,2-ethenediol. The transition structures obtained from the DFT calculation were shown in Figure 3. The four-membered ring-like structure at transition state can be formed from acrolein (TS4) and 1,2-ethenediol by means of tautomerism reaction (TS6). The threshold energy of the reactions were 313.5 kJ/mol and 252.6 kJ/mol from acrolein and 1,2-ethenediol, respectively. The dehydration from 1,2,3-propenetriol gives acrolein via six-membered

ring-like structure, which forms intramolecular hydrogen bonding (TS5).   It lowers the reaction barrier and the threshold energy becomes 99.2 kJ/mol.
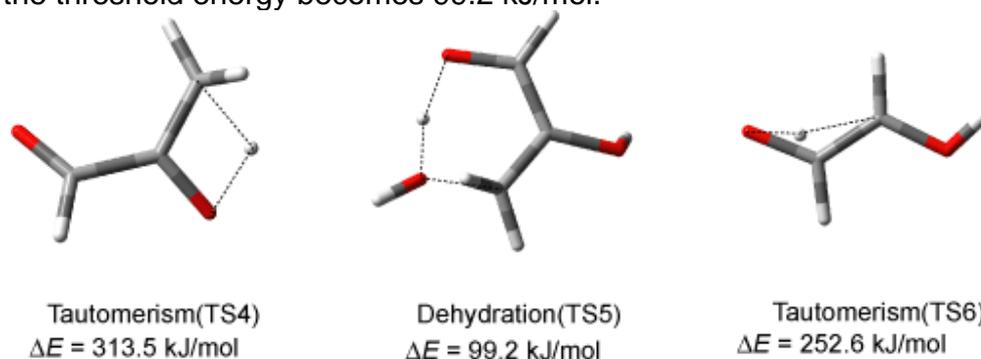

Tautomerism(TS4)
ΔE = 313.5 kJ/mol

Dehydration(TS5)
ΔE = 99.2 kJ/mol

Tautomerism(TS6)
ΔE = 252.6 kJ/mol

Figure 3.   Optimized transition state structures on the reactions of the tautomerism and the dehydration.

The water-assisted mechanism of glyceraldehyde conversion has been discussed in terms of the dehydration and the tautomerism, which gives acrolein and 1,2,3-propenetriol, respectively.   The reactant and the transition state structures are shown in Figure 4.
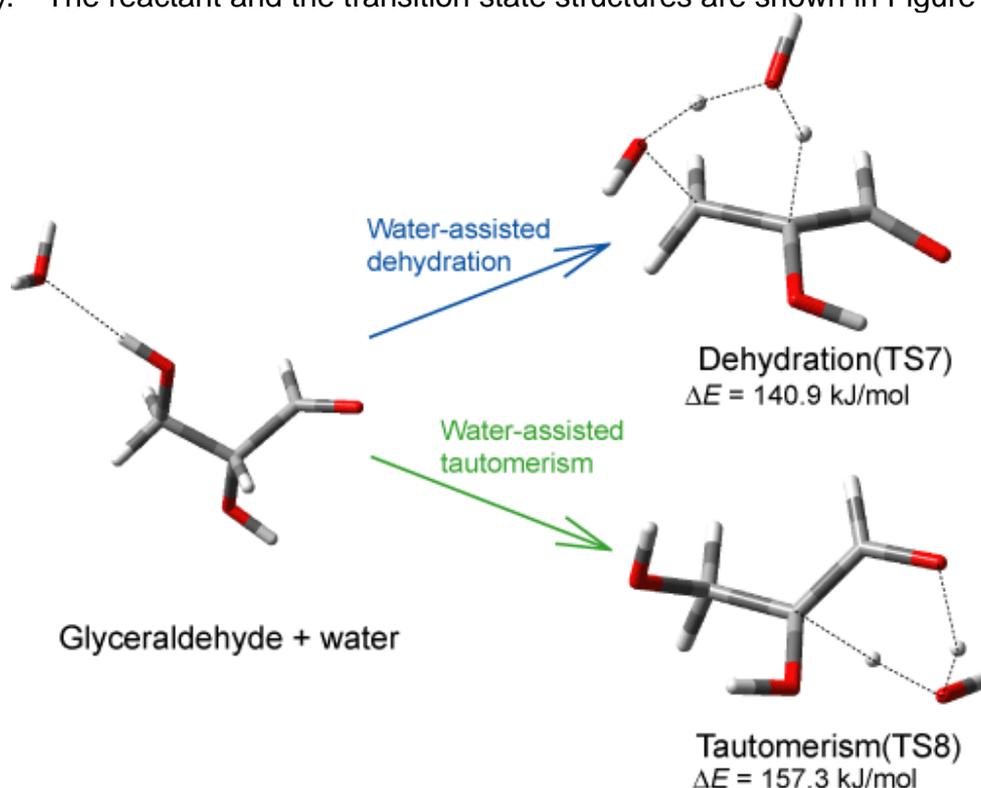

Water-assisted
dehydration

Dehydration(TS7)
ΔE = 140.9 kJ/mol

Water-assisted
tautomerism

Glyceraldehyde + water

Tautomerism(TS8)
ΔE = 157.3 kJ/mol

Figure 4.   Hydrogen bonded glyceraldehyde complex and optimized transition state structures on water-assisted dehydration and water-assisted tautomerism.

The calculated transition state structure has the six-membered ring-like water bridge, which is a proper configuration for the hydrogen migration.   Threshold energies of water-assisted dehydration (TS7) and tautomerism (TS8) are 140.9 kJ/mol and 157.3 kJ/mol

from glyceraldehyde, respectively. The addition of water molecules can form rather static transition state and it lowers the barriers by 90.5 kJ/mol and 131.2 kJ/mol for the dehydration and the tautomerism, respectively. We also have discussed the water-assisted tautomerism of acrolein, which can be converted into pyruvaldehyde. As mentioned above, the six-membered ring-like structure of the water-assisted tautomerism can be formed from acrolein on the transition state, the threshold energy became 110.0 kJ/mol was less than unimolecular mechanism.

Table 1. Threshold energies glyceraldehyde conversion. Units in threshold energy is kJ/mol.

Reactant	Product	Number of water	Threshold energy	Threshold energy (Reverse)
Glyceraldehyde	Acrolein	0	231.4 (TS1)	225.7
Glyceraldehyde	Acrolein	1	140.9 (TS7)	185.4
Glyceraldehyde	1,2,3-propenetriol	0	288.5 (TS2)	246.5
Glyceraldehyde	1,2,3-propenetriol	1	157.3 (TS8)	250.3
Glyceraldehyde	Formaldehyde + 1,2-ethenediol	0	128.7 (TS3)	32.7
Acrolein	Pyruvaldehyde	0	313.5 (TS4)	270.6
Acrolein	Pyruvaldehyde	1	110.0	151.6
1,2,3-propenetriol	Acrolein	0	99.2 (TS5)	135.6
1,2-ethenediol	Glycolaldehyde	0	252.6 (TS6)	292.9

The threshold energies of the forward and backward reactions are listed in Table 1. The threshold energies on the reverse reactions were estimated by subtracting single point energy of the product from one of the transition state structure. The most of inverse reactions are comparable threshold energies, however, in case of aldol condensation, it should be noted that the threshold energy was substantially lower than the retro-aldol reaction, which has an important influence on the reaction network.

According to the literatures, at lower density condition, glyceraldehyde tends to be converted into glycolaldehyde via the retro-aldol reaction. This trend can be explained by means of the reaction network and threshold energies estimated by the DFT calculation. The reaction network is described in Figure 5.
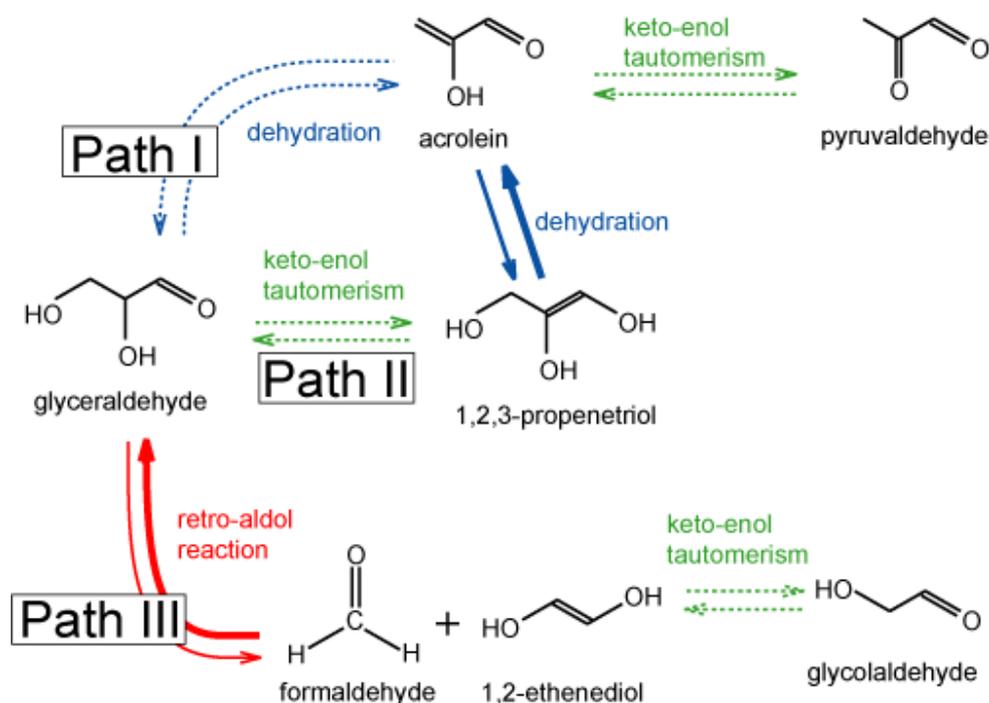
Figure 5. Reaction network on glyceraldehyde conversion.

The retro-aldol reaction is the lowest threshold energy among glyceraldehyde reaction, and it gives formaldehyde and 1,2-ethenediol, the latter compound can be converted into glycolaldehyde by tautomerism. The threshold energy of the tautomerism reaction was relatively higher, but it was lower than that to form pyruvaldehyde. We have to take account of the aldol condensation, which has significantly lower threshold energy and tends to form glyceraldehyde. The other reaction pathway from glyceraldehyde is converted into acrolein by dehydration. But it prefer to convert into glyceraldehyde via 1,2,3-propenetriol. Finally, the non-water-assisted mechanism point to form the glycolaldehyde by means of the retro-aldol reaction and the tautomerism.

The reaction network involving the water-assisted mechanisms was shown in Figure 6.
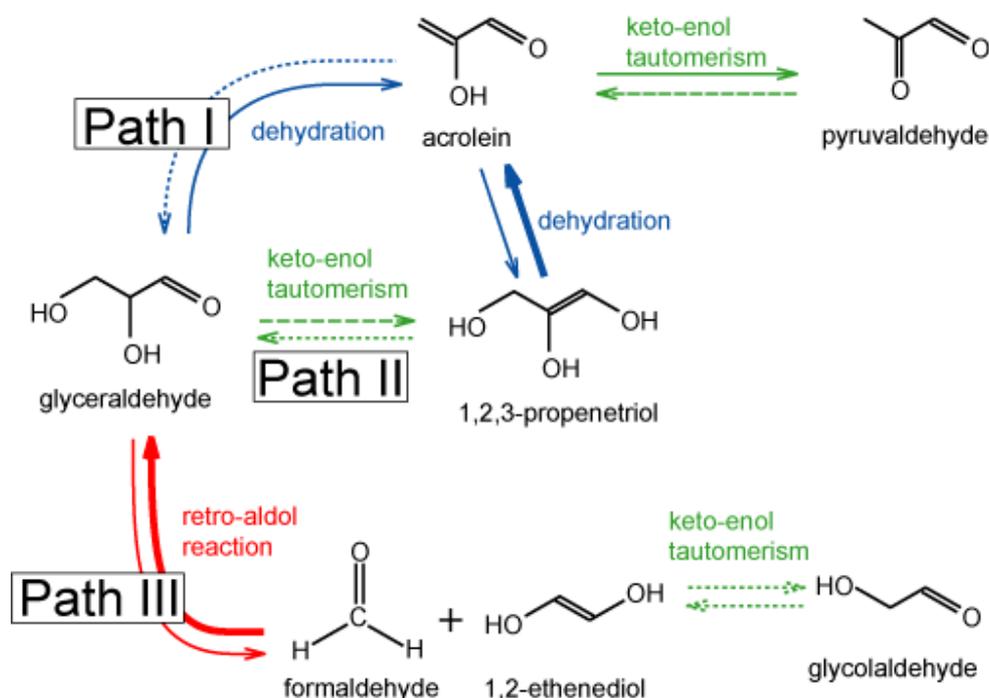
Figure 6. Reaction network on glyceraldehyde conversion along with water-assisted mechanisms.

In spite of the catalytic water molecules promote the dehydration and the tautomerism, the retro-aldol reaction was the lowest threshold energy among the reactions starting from the glyceraldehyde. Nevertheless, its reverse reaction, the aldol condensation, is lower barrier, which indicates the retro-aldol reaction is equilibrium reaction. The glyceraldehyde can be converted into acrolein by the water-assisted dehydration, and it can form pyruvaldehyde by the water-assisted tautomerism. The both of the dehydration and the tautomerism were scarcely reversible reactions. The water-assisted tautomerism gives acrolein via 1,2,3-propenetriol by dehydration, it was not a main pathway because the threshold energy of the tautomerism is higher than that of the dehydration. It may be concluded that the pathway glyceraldehyde → acrolein → pyruvaldehyde is an important route for the water-assisted glyceraldehyde conversion.

Conclusion

The three decomposition pathways, dehydration, keto-enol tautomerism, and retro-aldol reaction of glyceraldehyde conversion in the presence of water have been studied by means of DFT calculation at the B3LYP/AUG-cc-pVDZ level. A six-membered ring-like transition structure by retro-aldol reaction lowered the threshold energy by means of relaxing bond angle. On the other hand, dehydration and tautomerism on glyceraldehyde conversion gives energetically unfavorable four-membered ring-like structure. Nevertheless, in the case of water-assisted dehydration and tautomerism, the transition state structure substantially reduced the threshold energy by forming six-membered ring-like water bridge to migrate hydrogen atom. The peculiarity of supercritical water such as solvation dynamics or local enhancement around reactants should be involved the analysis by means of the quantum mechanics / molecular

mechanics study, which will be discussed in the future study.

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