

Density functional theory study of glyceraldehyde conversion in supercritical water



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ABSTRACT

Density functional theory calculations of glyceraldehyde conversion were performed to elucidate the relative reactivity between dehydration and retro-aldol reaction. In this study, structures and energies of the reaction system were determined by B3LYP/AUG-cc-pVDZ level of theory to explore the catalytic role of water molecule. The water-assisted retro-aldol reaction is the most favorable pathway among glyceraldehyde conversion. Water molecule participation in the reaction system lowered the threshold energies for both reaction pathways, suggesting that a water molecule acts as homogeneous catalyst. Comparing the threshold energy values between non-water and water-assisted mechanisms, the threshold energy difference in dehydration was found to be greater than that in the retro-aldol reaction. This large catalytic water influence on the dehydration means that the glyceraldehyde dehydration is more enhanced at fairly higher density conditions. The reaction analysis in terms of water molecule participation can explain the influence of supercritical water density upon the glucose conversion and the catalytic role of water molecule in molecular level.

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1. Introduction

Glucose conversion in supercritical water into valuable chemicals such as 5-hydroxymethylfurfural [1–3], furfural [2], and lactic acid [4,5] is important for considering the downstream chemical processing of biomass resources [6]. Kabyemela et al. studied glucose decomposition kinetics in subcritical and supercritical water [7–11]. A pressure effect of the reaction rate on the glucose conversion suggested the possibility of controlling the selectivity in the formation of the valuable chemicals [11]. Typical monosaccharide conversion was performed by Lu and Saka in a batch-type experiment to investigate monosaccharides' isomerization, dehydration, and fragmentation (retro-aldol reaction) [12]. They concluded that the isomerization, dehydration, and fragmentation reactions are not only determined by initial monosaccharides but also the reaction condition. In addition, they suggested that dehydration possibly first occur where after fragmentation reaction follows. Caetero et al. performed cellulose depolymerization in near critical water by flow-type reactor.

The rate constants of 5-hydroxymethylfurfural formation were increased when temperature is increased if water concentration was taken into account in the reaction. Therefore, they concluded that the 5-hydroxymethylfurfural formation reaction rate would be highly influenced by the density (water concentration) of the reaction medium. Sasaki et al. investigated the temperature and pressure influences on the glucose conversion to clarify major pathways with the aim of constructing the conversion network [13,14]. They found that the major pathway of the glucose conversion was retro-aldol reactions under lower density conditions and the dehydration was enhanced in higher water density conditions.

This difference in density dependence between the dehydration and the retro-aldol reaction could be easily estimated to result from the catalytic role of water molecules. However, numerous reaction products and unstable intermediates obtained from the parallel and the sequential reaction networks prevent us to elucidate quantitatively the glucose conversion networks. Thus, a simpler starting compound as a model species of glucose would be preferable to elucidate the relative reactivity between the dehydration and retro-aldol reactions. Glyceraldehyde is a simple and an important intermediate compound in the glucose conversion in supercritical water, because the glyceraldehyde can be converted into pyruvaldehyde by dehydration, and glycolaldehyde can be formed from glyceraldehyde by retro-aldol reaction. Therefore,

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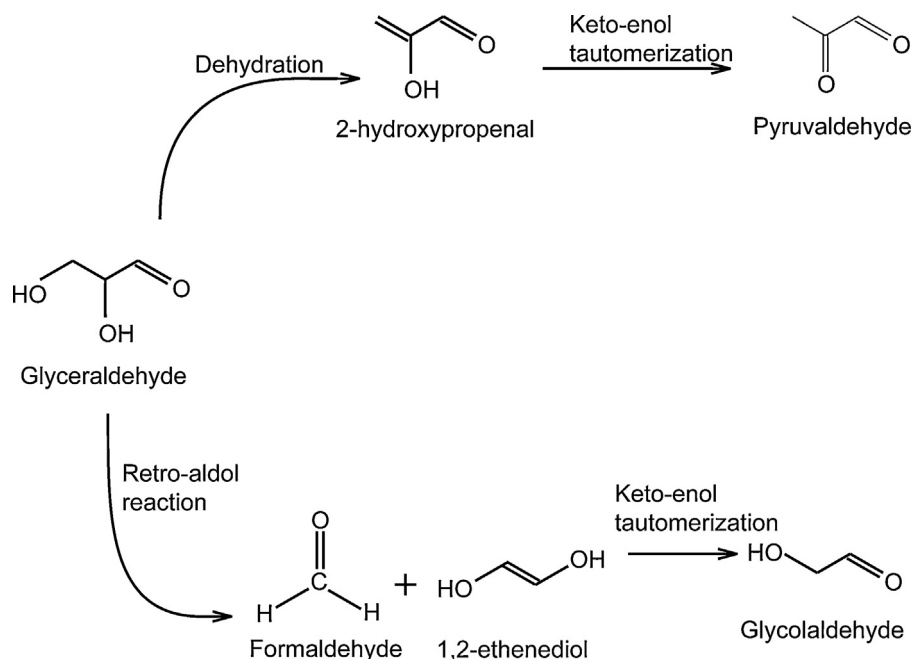


Fig. 1. Glyceraldehyde conversion pathways considered the present study.

exploring the glyceraldehyde conversion in molecular level would give us a clear explanation for the role of catalytic water molecule on both of dehydration and retro-aldol reaction.

Ab initio calculations for organic reactions in supercritical water have been reported to elucidate the catalytic role of water molecules [15–19]. Akiya and Savage performed ab initio calculations of formic acid decomposition and revealed that the reduction of the threshold energy was reduced by the presence of water molecules in the transition state complex [20]. They also suggested that the water molecules behave as homogeneous catalyst for both of the dehydration and the decarboxylation. Takahashi et al. performed density functional theory calculations of ethanol oxidation to acetaldehyde for elucidating the catalytic role of water molecules in supercritical conditions [21]. They found that water molecules participating the transition state reduced the threshold energy by forming ring-like water-wired structure. Fujii et al. investigated an acid-catalyzed mechanism of formic acid dehydration in hot-compressed water by density functional theory. They found that the dehydration proceeds via the protonation of the hydroxyl oxygen of formic acid. In addition, they suggested that the reaction rate could be manipulated by tuning water properties such as the ion product, which is controllable by temperature and pressure. In this study, density functional theory calculations of glyceraldehyde conversion were performed to clarify the reaction mechanism in terms of the catalytic role of water molecule on both of the dehydration and the retro-aldol reaction in supercritical water.

2. Computational details

We performed density functional theory calculations of glyceraldehyde conversion for investigating relative reactivity between dehydration and retro-aldol reaction. The glyceraldehyde conversion pathways considered in the present study are shown in Fig. 1. The dehydration pathway converts glyceraldehyde into 2-hydroxypropenal via dehydration, and then produces pyruvaldehyde via keto-enol tautomerization. Retro-aldol reaction of glyceraldehyde produces formaldehyde and 1,2-ethenediol. The latter compound is converted into glycolaldehyde by means of keto-enol tautomerization.

Density functional theory calculations at the B3LYP [22] and AUG-cc-pVDZ [23–26] levels of theory were performed by Gaussian 03 revision C.2 [27]. The equilibrium geometries of reactants and products were optimized by the Berny optimization method. The transition state structure is located by the synchronous transit-guided quasi-Newton method according to the structures of reactants and products. Intrinsic reaction coordinate calculations were conducted to confirm that the transition structures do led to the expected product molecular structures and the reactants. All calculations were performed in the supercritical conditions by take into account of the zero-point and the thermal energy collections at 400 °C and 250 atm (25.3 MPa).

3. Results and discussions

3.1. Glyceraldehyde conversion without catalytic water molecule

Fig. 2a shows the optimized structure of the reactant for the glyceraldehyde dehydration without catalytic water molecule. The reactant structure is D-glyceraldehyde. We also calculated a reaction network originated from L-glyceraldehyde, but no significant energy differences were found against the case of D-glyceraldehyde as starting compound. Therefore, the following results were shown D-glyceraldehyde as a departure compound on the conversion network.

Fig. 3a shows the reactant species of the retro-aldol reaction of glyceraldehyde. The hydroxyl group connected to the side carbon (10O–12H) turned toward the carbonyl oxygen due to the formation of the intramolecular hydrogen bond.

Table 1
Relative energies and threshold energies on the glyceraldehyde conversion without catalytic water molecule.

Reaction	Reactant (kJ/mol)	Transition state (kJ/mol)	Threshold energy (kJ/mol)
Dehydration	0	230.209	230.209
Retro-aldol	–1.053	127.851	128.904

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