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# Kinetics and Mechanism of Glucose Decomposition in Hot-Compressed Water: Effect of Initial Glucose Concentration

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**ABSTRACT:** At a given reaction temperature (175–275 °C), the reaction rate constant of glucose decomposition in hot-compressed water (HCW) is found to decrease by almost 1 order of magnitude with increasing the initial glucose concentration from 0.01 to 1000 mg L<sup>-1</sup> (equivalent to  $5.6 \times 10^{-8}$ –0.0056 M). The results demonstrate a clear shift in the glucose decomposition mechanism at various initial glucose concentrations. Fructose is always the dominant reaction product with a high selectivity at the early stage of glucose decomposition, suggesting that it is a key primary product from glucose decomposition in HCW. The initial glucose concentration also influences the selectivity of glucose decomposition products substantially. The hydroxyl ion appears to play a controlling role in catalyzing the isomerization and retro-aldol reactions under all conditions in this study. At an initial glucose concentration less than 10 mg L<sup>-1</sup> (i.e.,  $5.6 \times 10^{-5}$  M), particularly when it is close to or less than the molar concentration of the ion product in HCW, the hydroxyl ions play a dominant role in catalyzing the isomerization and retro-aldol condensation reactions to produce fructose, glyceraldehydes and/or glycolaldehyde, erythrose, etc. However, at an initial glucose concentration higher than 10 mg L<sup>-1</sup> (i.e.,  $5.6 \times 10^{-5}$  M), the selectivity of 5-hydroxymethylfurfural increases substantially, indicating that hydrogen ions play an enhanced role in catalyzing dehydration reactions under the conditions. The shift in glucose decomposition mechanism is also reflected in the change in apparent activation energy that increases with an increasing initial glucose concentration, mainly due to an increasing selectivity of acid-catalyzed dehydration reaction that has a higher activation energy.

## 1. INTRODUCTION

Green chemicals production from biomass-derived sugars is essential to future sustainable development in a carbon-constrained world.<sup>1,2</sup> Glucose, as a monosugar produced from biomass hydrolysis, is known to be an ideal feedstock for the production of target chemical products such as furanics, e.g., 5-hydroxymethylfurfural (5-HMF)<sup>3–5</sup> and 2,5-dimethylfuran (DMF),<sup>6</sup> and organic acids, e.g., levulinic acid<sup>7,8</sup> and lactic acid.<sup>9</sup> Such production routes can achieve high selectivities; e.g., glucose can be converted to 5-HMF with a yield near 70%, catalyzed by metal chlorides in ionic liquid.<sup>3</sup> Hot-compressed water (HCW) is a promising reaction medium for synthesizing chemicals from cellulose/biomass.<sup>10–23</sup> Recent work also showed that hydrolysis of cellulose in nonchemical hot-compressed water (HCW) can produce a primary hydrolysis product containing various sugars with a wide range of degrees of polymerization (DPs) under mild conditions (e.g., <300 °C).<sup>24–28</sup> It is envisaged that further conversion of these products in HCW may lead to the formation of glucose and some useful chemicals, potentially realizing a possible route for green chemicals production directly from cellulose/biomass in HCW.

Decomposition of glucose in HCW is complex and may involve a variety of parallel reactions such as isomerization, retro-aldol condensation, and dehydration reactions.<sup>29–35</sup> Under noncatalytic reactions in HCW, glucose will decompose to a mixture of products including aldehydes, furfurals, phenols, acids, etc.<sup>17</sup> The complexity of these reactions lies in the fact that, as a result of high ionic product in HCW,<sup>12</sup> glucose decomposition in HCW involves both acid and base catalyzed reactions. For example, it is known that 5-HMF is generally accepted as a major

product from acidic glucose degradation. However, 5-HMF can also be produced indirectly from glucose through first converting glucose into fructose by the aldose–ketose isomerization reaction via the Lobry de Bruyn–Alberda van Ekenstein (LdB–AvE) transformation,<sup>36</sup> followed by the dehydration of fructose.<sup>37</sup> Under acidic conditions, a previous ab initio molecular dynamic simulation<sup>38</sup> suggests that glucose initially forms a 2,5-anhydride intermediate by protonation of the OH group on position C2, followed by the further elimination of water to form 5-HMF. However, under HCW conditions, both H<sup>+</sup> and OH<sup>-</sup> coexist, with the ionic concentrations known to be substantially higher (by 3 orders of magnitude) than those in ambient water.<sup>12,39</sup> Therefore, it is still largely unknown which ion (H<sup>+</sup> or OH<sup>-</sup>) plays a more important role and what are the dominant reaction pathways in glucose degradation under various HCW conditions.

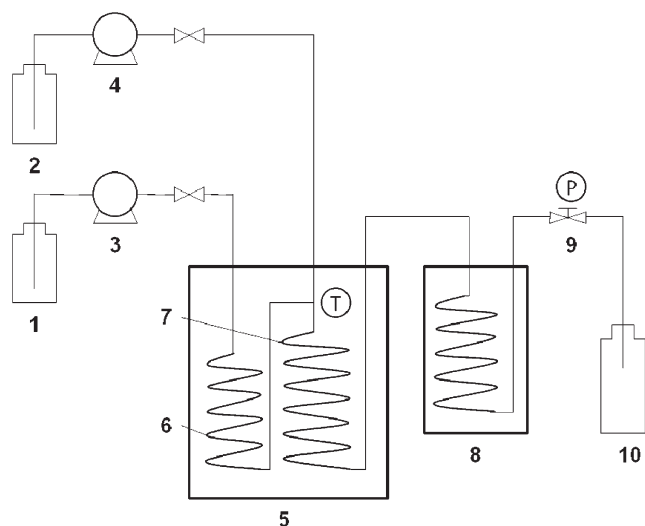
Glucose decomposition in HCW generally follows first-order reaction kinetics under catalytic<sup>40–42</sup> or noncatalytic<sup>30,43,44</sup> conditions. It was also found that the reaction order decreases from 1 at 448 K to 0.7 at 673 K and the concentration of glucose solution appears to have some influence on the reaction rate of glucose decomposition in HCW.<sup>43</sup> Unfortunately, thus far little work has been done on the effect of initial glucose concentration on glucose decomposition kinetics and the fundamental mechanism governing such effects. These are the main objectives of this study, which carries out a systematic study on glucose decomposition

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**Figure 1.** Schematic diagram of the continuous reactor system used in this study: 1, water reservoir; 2, glucose solution reservoir; 3, HPLC pump; 4, HPLC pump; 5, fluidized sand bath; 6, water preheating tube; 7, tube reactor; 8, cooling unit; 9, back-pressure regulator; 10, liquid product collector.

experiments using a continuous reactor system. A wide range of initial glucose concentration is carefully chosen to highlight the significant effect of initial glucose concentration on glucose decomposition in HCW.

## 2. EXPERIMENTAL SECTION

**2.1. Materials and Reactor System.** The glucose sample (monohydrate, Product No. 49158) and some high-purity standards and reagents were purchased from Sigma-Aldrich. A continuous reactor system was used in this study for glucose decomposition in HCW, with the schematic diagram shown in Figure 1. Water delivered by an HPLC pump was preheated in the fluidized sand bath. The preheated water was mixed with the glucose solution fed by another HPLC pump to rapidly heat the solution to desired reaction temperatures. A thermocouple was located at the inlet of the stainless tube reactor for monitoring the temperature of the reactant solution after mixing. The reaction residence time was adjusted by the length of the stainless steel (SUS 316) tube reactor. The outer diameter (o.d.) and inner diameter (i.d.) of the reactor tube were generally 25.4 and 4.572 mm, respectively, although smaller tubes (o.d., 1.6 mm; i.d., 0.508 mm) were used in the experiments at high temperatures (250 °C or above) in order to achieve a short residence time as the decomposition reactions are rapid. The effluent from the tube reactor was immediately cooled in an ice–water bath and then collected for analysis.

To understand the role of ions in glucose decomposition in HCW, a wide range of glucose concentration ( $0.01\text{--}1\,000\text{ mg L}^{-1}$ , equivalent to  $5.6 \times 10^{-8}\text{--}0.0056\text{ M}$ ) was carefully chosen in the experiments. It is noteworthy that the lowest glucose concentration used in this study is even lower than the concentration of  $\text{H}^+$  or  $\text{OH}^-$  in HCW by 1 order of magnitude, realizing a ratio of  $\text{H}^+$  and glucose similar to that under acidic conditions. In all experiments, the ratio of the flow rates of preheated water to glucose solution was 2:1, so the concentration of glucose solution fed by the HPLC pump is 3 times higher than the desired

concentration. Generally, a flow rate of  $10\text{ mL min}^{-1}$  was used to feed the glucose solution. A series of experiments were carried out at reaction temperatures ranging from 175 to 275 °C with a 25 °C temperature interval and at a constant pressure of 10 MPa which was controlled by a back-pressure regulator.

**2.2. Liquid Product Analysis.** Glucose concentrations in the liquid products collected were quantified by high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The HPAEC-PAD analysis was carried out using a Dionex ICS-3000 ion chromatography (IC) system equipped with a CarboPac PA20 analytic column ( $3 \times 150\text{ mm}$ ) and a guard column ( $3 \times 30\text{ mm}$ ), with a 50 mM NaOH solution as the eluent. HPAEC is known to be capable of direct quantification of sugar compounds in solutions at low-picomole levels,<sup>24</sup> enabling experiments to be carried out at a very low initial glucose concentration, even similar to those of  $\text{H}^+$  or  $\text{OH}^-$  in HCW. For the liquid samples produced at high glucose concentrations, the samples were diluted to ensure that the glucose concentrations of diluted samples were within the linear response range of the HPAEC-PAD detection system.

HPAEC-PAD is also capable of identifying and quantifying other low concentration reaction products in the samples. A series of high-purity standards, such as glucose, fructose, glyceraldehyde, glycolaldehyde, erythrose, 5-HMF, 1,6-anhydroglucose, and cellobiose, have been used to identify and quantify the reaction products in the samples. The selectivity ( $S_i$ ) of glucose decomposed to a certain product  $i$  can be determined by

$$S_i = \frac{C_i}{G_0 - G} \quad (1)$$

where  $G_0$  and  $G$  ( $\text{mg L}^{-1}$ ) are the glucose concentrations before and after decomposition and  $C_i$  ( $\text{mg L}^{-1}$ ) is the concentration of product  $i$  after decomposition. The total C in a liquid solution was determined by a total organic carbon (TOC) analyzer (Shimadzu TOC-V<sub>CPH</sub>). The carbon balance was found to be  $\sim 100\%$  even at 275 °C, indicating that the gas produced from glucose decomposition under the reaction conditions in this study is negligible.

## 3. RESULTS AND DISCUSSION

**3.1. Kinetics of Glucose Decomposition in HCW at Various Initial Concentrations.** Based on the glucose concentrations quantified by HPAEC-PAD at various residence times, the reaction rate constant of glucose decomposition in HCW can be determined. Assuming the glucose decomposition follows first-order kinetics, we have

$$-\ln\left(\frac{G}{G_0}\right) = k\tau \quad (2)$$

where  $G_0$  and  $G$  ( $\text{mg L}^{-1}$ ) are the glucose concentrations before and after decomposition and  $k$  ( $\text{s}^{-1}$ ) is the reaction rate constant.  $\tau$  (s) is the residence time and can be calculated by

$$\tau = V \frac{\rho}{F} \quad (3)$$

where  $V$  ( $\text{m}^3$ ) is the reactor volume that changes with tube length,  $\rho$  ( $\text{kg m}^{-3}$ ) is the water density under the reaction conditions, and  $F$  ( $\text{kg s}^{-1}$ ) is the total mass flow rate of water and glucose solution.

The relationships between  $-\ln(G/G_0)$  and residence time at various temperatures and initial glucose concentrations are then

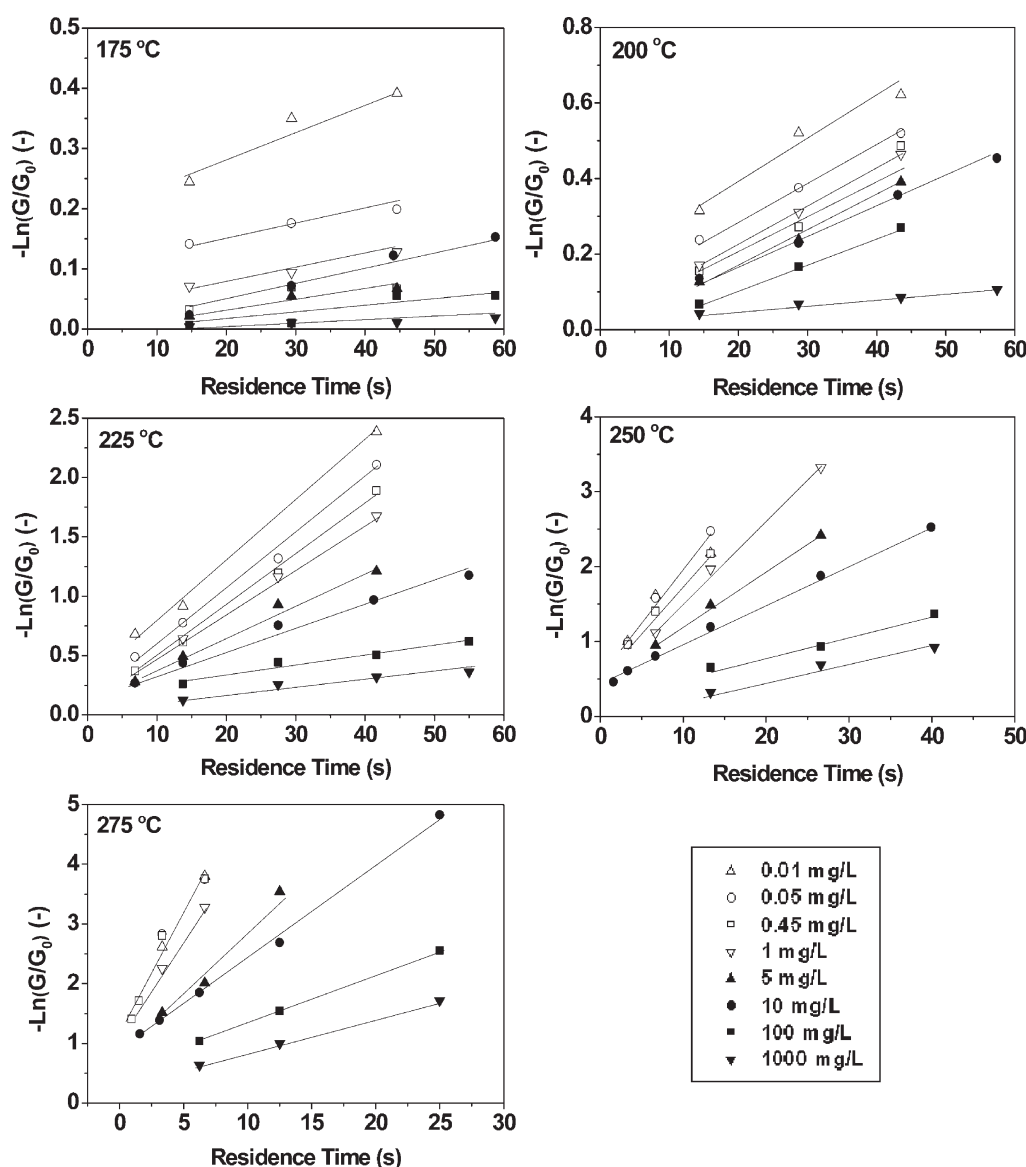
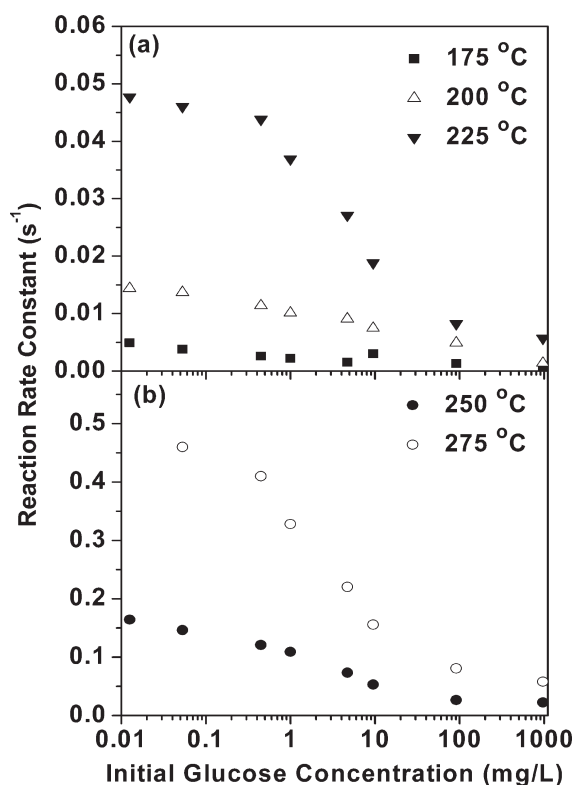


Figure 2. Correlations between  $-\ln(G/G_0)$  and residence time at various temperatures.

plotted in Figure 2. As shown in Figure 2, a linear relationship between  $-\ln(G/G_0)$  and residence time is clearly evident, suggesting that glucose decomposition is indeed first order with respect to glucose concentration under all conditions. Based on the data presented in Figure 2, the reaction rate constant of glucose decomposition in HCW,  $k$ , can then be determined according to eq 2 then plotted in Figure 3 as a function of initial glucose concentration. While at the same glucose concentration the glucose decomposition rate constant increases with reaction temperature as expected, the data in Figures 2 and 3 clearly demonstrate that the initial glucose concentration has a substantial effect on the reaction rate constant of glucose decomposition in HCW. At any given temperature, the glucose decomposition rate constant decreases as the initial glucose concentration increases, by almost 1 order of magnitude from 0.01 to 1000 mg L<sup>-1</sup>. Such a significant effect of initial glucose concentration on the glucose decomposition rate constant in HCW was not reported or generally ignored in past studies.<sup>30,43,44</sup> This is mainly due to the high initial glucose concentrations used in those studies, i.e.,

0.02–0.5 M (i.e., 3600–90 000 mg L<sup>-1</sup>), much higher than the highest concentration (1000 mg L<sup>-1</sup>, i.e., 0.0056 M) used in this study. As shown in Figure 3, at an initial glucose concentration >100 mg L<sup>-1</sup> (i.e.,  $5.6 \times 10^{-4}$  M), initial glucose concentration has an insignificant effect on the reaction rate constant of glucose decomposition. For example, at 250 °C, the glucose reaction rate constant only reduces from  $\sim 0.027$  to  $\sim 0.023$  s<sup>-1</sup> even when the initial glucose concentration increases by 10 times from 100 to 1000 mg L<sup>-1</sup>. While previous studies used initial glucose concentrations much higher than 1000 mg L<sup>-1</sup> (equivalent to  $\sim 0.0056$  M or  $\sim 0.1$  wt %), the data in this study clearly suggest that, at an initial glucose concentration of <100 mg L<sup>-1</sup> (i.e.,  $5.6 \times 10^{-4}$  M), the glucose decomposition rate constant is highly sensitive to initial glucose concentration, particularly when the glucose concentration is close to the concentration of H<sup>+</sup> or OH<sup>-</sup> in HCW (see discussion below).

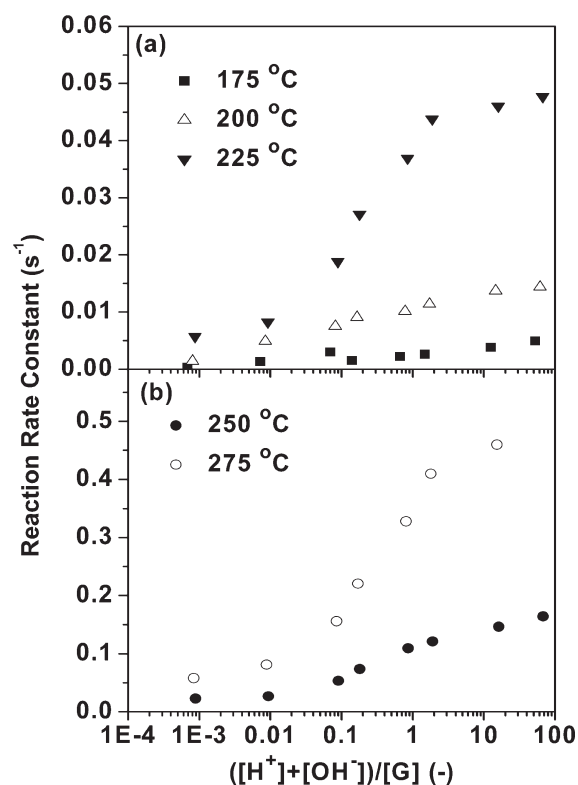
Given the importance of the ion product in HCW,<sup>12</sup> the significant effect of the initial glucose concentration on its decomposition rate in HCW is most likely due to the catalytic



**Figure 3.** Reaction rate constant ( $k$ ) of glucose decomposition in HCW as a function of initial glucose concentration at various temperatures: (a) 175, 200, and 225 °C; (b) 250 and 275 °C.

effect of the ion product in HCW. Previous *ab initio* molecular dynamic simulations suggested that the rate-limiting step for glucose decomposition reactions in aqueous solution is the protonation of OH groups on the glucose molecule and the subsequent breaking of the C–O bond of the protonated OH group from the sugar rings.<sup>38,45</sup> Therefore, it is reasonable to hypothesize that the decomposition reaction of glucose in HCW is likely to be initialized from the OH groups catalyzed by the ion product in HCW. It is known that the concentration of  $H^+$  is same as that of  $OH^-$  in HCW, about 3 orders of magnitude higher than those in ambient water. For example, the HCW has an  $H^+$  or  $OH^-$  concentration of  $\sim 2.4 \times 10^{-6}$  mol L<sup>-1</sup> at  $\sim 250$  °C and  $\sim 10$  MPa.<sup>39</sup> To achieve the same concentration as  $H^+$  or  $OH^-$ , the initial glucose concentration needs to be  $\sim 0.43$  mg L<sup>-1</sup>. As shown in Figures 2 and 3, indeed, the reaction rate constant increases significantly with decreasing the initial glucose concentration when the initial glucose concentration is below 0.5 mg L<sup>-1</sup>.

Therefore, it is plausible to plot the decomposition reaction rate constant as a function of the ratio between the molar concentration ion product in HCW and the molar concentration of glucose in HCW, or the ion–glucose molar ratio, i.e.,  $([H^+] + [OH^-])/[G]$ , under various reaction conditions, as shown in Figure 4. Clearly, it can be seen that the reaction rate constant of glucose decomposition increases as the ion–glucose molar ratio increases, but not in a linear relationship. It is interesting to note that the reaction rate constant increases substantially at ion–glucose molar ratio  $< 2$ . At ion–glucose molar ratio  $\geq 2$ , the reaction rate constant only increases slightly with the ion–glucose molar ratio. The results in Figure 4 clearly demonstrate that

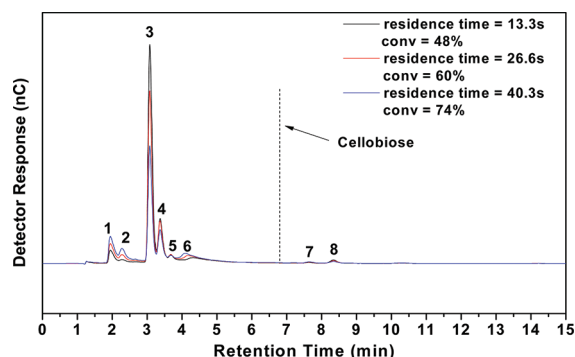


**Figure 4.** Reaction rate constant ( $k$ ) of glucose decomposition as a function of the molar ratio of ion product and glucose ( $([H^+] + [OH^-])/[G]$ ) in HCW at various temperatures: (a) 175, 200, and 225 °C; (b) 250 and 275 °C.

the ions in HCW,  $H^+$  and/or  $OH^-$ , have strong catalytic effects on enhancing the glucose decomposition reactions. It seems that, at  $([H^+] + [OH^-])/[G] < 2$ , the ion product plays a controlling role in determining the reaction rate of glucose decomposition in HCW, evidenced by the substantial increase in the reaction rate with increasing  $([H^+] + [OH^-])/[G]$ . At  $([H^+] + [OH^-])/[G] \geq 2$ , the system appears to have a sufficient amount of  $H^+$  and/or  $OH^-$  so that the reaction rate constant only increases slightly with further increase in  $([H^+] + [OH^-])/[G]$ , exhibiting a saturation effect. Such interesting observations may be explained from the point of view of glucose molecular structure. A glucose molecule has five OH groups in its structure; for the decomposition reaction of a glucose molecule in HCW to likely proceed to saturation, a minimum of one  $H^+$  or  $OH^-$  is required for each glucose molecule, i.e.,  $([H^+] + [OH^-])/[G] = 2$ . At  $([H^+] + [OH^-])/[G] < 2$ , the reaction system has an insufficient amount of  $H^+$  and/or  $OH^-$  so that an increase in the ion–glucose molar ratio is likely to substantially increase the glucose decomposition reaction rate. Oppositely, at  $([H^+] + [OH^-])/[G] \geq 2$ , glucose decomposition would be less likely controlled by the availability of ions as each glucose molecule would already have one  $H^+$  or  $OH^-$ , leading to much less catalytic effect of additional ions in the system on enhancing glucose decomposition reactions.

The data in Figures 2–4 demonstrate that glucose decomposition in HCW can be limited by the availability of ions in HCW, depending on the initial glucose concentration in the reaction solutions. Such a substantial increase in the reaction rate constant with decreasing initial glucose concentration also reflects a shift in the reaction mechanism and pathways of glucose



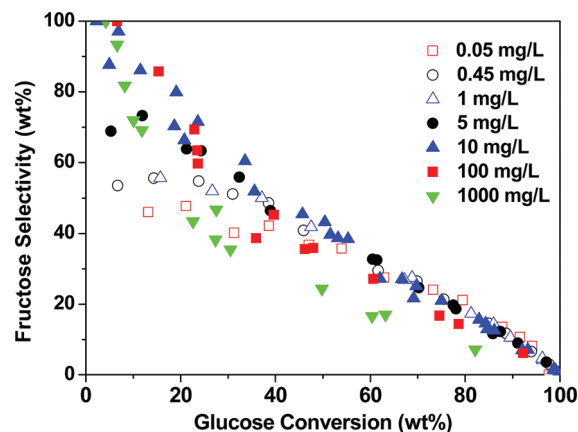


**Figure 5.** IC chromatograms of liquid products from glucose decomposition in HCW at 250 °C and an initial glucose concentration of 100 mg L<sup>-1</sup>. Peaks: 1, glyceraldehyde and glycolaldehyde; 2, 5-HMF; 3, glucose; 4, fructose; 5, erythrose; 6–8, unknown. The dashed line indicates the retention time at which the peak of cellobiose standard would appear.

decomposition, most likely as a result of strong catalytic effects of ions in HCW. However, it is still not clear which ion (H<sup>+</sup> and/or OH<sup>-</sup>) plays a more important role in glucose decomposition reactions and the fundamental mechanism governing such reactions. Therefore, attempts were then taken to analyze the liquid products from glucose decomposition under various conditions, with the results reported in section 3.2.

**3.2. Liquid Products from Glucose Decomposition in HCW at Various Initial Concentrations.** To further investigate the mechanism of glucose decomposition in HCW, HPAEC-PAD was used to characterize the liquid products of glucose decomposition under various conditions. Figure 5 presents typical IC chromatograms of the liquid products produced from glucose decomposition at 250 °C at various conversion levels. It can be found that the main products from glucose decomposition in HCW are fructose, glyceraldehydes and/or glycolaldehyde, erythrose, 5-HMF, etc. It should be noted that the method used in the IC was not able to separate glycolaldehyde and glyceraldehydes which end with a single peak in the chromatogram, plus unknown products which cannot be identified.

HPAEC-PAD is capable of identifying very low concentrations of 1,6-anhydroglucose. However, there is no peak of 1,6-anhydroglucose identified in the chromatograms of the liquid product as shown in Figure 5. Clearly, 1,6-anhydroglucose is not present in the liquid products of glucose decomposition under the reaction conditions in this study. This is an interesting observation because, in previous studies,<sup>44,46</sup> 1,6-anhydroglucose was reported to be one of the main compounds in the liquid products from glucose decomposition in HCW. A close examination of the experimental conditions used in the two studies reveals that the initial glucose concentrations were much higher. For example, in those studies,<sup>44,46</sup> 0.51 and 0.05 M glucose solutions were used, which were almost 100 and 10 times higher than the concentration used in this study, respectively. Therefore, the results in this study suggest that, at a low glucose concentration (<0.0056 M), glucose decomposition reactions follow a pathway what does not favor the formation of 1,6-anhydroglucose. It should also be noted that in Figure 5 the chromatograms also show the presence of unknown reaction products (e.g., peaks 7 and 8 in Figure 5) in the liquid product. Generally, sugar compounds with a higher molecular weight need a longer time to flow through the column during HPAEC-PAD analysis, therefore shown in the chromatogram at a

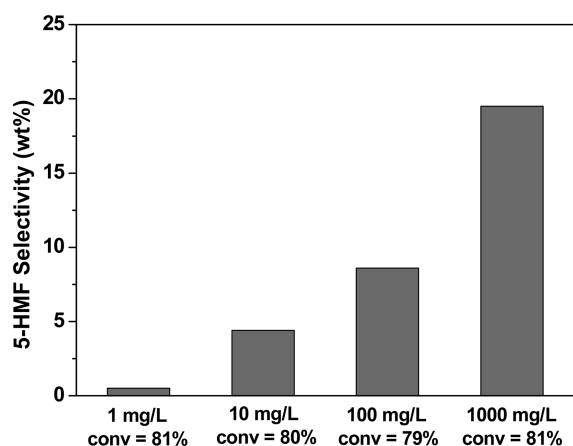


**Figure 6.** Selectivity of fructose as a function of glucose conversion under various reaction conditions. The datum points were obtained from glucose decomposition experiments at various initial glucose concentrations and different temperatures.

later retention time.<sup>24</sup> Such unknown products appear to have molecular weights higher than glucose, indicating that the polymerization reactions might have also taken place during glucose decomposition in HCW. This appears to be consistent with the previous reports on the fact that polymerization reactions can take place during the acidic degradation of glucose in HCW.<sup>45,47</sup> This is possible because, at low initial glucose concentrations in this study, the [H<sup>+</sup>]/[G] ratio is close to that under acidic condition so that polymerization reactions are likely to take place.

The selectivity of fructose is also plotted in Figure 6 as a function of glucose conversion for glucose decomposition experiments at various initial glucose concentrations and temperatures. It can be seen in Figure 6 that fructose has a very high selectivity at an early stage of glucose decomposition in HCW, which was also reported elsewhere.<sup>44</sup> Clearly, at an initial glucose concentration of >10 mg L<sup>-1</sup>, the selectivity of fructose is >90% at low glucose conversions (<10%), indicating that the isomerization reaction is dominant as the first step of glucose decomposition in HCW at high glucose concentrations (>10 mg L<sup>-1</sup>, i.e.,  $5.6 \times 10^{-5}$  M). However, fructose is prone to decomposition for producing smaller compounds,<sup>32,48</sup> such as glyceraldehydes and/or glycolaldehyde, erythrose, and 5-HMF. At a given reaction temperature, the reaction rate of fructose decomposition is known to be much faster than that of glucose decomposition.<sup>30</sup> Therefore, it is expected that the selectivity of fructose would decrease substantially with glucose conversion, as exactly shown in Figure 6.

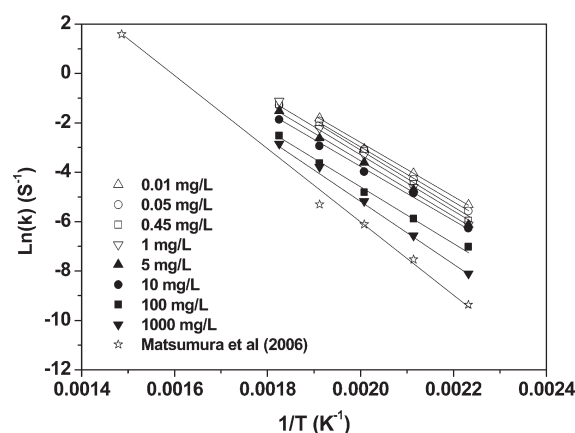
In addition, the data in Figure 6 also suggest that, at the same glucose conversion level, the selectivity of fructose strongly depends on the initial glucose concentrations. At higher concentrations (e.g., 100–1000 mg L<sup>-1</sup>), isomerization is still the dominant reaction at the early stage of glucose decomposition. However, as the decomposition reaction progresses, at the same glucose conversion, the selectivity of fructose is lower than that of glucose decomposition at an initial glucose concentration of 10 mg L<sup>-1</sup>. The data suggest that, at a higher initial glucose concentration, the rate of fructose formation from glucose decomposition is slower than the rate of fructose decomposition. This is more likely due to the hydroxyl ion, since the isomerization reaction to produce fructose and fructose decomposition reactions are all hydroxyl ion catalyzed reactions.<sup>17</sup> At a high glucose concentration, the hydroxyl ions are insufficient for all



**Figure 7.** Selectivity of 5-HMF at a similar conversion level but various initial glucose concentrations during glucose decomposition in HCW.

the glucose molecules. Once the fructose is produced, at least part of hydroxyl ions will participate in catalyzing the fructose decomposition reaction because the reaction is known to have a low activation energy.<sup>44</sup> On one hand, the reduction of fructose will be promoted by hydroxyl ion. On the other hand, the isomerization reaction to produce fructose will be partially inhibited due to the reduced availability of hydroxyl ion. The balance of these two factors appears to result in a net reduction in fructose selectivity during glucose decomposition at high initial glucose concentrations (e.g., >100 mg L<sup>-1</sup>). At a lower concentration <100 mg L<sup>-1</sup>, such effects would become less significant as a result of increasing [OH<sup>-</sup>]/[G] molar ratio, leading to slightly increased selectivity. However, at a very low concentration (e.g., 0.05–1 mg L<sup>-1</sup>), the selectivity of fructose is only ~50% even at conversions of <10%, suggesting that there are other parallel reactions taking place along with the isomerization reaction. The IC chromatograms show that erythrose, glyceraldehyde, and/or glycolaldehyde are detected in the liquid products at lower glucose concentration. Clearly, retro-aldol condensation reactions have taken place at a very low glucose concentration, as a result of the high [OH<sup>-</sup>]/[G] molar ratio under the conditions.

The data presented in Figures 2–6 demonstrate that the initial glucose concentration affects not only the reaction rate but also the reaction pathways during glucose decomposition in HCW. This may lead to substantial differences in the compositions of liquid products produced from glucose decomposition at various initial glucose concentrations, as a result of the significant ion product in HCW. To illustrate this point, the IC chromatograms of liquid products from glucose decomposition in HCW at 275 °C for different initial glucose concentrations were compared at a similar conversion. While the main compounds in the liquid products from different initial glucose concentrations are similar, their selectivities are largely different. The most significant difference is in the 5-HMF data, the selectivity of which are presented in Figure 7. While 5-HMF is hardly detected in the liquid product produced from glucose decomposition at an initial glucose concentration of 1 mg L<sup>-1</sup>, the selectivity of 5-HMF increases substantially with the initial glucose concentration, from nearly zero at 1 mg L<sup>-1</sup> to ~20% at 1000 mg L<sup>-1</sup>. Thus far, the reaction mechanism of 5-HMF formation from glucose decomposition in HCW is still not well understood. Generally 5-HMF is regarded as a typical product of fructose acidic decomposition reaction,<sup>37,49,50</sup> but molecular dynamic



**Figure 8.** Arrhenius plots of glucose decomposition in HCW at various initial glucose concentrations.

simulations suggest direct formation from glucose decomposition is still possible.<sup>38</sup> Under the current reaction conditions, 5-HMF from glucose decomposition in HCW is more likely produced via the intermediate fructose dehydration,<sup>51,52</sup> since fructose is produced with a high selectivity as shown in Figure 6. The increasing selectivity of 5-HMF indicates that the acid catalyzed dehydration reaction to form 5-HMF become increasingly important at high initial glucose concentrations (>10 mg L<sup>-1</sup>).

Further efforts were then made to investigate the reasons responsible for increasing the selectivity of 5-HMF with increasing initial glucose concentration. Experiments on fructose decomposition in HCW were then carried out at 10 and 1000 mg L<sup>-1</sup>. The results show that, similar to glucose decomposition in HCW, 5-HMF is only produced from fructose decomposition with a high selectivity at 1000 mg L<sup>-1</sup>. A possible explanation is that OH<sup>-</sup> is more effective than H<sup>+</sup> in catalyzing the decomposition reactions of glucose and fructose in HCW. Such a hypothesis seems to be plausible because alkali catalysts are known to greatly promote glucose isomerization<sup>51,53</sup> and retro-aldol condensation<sup>54,55</sup> while the effect of acid catalysts is negligible.<sup>51</sup> For fructose, both acid and alkali catalysts have significant effects on its decomposition in HCW.<sup>51</sup> At initial glucose concentrations of >10 mg L<sup>-1</sup>, the intermediate fructose as the main primary reaction product also has a high concentration, as shown in Figure 6. Obviously, there are insufficient OH<sup>-</sup> ions for catalyzing all the fructose molecules in the solutions, therefore leaving more chances for H<sup>+</sup> ions to catalyze the dehydration reaction to form 5-HMF. In summary, the results presented in this study suggest that OH<sup>-</sup> ions have a higher priority than H<sup>+</sup> ions in catalyzing the decomposition reactions of glucose and fructose in HCW. The production of 5-HMF is largely due to acid catalyzed dehydration reactions from the intermediate fructose after OH<sup>-</sup> ions become less available at initial glucose concentrations of >10 mg L<sup>-1</sup>. Once 5-HMF is formed, it may be further decomposed to other organic acids depending on reaction conditions;<sup>7,8,56</sup> therefore, the glucose decomposition reaction at high conversions may also be catalyzed by the formed acids.

**3.3. Reaction Pathways of Glucose Decomposition in HCW at Various Initial Glucose Concentrations.** Figure 8 presents the Arrhenius plots of glucose decomposition in HCW at various initial glucose concentrations. Further processing of the data

shows that the apparent activation energy of glucose decomposition decreases with decreasing initial glucose concentration (see Figure 9), from  $\sim 109 \pm 5 \text{ kJ mol}^{-1}$  at  $1000 \text{ mg L}^{-1}$  to  $\sim 90 \pm 4 \text{ kJ mol}^{-1}$  at  $0.01 \text{ mg L}^{-1}$ , consistent with  $121 \text{ kJ mol}^{-1}$  reported in a previous study<sup>43</sup> that used a considerably higher initial glucose concentration. Additionally, when the initial glucose concentration is sufficiently low ( $< 5 \text{ mg L}^{-1}$ ), there is little change in the apparent activation energy with further decrease in initial glucose concentration while the reaction rate of glucose decomposition still significantly increases with decreasing glucose concentration. Clearly, this indicates that the preexponential factor must increase with decreasing glucose concentration from 1 to  $0.01 \text{ mg L}^{-1}$ . This is exactly the result shown in Figure 9b, most likely due to increased  $([\text{H}^+] + [\text{OH}^-])/[\text{G}]$  ratio under the prevailing conditions.

The increase in 5-HMF selectivity (see Figure 7) and apparent activation energy (see Figure 9a) of glucose decomposition in HCW clearly indicate a shift in reaction pathways as the initial glucose concentration increases. At initial glucose concentrations higher than  $10 \text{ mg L}^{-1}$ ,  $\text{H}^+$  ions start to play a more important role in catalyzing the dehydration reaction, leading to the increasing formation of 5-HMF. At initial glucose concentrations  $< 10 \text{ mg L}^{-1}$ , it is still  $\text{OH}^-$  ions that play the dominant role in catalyzing glucose isomerization and retro-aldol condensation to form fructose, glyceraldehyde, erythrose, glycolaldehyde, etc. It is also very likely that  $\text{H}^+$  catalyzed dehydration reactions may have a higher activation energy than  $\text{OH}^-$  catalyzed reactions (i.e., isomerization or retro-aldol condensation reactions). As shown in a previous study,<sup>44</sup> under subcritical HCW conditions, the glucose isomerization reaction to form fructose has the lowest apparent activation energy of  $78.6 \text{ kJ mol}^{-1}$ , while the glucose retro-aldol reactions to form erythrose and glyceraldehyde have higher activation energies of  $96.2 \text{ kJ mol}^{-1}$  and  $95.6 \text{ kJ mol}^{-1}$ , respectively. Indeed, this is very close to the apparent activation energy ( $\sim 90 \text{ kJ mol}^{-1}$ ) determined at low glucose concentrations in this study. The dehydration reaction to form 5-HMF was found to have an apparent activation energy of  $125.9 \text{ kJ mol}^{-1}$ .<sup>44</sup> This further explains why the apparent activation energy of glucose decomposition increases with initial glucose concentration, mainly due to the increased selectivity of dehydration reactions to form 5-HMF at high glucose concentrations.

Based on the results and discussion in this study, the effects of initial glucose concentration on the mechanisms of glucose decomposition in HCW can be summarized in Figure 10.  $\text{OH}^-$  ions appear to have higher priority over  $\text{H}^+$  ions in catalyzing the isomerization and retro-aldol condensation reactions so that those reactions will be promoted at low initial glucose concentrations ( $< 10 \text{ mg L}^{-1}$ ). However, at high initial glucose concentrations ( $\geq 10 \text{ mg L}^{-1}$ ), as there are insufficient  $\text{OH}^-$  ions available for all the glucose molecules,  $\text{H}^+$  ions become more important in catalyzing the dehydration reaction to produce 5-HMF. Under all reaction conditions in this study, the formation of 1,6-anhydroglucose by the dehydration reaction of glucose is inhibited, most likely due to the high activation energy required for this reaction to take place. It is known that the glucose dehydration reaction to form 1,6-anhydroglucose has a high activation energy of  $193.2 \text{ kJ mol}^{-1}$ ,<sup>44</sup> which is substantially higher than the apparent activation energy ( $\sim 90 \pm 4$ – $109 \pm 5 \text{ kJ mol}^{-1}$ ) of glucose decomposition measured in this study. The results in this study also clearly show that, for modeling sugar

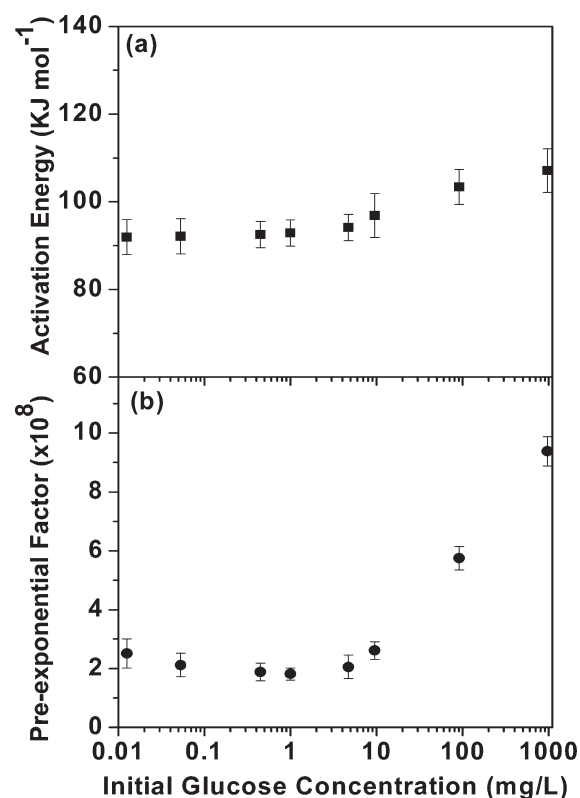


Figure 9. Activation energy and preexponential factor of glucose decomposition in HCW as a function of initial glucose concentration.

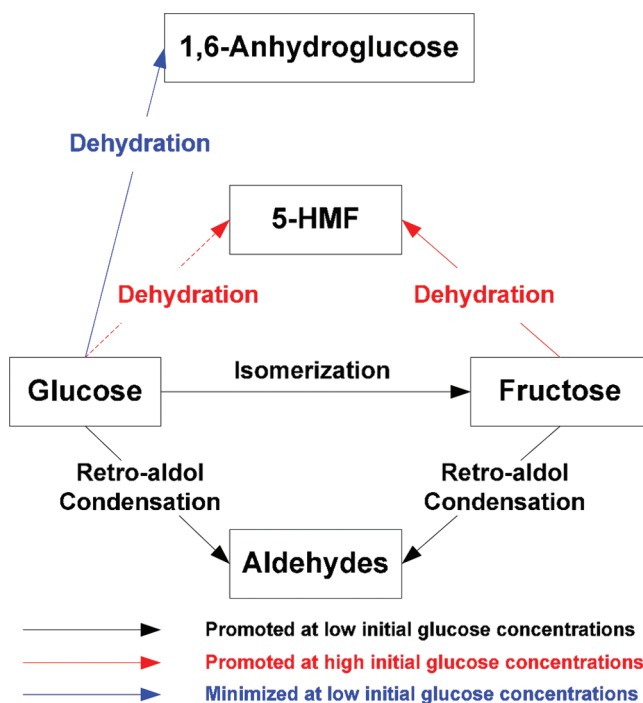


Figure 10. Effect of initial glucose concentration on reaction pathways during glucose decomposition in HCW.

decomposition in HCW, the influence of initial glucose concentration on the glucose decomposition kinetics and product distribution must be considered.



## 4. CONCLUSIONS

This study provides new insights into the mechanism of glucose decomposition in HCW at various initial glucose concentrations, by investigating the kinetics of glucose decomposition reactions at a low concentration level down to that of the ion product in HCW. The reaction rate constant increases substantially with decreasing initial glucose concentration, suggesting a shift in the glucose decomposition reaction pathway at various initial glucose concentrations. Selectivity of fructose is very high at the early stage of glucose decomposition reactions, indicating that fructose is a major primary product from glucose decomposition in HCW. The distribution of major compounds in the liquid product greatly changes with the initial glucose concentration. The selectivity of 5-HMF increases with glucose concentration, indicating that the  $H^+$  catalyzed dehydration reaction plays a more important role at higher initial glucose concentration. However, at low initial glucose concentration, the  $OH^-$  catalyzed isomerization and retro-aldol reactions play a dominant role, leading to the formation of fructose, erythrose, glycolaldehyde, and/or glyceraldehyde, etc. The change in the selectivity of various reaction pathways at different initial glucose concentrations also leads to changes in the apparent activation energy of glucose decomposition in HCW. The apparent activation energy of glucose decomposition increases with increasing initial glucose concentration, as a result of the favored acid catalyzed dehydration reaction of high activation energy.

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