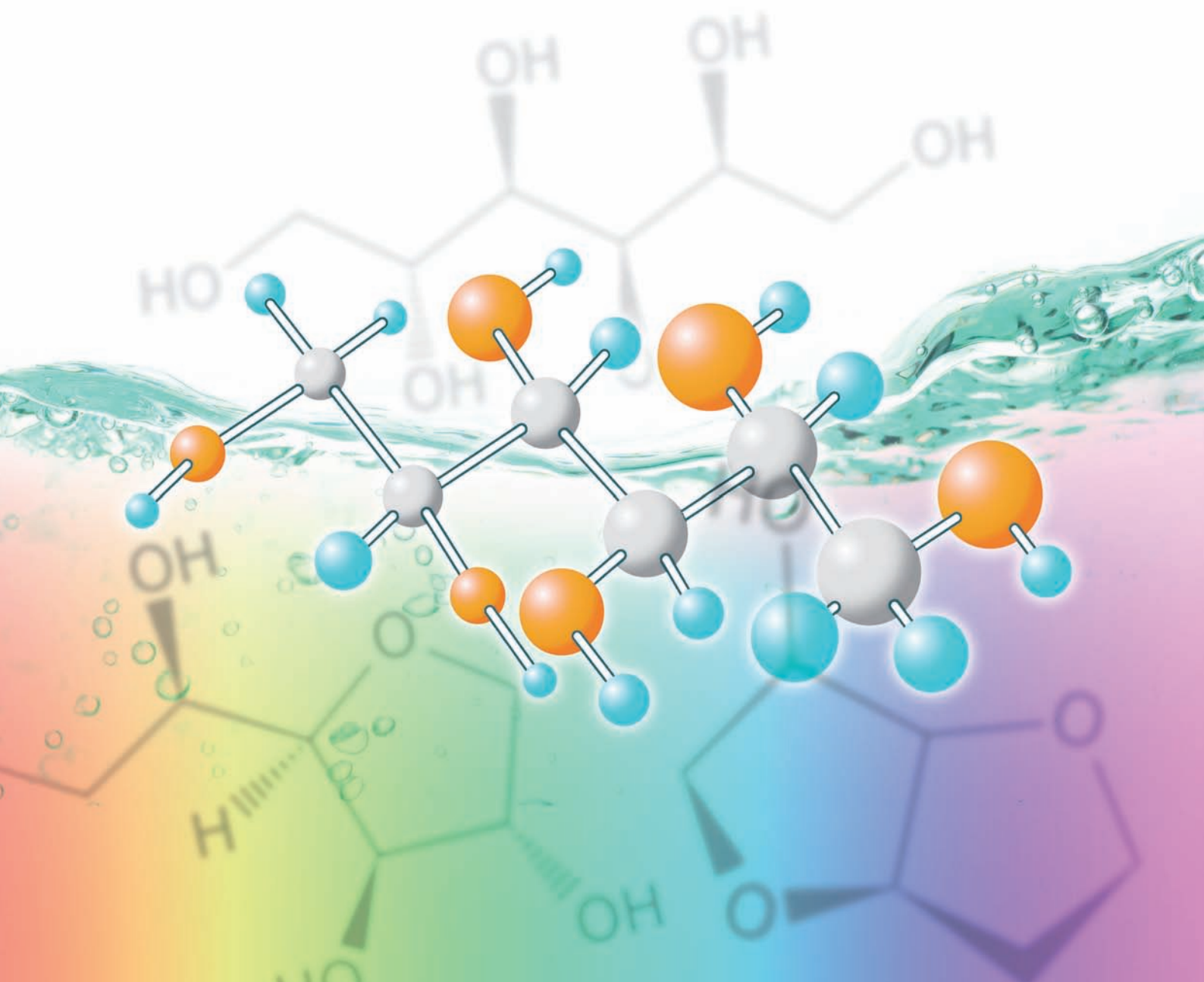


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PAPER

Sorbitol dehydration in high temperature liquid water

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Sorbitol dehydration in high temperature liquid water proceeded at 523–573 K without adding any acid catalysts. Anhydrosorbitols (1,4-anhydrosorbitol (1,4-AHSO), 2,5-anhydrosorbitol (2,5-AHSO) and 1,5-anhydrosorbitol (1,5-AHSO)) were produced by the monomolecular dehydration of sorbitol, and isosorbide was produced by the stepwise dehydration of 1,4-AHSO. The formation rates of 1,4-AHSO and 2,5-AHSO (five-membered cyclic ethers) from sorbitol dehydration were much larger than that of 1,5-AHSO (six-membered cyclic ether), and 1,4-AHSO was the main product of the monomolecular dehydration of sorbitol. The dehydration rate of sorbitol to 1,4-AHSO was faster than that of 1,4-AHSO to isosorbide; therefore, 1,4-AHSO could be obtained as an intermediate product. A kinetic analysis of sorbitol dehydration in high temperature liquid water showed that the maximum yield of 1,4-AHSO from the dehydration of sorbitol increased with decreasing reaction temperature (for example, 80% at 500 K) and that the maximum yield of isosorbide was 57% at 590 K for 1 h. 1,4-AHSO and isosorbide could be produced selectively from sorbitol dehydration in high temperature liquid water by controlling both the reaction temperature and reaction time.

1. Introduction

The production of chemicals and fuels from renewable biomass has attracted much attention for a sustainable society.¹ The conversion of the non-edible fraction of biomass, such as cellulose, to valuable chemicals using environmentally-friendly techniques is crucial. Sorbitol is a promising biomass-derived material from cellulose for providing chemicals.^{2–4} Cellulose can be depolymerized to glucose by hydrolysis,^{5–7} and glucose can be hydrogenated to sorbitol using ruthenium or nickel catalysts.^{8–10} Recently, Fukuoka and Dhepe succeeded in producing sorbitol by the one-step cracking of cellulose using a platinum catalyst and hydrogen in water.^{11,12} The dehydration of sorbitol can provide valuable chemicals: both anhydrosorbitol (sorbitan) by monomolecular dehydration and isosorbide by bimolecular dehydration. Anhydrosorbitol is a key material for producing sorbitan fatty acid esters, which are used as naturally-derived surfactants or non-toxic food additives. Isosorbide and isosorbide nitrate are drug medicines used as osmotic diuretics and blood pressure lowering drugs, respectively. Also, isosorbide has attracted a great deal of attention because poly(ethylene terephthalate) (PET), containing isosorbide, has higher glass transition temperatures (T_g) than pure PET, broadening the applications of polyesters.¹³

Sorbitol dehydration has been studied since the mid-20th century.^{14–16} Some researchers have reported sorbitol dehydration with inorganic acid catalysts, such as sulfuric and hydrochloric acids, in the temperature range 377–408 K^{17,18} and with hydrofluoric acid at 293 K.¹⁹ In these processes, however, a neutralization procedure is essential to remove hazardous inorganic acid catalysts, and also the separation processes of the dehydration products from the salt solutions are troublesome. Environmentally benign techniques should be applied for biomass-derived material transformation, in which case hazardous materials are neither used nor produced. High temperature liquid water has attracted much attention as a promising reaction medium for acid- and base-catalyzed reactions.^{20–30} Savage *et al.* have reported that the dehydration of 1,4-butanediol to tetrahydrofuran proceeded in high temperature liquid water using the self-ionization of water,²³ which is more highly feasible at high temperature than that at ambient temperature, leading to high concentrations of proton and hydroxide ions. Sorbitol dehydration in high temperature liquid water does not require a neutralization step.

In this manuscript, we report the transformation of biomass-derived material to value-added chemicals, especially sorbitol dehydration to anhydrosorbitol and isosorbide in high temperature liquid water without adding any hazardous acid catalysts. We found that the formation rates of 1,4-anhydrosorbitol and 2,5-anhydrosorbitol (five-membered cyclic ethers) by sorbitol dehydration were much higher than that of 1,5-anhydrosorbitol (six-membered cyclic ether), and that 1,4-anhydrosorbitol was the main product of the monomolecular dehydration of sorbitol.

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Isosorbide was produced by a stepwise dehydration of 1,4-anhydrosorbitol. We investigated the reaction pathway and kinetics of the sorbitol dehydration in high temperature liquid water to produce anhydrosorbitol or isosorbide selectively.

2. Experimental

D-Sorbitol was purchased from Wako Pure Chemical Industries, Ltd. and used without any further purification.

The dehydration of sorbitol was carried out in a batch reactor (inner volume: 6 cm³) made of a SUS316 tube.^{31,32} After 3 cm³ of sorbitol aqueous solution had been loaded into the reactor, it was purged with argon gas to remove air. The reactor was then submerged into a molten salt bath at the desired reaction temperature for a given reaction time, and then submerged into a water bath for cooling quickly to ambient temperature after the reaction. The mixture of the reactant and liquid products was taken out from the reactor with distilled water and separated from the solid products by filtration.

Sorbitol dehydration was also carried out in a batch reactor with the addition of high pressure carbon dioxide.^{24–26} After 3 cm³ of sorbitol aqueous solution had been loaded in the reactor, it was purged with argon gas to remove air, and carbon dioxide was then loaded into the reactor at 323 K. After the reaction, carbon dioxide was removed by depressurization, and then the mixture of the reactant and liquid products was taken out from the reactor with distilled water and separated from the solid products by filtration.

Quantitative analysis of the unreacted reactant and liquid products was conducted by a high performance liquid chromatograph (HPLC, Gilson, Inc.) with an evaporative light scattering detector (model 300S ELSD, SofTA Corporation) and a UV-vis detector (UV/VIS-152, Gilson, Inc.) equipped with a Carbomix Ca NP5 column (Sepax Technologies, Inc.). The products were identified by comparing them with the retention times of the standard materials: 1,4-anhydro-D-sorbitol (1,4-AHSO, Tronto Research Chemicals Inc.), 1,5-anhydro-D-sorbitol (1,5-AHSO, Sigma-Aldrich), 2,5-anhydro-D-sorbitol (2,5-AHSO, Tronto Research Chemicals Inc.) and 1,4-3,6-dianhydro-D-sorbitol (isosorbide, Alfa Aesar). The other possible dehydrated product, 3,6-anhydro-D-sorbitol (3,6-AHSO), could not be separated from 1,4-AHSO by HPLC because 3,6-AHSO is an epimer of 1,4-AHSO; therefore, the measured amount of 1,4-AHSO in this manuscript includes a quantity of 3,6-AHSO. The ratio of 3,6-AHSO to 1,4-AHSO is reported to be very low (less than 0.1), as determined by ¹³C NMR spectroscopy.¹⁷

3. Results and discussion

3.1. Dehydration of sorbitol at different temperatures

The dehydration of sorbitol (1.0 mol dm⁻³) proceeded at 523 K in high temperature liquid water, and 1,4-AHSO, 2,5-AHSO, 1,5-AHSO, and isosorbide were obtained (Fig. 1(a)). The material balance, which is defined as the sum of the unreacted sorbitol and the detected products (1,4-AHSO, 2,5-AHSO, 1,5-AHSO and isosorbide), was more than 90% at 523 K, even for a 36 h reaction. The major product obtained from monomolecular dehydration was 1,4-AHSO, with the highest yield of 69% at

523 K for 24 h, and the yield of isosorbide obtained from the bimolecular dehydration of sorbitol increased with reaction time. On the other hand, 2,5-AHSO was obtained with a yield of 10% at 523 K after 18 h and it did not change with reaction time after 18 h. The yield of 1,5-AHSO was always less than 1% at 523 K (data not shown in Fig. 1(a)).

At a lower reaction temperature of 473 K, sorbitol dehydration proceeded very slowly on a 24 h scale (sorbitol conversion 14% after 24 h).

The dehydration of sorbitol was also carried out at 548, 560 and 573 K in high temperature liquid water (Fig. 1(b), (c) and (d)). The material balance decreased with an increase of reaction temperature and reaction time. For example, at 573 K, the material balance at a reaction time of 5 h was 75% from HPLC analysis. On the other hand, the amount of total organic carbon in the liquid phase, which was analyzed by a total organic carbon analyzer Shimadzu TOC-V_{CSN}, was 90% of the reactant sorbitol. The difference between the material balance by HPLC analysis and total organic carbon in the liquid phase indicates that by-products caused by the polymerization and/or degradation of sorbitol or anhydrosorbitol were dissolved in the liquid phase. Solid products should have been obtained up to 10%, as derived from the amount of total organic carbon (90%) in the liquid phase; however, the amount of solid products was not enough to be determined by a gravimetric method. The material balance also decreased with increasing reaction time (65% at 10 h at 573 K).

Over 593 K, the material balance of the reaction after 5 h was less than 50%, indicating that the degradation and polymerization of the products and/or reactant occurred notably over 593 K.

At all the temperatures (523–573 K), 1,4-AHSO and 2,5-AHSO were produced at the beginning of reaction (Fig. 1). The initial formation rates of 1,4-AHSO and 2,5-AHSO increased with increasing reaction temperature, and the 1,4-AHSO yield was higher than the 2,5-AHSO yield at the initial stage of the sorbitol dehydration. The 1,4-AHSO yield had a maximum and decreased with reaction time; on the other hand, the 2,5-AHSO yield was almost constant or started to decrease slightly at 573 K. Isosorbide was produced later than 1,4-AHSO and 2,5-AHSO because isosorbide “1,4-3,6-dianhydro-D-sorbitol” was formed by the stepwise dehydration of 1,4-AHSO (Scheme 1). Among the reaction conditions in Fig. 1, the maximum yield of 1,4-AHSO was 69% (at 523 K after 24 h) and that of isosorbide was 55% (at 573 K after 3 h). Isosorbide and 1,4-AHSO could be produced by the dehydration of sorbitol in high temperature liquid water without adding any acid catalysts.

The yields of 1,5-AHSO were always less than 1% under the experimental conditions of our work (the data are not shown in Fig. 1). This result shows that the formation rates of 1,4-AHSO and 2,5-AHSO (five-membered cyclic ethers) are much higher than that of 1,5-AHSO (six-membered cyclic ether). A similar result was observed in our previous reports, where the dehydration rate of 1,4-butanediol to tetrahydrofuran (five-membered cyclic ether) was much higher than that of 1,5-pentanediol to tetrahydropyran (six-membered cyclic ether).^{25,33} The dehydration reactions of polyalcohol compounds, including sorbitol, to five-membered cyclic ethers would rather proceed through a transition state of lower energy than undergo

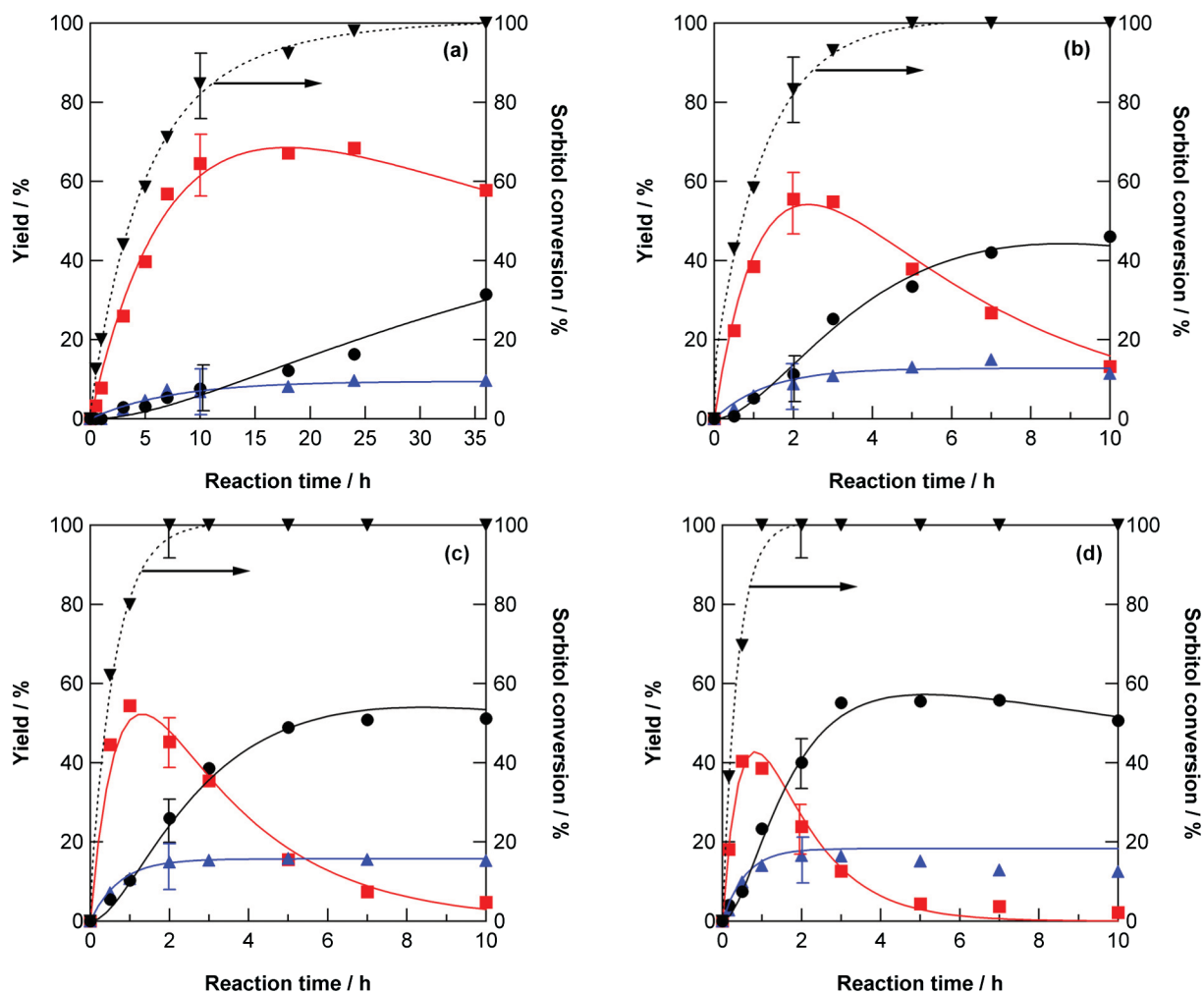


Fig. 1 Yields of 1,4-AHSO (■), 2,5-AHSO (▲) and isosorbide (●), and sorbitol conversion (▼), as a function of elapsed time for the sorbitol dehydration reaction at (a) 523, (b) 548, (c) 560 and (d) 573 K in water (initial sorbitol concentration: 1.0 mol dm^{-3}). The lines show the best fit for the obtained data to the equations in the appendix with the kinetic parameters in Table 1.

dehydration reactions to six-membered cyclic ethers because the initial dehydration rates should be determined by kinetic factors.

3.2. Dehydration of 1,4-anhydro-D-sorbitol in high temperature liquid water

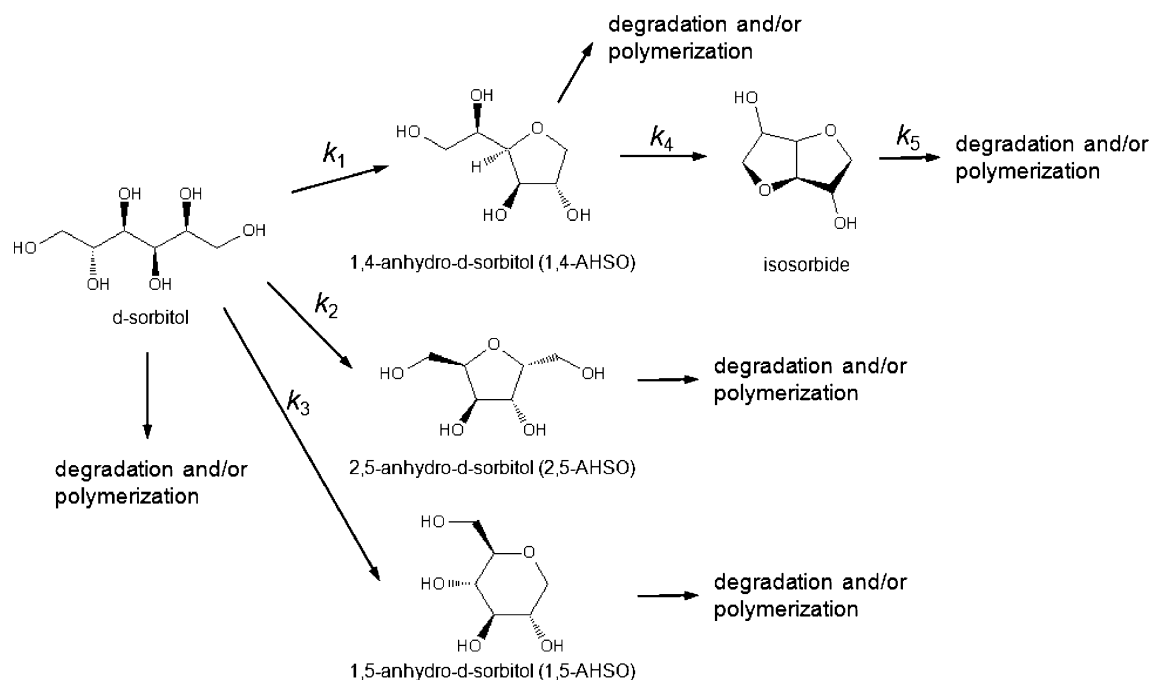
We also carried out the dehydration of 1,4-AHSO (1.0 mol dm^{-3}) in high temperature liquid water by following the same procedure as that for sorbitol dehydration (Fig. 2). The material balance also decreased with increasing reaction temperature and reaction time. For example, at 573 K, the material balance at a reaction time of 3 h was 85% by HPLC analysis. The product was only isosorbide, and sorbitol could not be detected, indicating that the hydration of 1,4-AHSO to sorbitol did not proceed in high temperature liquid water and that the dehydration of sorbitol to 1,4-AHSO was irreversible. The isosorbide yields from 1,4-AHSO dehydration were 6, 23 and 48% at 548, 560 and 573 K after 3 h, respectively (Fig. 2); however, the isosorbide yields from sorbitol dehydration were 25, 39 and 56% at 548, 560 and 573 K after 3 h, respectively (Fig. 1). These results indicate that the dehydration of 1,4-AHSO to isosorbide during sorbitol dehydration was faster than that during 1,4-AHSO dehydration.

This phenomenon will be discussed in detail in section 3.5 by using kinetics and the mechanism of the reactions.

The stability of isosorbide in high temperature liquid water was investigated at 573 K in the same procedure as the sorbitol dehydration reaction by using a 1.0 mol dm^{-3} isosorbide aqueous solution instead of a sorbitol aqueous solution. The reverse reactions (the formation of 1,4-AHSO, sorbitol and so on) did not proceed and the recovery yield of isosorbide was more than 97% after 5 h at 573 K, indicating that isosorbide molecules themselves are stable in water at 573 K. In contrast to this result, the isosorbide yields from the sorbitol dehydration at 573 K decreased from 5 h (55%) to 10 h (50%) (Fig. 1(d)), indicating that polymerization of isosorbide with the other products, such as 2,5-AHSO and degradation products, occurs during sorbitol dehydration.

3.3. Dehydration of sorbitol at different initial concentrations

Sorbitol dehydration behavior was investigated at different initial sorbitol concentrations ($1.0\text{--}3.0 \text{ mol dm}^{-3}$) in high temperature liquid water at 573 K (Fig. 3). The product yields of 1,4-AHSO and 2,5-AHSO from different initial reactant



Scheme 1 The reaction pathway of sorbitol dehydration.

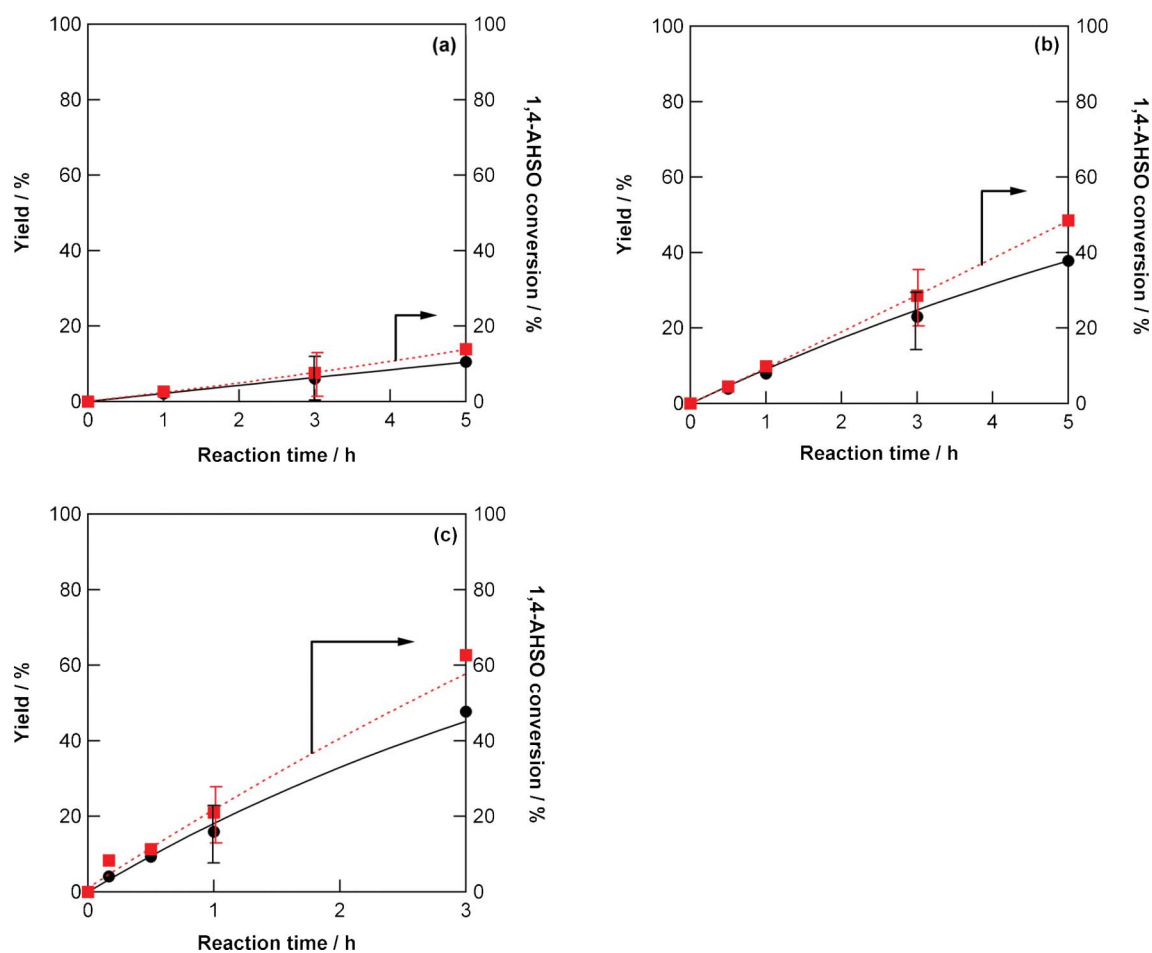


Fig. 2 Yields of isosorbide (●) and the conversion of 1,4-AHSO (■) as a function of elapsed time for the 1,4-AHSO dehydration reaction at (a) 548, (b) 560 and (c) 573 K in water (initial 1,4-AHSO concentration: 1.0 mol dm⁻³).

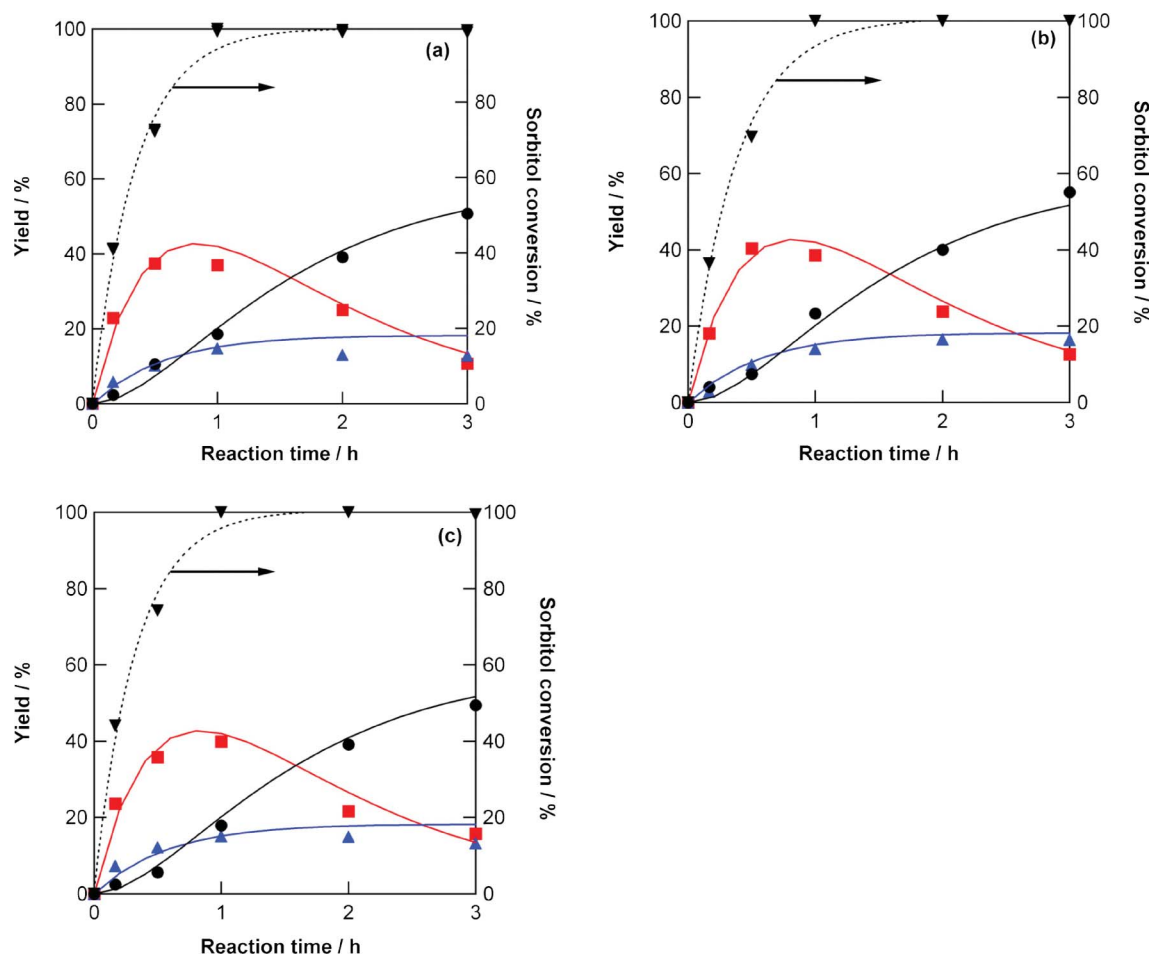


Fig. 3 Yields of 1,4-AHSO (■), 2,5-AHSO (▲) and isosorbide (●), and sorbitol conversion (▼), as a function of elapsed time for the sorbitol dehydration reaction at 573 K in water (initial sorbitol concentration: (a) 1.0 (same data as in Fig. 1(d)), (b) 2.0 and (c) 3.0 mol dm⁻³). The lines of the three figures are same to clarify the differences between the plots, showing the best fit for the obtained data of 1.0 mol dm⁻³ sorbitol dehydration, as shown in Fig. 1(d).

concentrations (1.0, 2.0 and 3.0 mol dm⁻³ sorbitol aqueous solutions) were quite similar to each other, indicating that the dehydration of sorbitol follows a first-order dependence with respect to sorbitol concentration. The isosorbide yields from different initial sorbitol concentrations were also similar to each other. From this result, the dehydration reaction of 1,4-AHSO to isosorbide should have a first-order dependence on 1,4-AHSO concentration because the 1,4-AHSO concentration depended on the initial sorbitol concentration proportionally.

3.4. Dehydration of sorbitol with high pressure carbon dioxide

The dehydration of sorbitol (1.0 mol dm⁻³) was carried out in high temperature liquid water with 10 MPa of carbon dioxide at 523 and 573 K (Fig. 4) to investigate the effect of carbonic acid, which is derived from water and carbon dioxide. The rates of sorbitol consumption, and the production of 1,4-AHSO, 2,5-AHSO and isosorbide, were almost the same with or without carbon dioxide (Fig. 4), indicating that the dehydration rate is not enhanced by the addition of carbon dioxide (10 MPa). This result shows that the dehydration reaction of sorbitol has an almost zero-order dependence on proton concentration in the

range of temperatures 523–573 K and proton concentrations with/without carbonic acid.

We have reported that high pressure carbon dioxide dissolved in high temperature liquid water accelerates the dehydration reactions of diol and triol compounds to cyclic ethers by protons derived from carbonic acid;^{24,25} the apparent reaction orders of protons for the polyalcohol dehydration reactions were estimated to be 0.6 and 0.2 at 573 K²⁵ for 3-hydroxytetrahydrofuran from 1,2,4-butanetriol and tetrahydrofurfuryl alcohol from 1,2,5-pentanetriol, respectively. Thus, we concluded that the dehydration of 1,2,4-butanetriol and 1,2,5-pentanetriol to cyclic ether compounds was not simply initiated by collisions between the polyalcohol molecule and proton. On the other hand, the dehydration reaction of sorbitol had an almost zero-order dependence on proton concentration. This result can be explained by two possible reasons. (i) Protonation (–OH₂⁺) of hydroxyl groups (–OH) was not a rate-determining step, and that the other elementary steps of dehydration, such as the attack of an O atom in –OH at a C atom with –OH₂⁺ (S_N2 substitution mechanism) and the simultaneous elimination of water, would be rate-determining under our reaction conditions. (ii) Water molecules play a role as a proton donor, and the hydroxyl group of sorbitol was protonated by water molecules in high

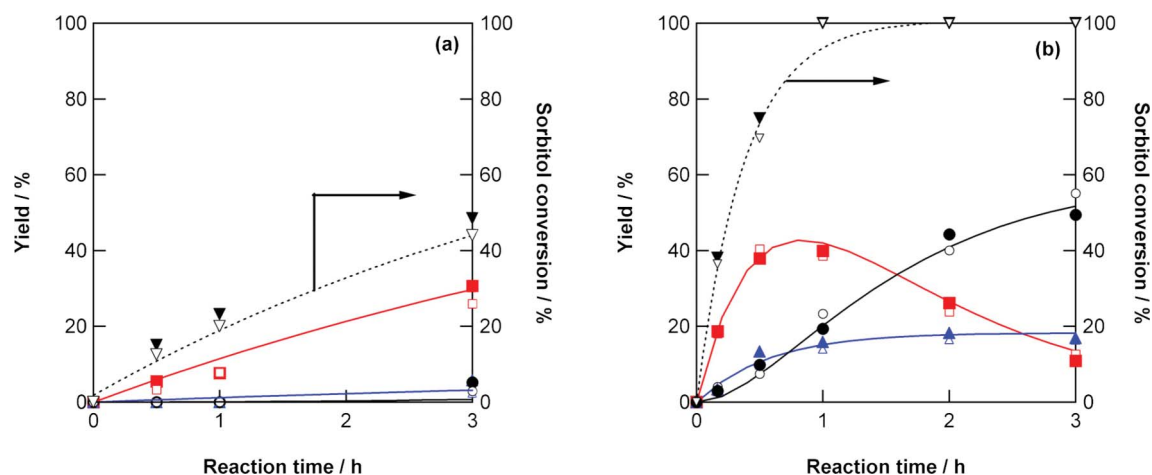


Fig. 4 Yields of 1,4-AHSO (■/□), 2,5-AHSO (▲/△) and isosorbide (●/○), and sorbitol conversion (▼/▽), as a function of elapsed time for the sorbitol dehydration reaction at (a) 523 and (b) 573 K in water (initial sorbitol concentration: 1.0 mol dm⁻³, initial carbon dioxide pressure: 0 (open symbols) and 10 (closed symbols) MPa). The lines show the best fit for the obtained data of sorbitol dehydration without carbon dioxide, as shown in Fig. 1.

temperature water.^{23,34,35} Savage *et al.* have reported that the hydrolysis rates of organic compounds such as dibenzyl ether and methyl benzoate were not affected by proton concentration in high temperature liquid water at 473–573 K in the pH range 4 to 7.^{34,35} They claimed that the acid-catalyzed reaction could proceed not only by protons but also by water molecules in high temperature liquid water.^{23,34,35} The pH range of sorbitol dehydration with and without carbon dioxide in this study is estimated to be 3.5 and 6.0, respectively,³⁴ the range in which Savage *et al.* reported that water molecules mainly caused an acid-catalyzed reaction.^{23,34,35}

In contrast, it has been reported that the dehydration rates of sorbitol by acid catalysts at 408 K under vacuum are changed by the identity of the acid catalyst,¹⁸ and that the order of dehydration activity among the acid catalysts studied was sulfuric acid \approx hydrochloric acid > phosphoric acid. It has also been reported that the dehydration rate decreases with decreasing acid concentration (below 0.5%, sulfuric acid).¹⁸ The dehydration rates of sorbitol with strong acid catalysts under vacuum at 408 K increased with increasing numbers of protons. The authors claimed in the manuscript¹⁸ that sorbitol dehydration with strong acid catalysts under vacuum proceeded *via* a carbocationic intermediate species by the elimination of water from $-\text{OH}_2^+$ (S_N1 substitution mechanism) followed by cyclization. Sorbitol dehydration in high temperature liquid water proceeds in a different way from that in strong acid catalysts under vacuum.

3.5. Kinetics for sorbitol dehydration in high temperature liquid water

The dehydration of sorbitol in high temperature liquid water proceeded *via* the sequence of steps shown in Scheme 1. The reverse reaction did not proceed, as revealed by the reaction behavior of 1,4-AHSO and isosorbide in high temperature liquid water (section 3.2.). The amount of formed isosorbide decreased in high temperature liquid water (k_5 step in Scheme 1), as shown in Fig. 1(d). The dehydration reactions have a first-order

Table 1 Kinetic parameters for the dehydration reactions of sorbitol (initial sorbitol concentration: 1.0 mol dm⁻³)

Reaction T/K	523	548	560	573	Activation energy/kJ mol ⁻¹
$k_1/10^{-2} \text{ mol h}^{-1}$	0.13	0.65	1.2	1.4	127
$k_2/10^{-2} \text{ mol h}^{-1}$	0.013	0.11	0.22	0.32	166
$k_4/10^{-2} \text{ mol h}^{-1}$	0.016	0.18	0.36	0.78	195
$k_5/10^{-2} \text{ mol h}^{-1}$	0.0083	0.041	0.098	0.11	136

^a Parameters defined in Scheme 1 and the Appendix.

dependence on the reactant concentration (section 3.3.). The concentrations of the reactant and products are represented as eqns (6)–(10) using various rate constants (k_1 , k_2 , k_3 , k_4 and k_5 in Scheme 1), as shown in the Appendix. The polymerization and/or degradation of sorbitol and its products could proceed in high temperature liquid water; however, we adopted only k_5 as the polymerization and/or degradation of isosorbide for the simplicity of the rate equations. The concentration of 1,5-AHSO (less than 1% under all conditions) is ignorable; therefore, k_3 is zero. The rate constants (k_1 , k_2 , k_4 and k_5) were estimated (Table 1) using linear regression analyses with minimization of residuals for the data of 1,4-AHSO, 2,5-AHSO and isosorbide yields. Rate constant k_1 (sorbitol to 1,4-AHSO) was the highest compared with the other rate constants (k_2 , k_4 and k_5), indicating that the first dehydration step of sorbitol to 1,4-AHSO proceeds faster than the other dehydration steps and that 1,4-AHSO could be obtained as an intermediate product. The yields of reactant and products could be predicted from the rate constants in Table 1 and eqns (6)–(10), as shown in Fig. 1. The predicted lines of the yields are consistent with the experimentally yielded data, indicating that the dehydration of sorbitol in high temperature liquid water proceeded *via* the sequence of steps shown in Scheme 1, and that the dehydration of sorbitol and 1,4-AHSO has a first-order dependence on reactant concentration.

The final yield (%) of 2,5-AHSO became $k_2/(k_1 + k_2 + k_3) \times 100$ from eqn (8), without taking into account the degradation of 2,5-AHSO. The values of $k_2/(k_1 + k_2 + k_3) \times 100$ were 9.1, 14.5, 15.5

Table 2 Kinetic parameters for dehydration reaction of 1,4-AHSO to isosorbide (initial 1,4-AHSO concentration: 1.0 mol dm⁻³)

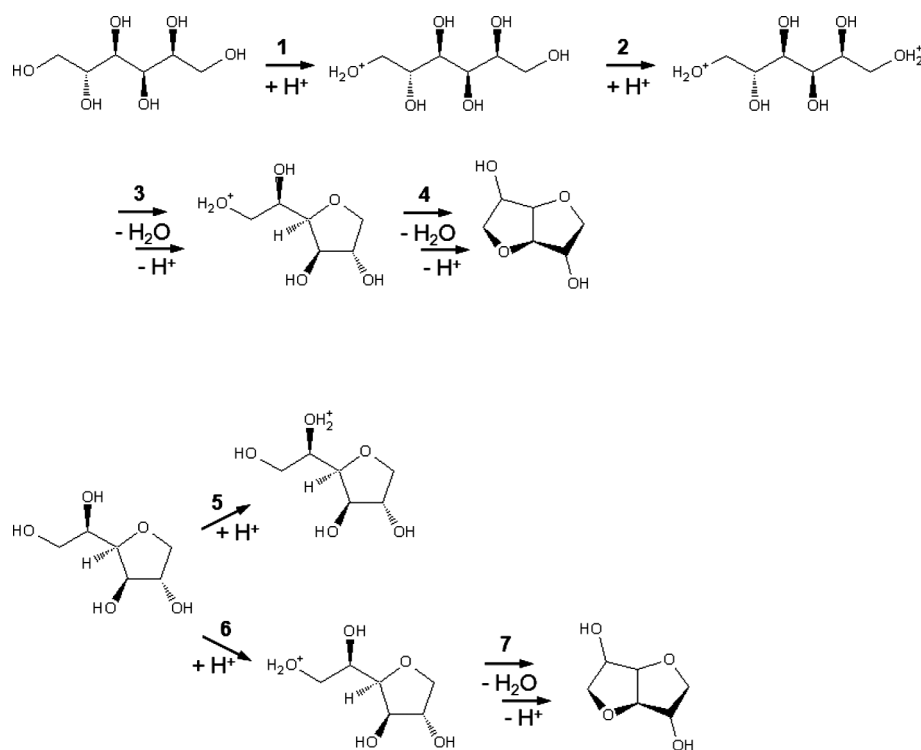
Reaction <i>T</i> /K	548	560	573
$k_4'/10^{-2}$ mol h ⁻¹	0.022	0.095	0.21

and 18.6 at 523, 548, 560 and 573 K, respectively, from Table 1, which are consistent with the final yields (%) of 2,5-AHSO (9.7, 14.9, 15.3 and 12.5 at 523, 548, 560 and 573 K, respectively), except for 573 K. The measured final yield of 2,5-AHSO at 573 K was lower than the predicted value, implying that the degradation and/or polymerization of 2,5-AHSO occurs in high temperature liquid water at 573 K.

We have shown the dehydration of 1,4-AHSO in high temperature liquid water (Fig. 2). The rate constant of 1,4-AHSO to isosorbide (k_4') during the 1,4-AHSO dehydration was estimated (Table 2). Rate constants k_4' were much lower than those from the sorbitol dehydration (k_4). The dehydration rates of 1,4-AHSO to isosorbide depended on the initial reactant (sorbitol or 1,4-AHSO) and those during the sorbitol dehydration were larger than those during the 1,4-AHSO dehydration. This result can be explained by protonation of the hydroxyl groups at both the C1 and C6 positions in the sorbitol dehydration (Scheme 2). The two hydroxyl groups at the C1 and C6 positions in sorbitol could both be preferentially protonated (steps 1 and 2 in Scheme 2), and then sorbitol was dehydrated to form 1,4-AHSO with $-\text{OH}_2^+$ at the C6 position (step 3 in Scheme 2). 1,4-AHSO with $-\text{OH}_2^+$ at the C6 position is easily dehydrated to form isosorbide (step 4 in Scheme 2). On the other hand, in the case of the 1,4-AHSO molecule, the hydroxyl group at the C5 position could be preferentially protonated (step

5 in Scheme 2) because of intramolecular hydrogen bonding between the hydroxyl groups at the C5 and C6 positions. We observed that the hydroxyl group at the C2 position in 1,2,5-pentanetriol was preferentially protonated because of the intramolecular hydrogen bond between the two hydroxyl groups at the C1 and C2 positions.^{25,36} The 1,4-AHSO molecule consists of a tetrahydrofuran structure having two hydroxyl groups and an 1,2-ethanediol group. The hydroxyl group at the C5 position in 1,4-AHSO, which corresponds to the C2 position in 1,2,5-pentanetriol, could be preferentially protonated (step 5 in Scheme 2) because of the intramolecular hydrogen bond. Thus, the dehydration of 1,4-AHSO occurred slowly because the reaction proceeds through the protonation of the hydroxyl group at the C6 position (step 6 in Scheme 2).

Fig. 5 shows Arrhenius plots for the rate constants (k_1 , k_2 , k_4 and k_5) in sorbitol dehydration in high temperature liquid water. The activation energies for the rate constants (k_1 , k_2 , k_4 and k_5) are shown in Table 1. The activation energy of k_4 (dehydration of 1,4-AHSO to isosorbide) was 195 kJ mol⁻¹, which was higher than that of k_1 (127 kJ mol⁻¹) (dehydration of sorbitol to 1,4-AHSO), indicating that the ratio of k_1/k_4 increased with decreasing reaction temperature and that the maximum yield of 1,4-AHSO increased at lower temperatures. The maximum yields of 1,4-AHSO and isosorbide as a function of temperature were calculated (Fig. 6) using eqn (7) and eqn (10), in which the rate constants were rewritten as functions of temperature using their activation energies. The maximum yield of 1,4-AHSO from the dehydration of sorbitol in high temperature liquid water increased with decreasing reaction temperature; however, the reaction time for the maximum yield of 1,4-AHSO increased with decreasing reaction temperature. For example, at 500 K, it reached almost 80%; however, it

**Scheme 2** Proposed reaction mechanism of dehydration reactions for sorbitol and 1,4-AHSO.

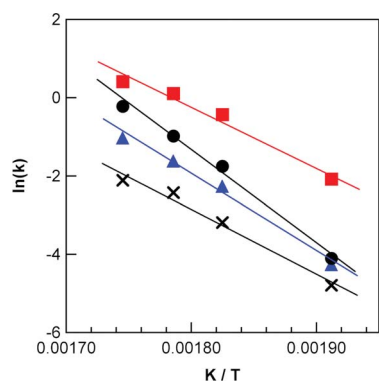


Fig. 5 Arrhenius plots of the rate constants (k_1 (■), k_2 (▲), k_4 (●) and k_5 (×) in Scheme 1) for sorbitol dehydration in high temperature liquid water.

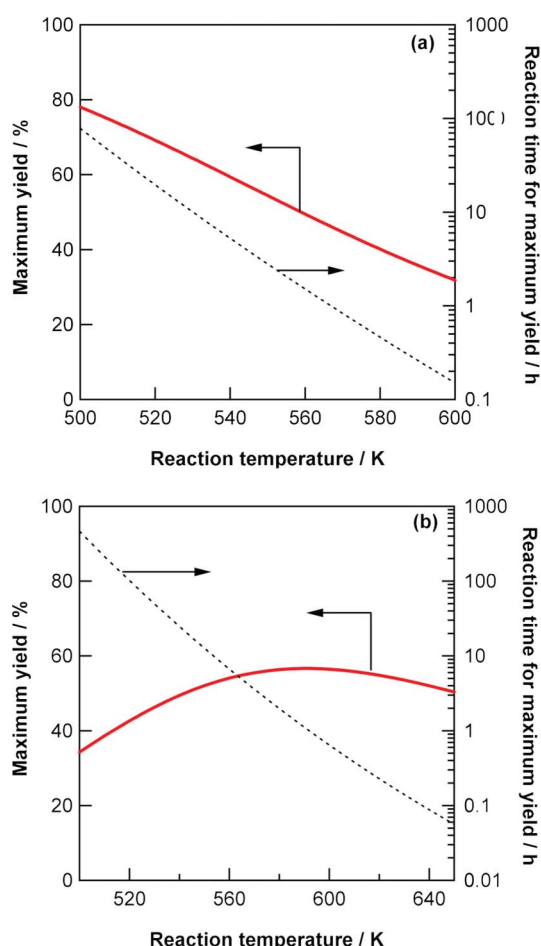


Fig. 6 Maximum yields of (a) 1,4-AHSO and (b) isosorbide, the reaction time for the maximum yield as a function of reaction temperature derived from eqn (7) and eqn (10), and the activation energies of the rate constants (k_1 , k_2 , k_4 and k_5).

took more than 3 d (78 h) to reach the maximum yield of 1,4-AHSO from the dehydration of sorbitol. The maximum yield of isosorbide from the dehydration of sorbitol became 57% at 590 K after 1 h. The experimental maximum yield of isosorbide was 55% at 573 K after 3 h among the reaction temperatures of 523, 548, 560 and 573 K.

3.6. Comparison of sorbitol dehydration in high temperature liquid water and in sulfuric acid

The maximum yield of isosorbide from sorbitol dehydration in high temperature liquid water was calculated to be 57% at 590 K after 1 h. Fleche and Huchette have reported that isosorbide can be obtained from sorbitol dehydration in water by sulfuric acid (ratio of acid to sorbitol = 0.01) at 408 K after 15 h with an isosorbide yield of 77%.¹⁸ The maximum yield of isosorbide in sorbitol dehydration with sulfuric acid (77%) was higher than that in high temperature liquid water (57%), and also the reaction temperature in sulfuric acid (408 K) was lower than that in high temperature liquid water (590 K). However, there are several advantages of undertaking sorbitol dehydration in high temperature liquid water, namely: the reaction time (1 h) is much shorter than that in sulfuric acid (15 h), and the dehydration reaction in high temperature liquid water does not require processes of neutralization, separation and purification. We have demonstrated that the synthesis of isosorbide or anhydrosorbitol from sorbitol can proceed in high temperature liquid water without any additive catalysts, which will lead to simple technologies for the conversion of biomass-derived material.

Conclusions

Sorbitol dehydration in high temperature liquid water proceeded at 523–573 K without adding any acid catalysts. Sorbitol dehydration proceeded *via* two steps: (i) sorbitol to 1,4-anhydrosorbitol or 2,5-anhydrosorbitol and (ii) 1,4-anhydrosorbitol to isosorbide. In the former step, 1,4-anhydrosorbitol was produced predominantly. The dehydration rate of sorbitol to 1,4-anhydrosorbitol was faster than that of 1,4-anhydrosorbitol to isosorbide; therefore, 1,4-anhydrosorbitol and isosorbide could be obtained selectively in high yields. A kinetic analysis of sorbitol dehydration in high temperature liquid water showed that the maximum yield of 1,4-anhydrosorbitol from the dehydration of sorbitol increased with decreasing reaction temperature and that the maximum yield of isosorbide from the dehydration of sorbitol became 57% at 590 K after 1 h. We controlled both the reaction temperature and the reaction time of the sorbitol dehydration to produce anhydrosorbitol or isosorbide selectively.

Appendix

The sequence of steps for the sorbitol dehydration reactions in high temperature liquid water are shown in Scheme 1. The concentrations of the reactant and products are represented in the form of differential equations as follows:

$$\frac{d[\text{Sorbitol}]}{dt} = -k_1[\text{Sorbitol}] - k_2[\text{Sorbitol}] - k_3[\text{Sorbitol}] \quad (1)$$

$$\frac{d[1,4\text{-AHSO}]}{dt} = k_1[\text{Sorbitol}] - k_4[1,4\text{-AHSO}] \quad (2)$$

$$\frac{d[2,5\text{-AHSO}]}{dt} = k_2[\text{Sorbitol}] \quad (3)$$

$$\frac{d[1,5\text{-AHSO}]}{dt} = k_3[\text{Sorbitol}] \quad (4)$$

$$\frac{d[\text{Isosorbide}]}{dt} = k_4[1,4\text{-AHSO}] - k_5[\text{Isosorbide}] \quad (5)$$

The concentrations can be represented as a function of time:

$$[\text{Sorbitol}] = [\text{Sorbitol}]_i \exp\{(-k_1 - k_2 - k_3)t\} \quad (6)$$

in which $[\text{Sorbitol}]_i$ represents the initial concentration

$$[1,4\text{-AHSO}] = \frac{k_1}{k_4 - k_1 - k_2 - k_3} [\text{Sorbitol}]_i \left[\exp\{(-k_1 - k_2 - k_3)t\} - \exp(-k_4 t) \right] \quad (7)$$

$$[2,5\text{-AHSO}] = \frac{k_2}{k_1 + k_2 + k_3} [\text{Sorbitol}]_i \left[1 - \exp\{(-k_1 - k_2 - k_3)t\} \right] \quad (8)$$

$$[1,5\text{-AHSO}] = \frac{k_3}{k_1 + k_2 + k_3} [\text{Sorbitol}]_i \left[1 - \exp\{(-k_1 - k_2 - k_3)t\} \right] \quad (9)$$

$$[\text{Isosorbide}] = \frac{k_4 k_1}{k_4 - k_1 - k_2 - k_3} [\text{Sorbitol}]_i \left[\frac{\exp\{(-k_1 - k_2 - k_3)t\} - \exp(-k_5 t)}{k_5 - k_1 - k_2 - k_3} - \frac{\exp(-k_4 t) - \exp(-k_5 t)}{k_5 - k_4} \right] \quad (10)$$

of sorbitol, and $[\text{Sorbitol}]$, $VV[1,4\text{-AHSO}]$, $[2,5\text{-AHSO}]$, $[1,5\text{-AHSO}]$ and $[\text{isosorbide}]$ represent the concentrations of sorbitol, 1,4-AHSO, 2,5-AHSO, 1,5-AHSO and isosorbide, respectively, at reaction time (t).

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