Thermodynamic Equilibria between Polyalcohols and Cyclic Ethers in High-Temperature Liquid Water[†]

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Thermodynamic equilibrium constants between polyalcohols and cyclic ethers in water at 573 K were determined by measuring their concentrations after the long-term reaction in a batch reactor. Intramolecular dehydration reactions of polyalcohols were important for conversion of biomass-derived carbohydrates; however, the yields of products were limited by thermodynamic equilibria between polyalcohols and products. All the thermodynamic equilibrium constants were estimated by the long-term dehydration reaction of 1 $mol \cdot dm^{-3}$ polyalcohol aqueous solutions at 573 K. The thermodynamic equilibrium constants between butanepolyols or pentanepolyols and five-membered or six-membered cyclic ethers were within a range from (39 to 337) $mol \cdot dm^{-3}$.

Introduction

Biomass has a large amount of oxygen atoms because plants combine carbon dioxide with water using solar energy to store oxygen as sugar building blocks, $(CH_2O)_n$. A selective removal of the oxygen atoms from biomass-derived carbohydrates, which are polyalcohols like fructose, sorbitol, and glycerol in most cases, by dehydration or hydrogenolysis is important to obtain valuable products with desired boiling points, water solubilities, octane numbers, and viscosities.[1] Kinetic studies of the intramolecular dehydration of polyalcohols were carried out;[2] however, yields of the products, cyclic ethers, were limited by thermodynamic equilibria between polyalcohols and cyclic ethers. In this work, we determined several thermodynamic equilibrium values between polyalcohols and cyclic ethers to develop an efficient conversion process of biomass derivatives to useful materials in water.[3]

High-temperature liquid water has attracted much attention as an alternative to harmful organic solvents because of its high proton concentration, which enhances rates of acid-catalyzed reactions such as dehydration in water without adding any hazardous acid.[4,5] Added carbon dioxide was dissolved in water to form carbonic acid, accelerating the acid catalysis of high-temperature water. We reported on a mechanism of the dehydration of polyalcohols having two or three hydroxyl groups, as simple model compounds of biomass-derived carbohydrates, to corresponding five- or six-membered cyclic ethers in water under high-pressure carbon dioxide at 573 K.[2] The thermodynamic equilibrium constants between polyalcohols and cyclic ethers are crucial for the efficient conversion process of biomass derivatives to useful materials; however, it is difficult to calculate the equilibrium constants of dehydration and hydration reactions in high-temperature liquid water using ΔG (Gibbs free energy) because of difficulty in determining hydrated structures for the reactants and products in high-temperature water.[6,7] Therefore, we determined the thermodynamic equilibrium constants by measuring the concentrations of polyalcohols and cyclic ethers after a long-term reaction in high-temperature liquid water.

Experimental Section

1,2,4-Butanetriol (1,2,4-BTO, Wako Pure Chemical Industries), 1,2,5-pentanetriol (1,2,5-PTO, Tokyo Chemical Industry), 1,4-butanediol (1,4-BDO, Wako Pure Chemical Industries), 1,4-pentanediol (1,4-PDO, Aldrich), and 1,5-pentanediol (1,5-PDO, Wako Pure Chemical Industries) were purchased and used without any further purification. The dehydration of polyalcohols was carried out in a batch reactor (inner volume: 6 cm^3) made of a SUS316 tube.[2,8] After 3 cm^3 of polyalcohol aqueous solution (1.0 $mol \cdot dm^{-3}$) was loaded in the reactor, the gas phase was purged with argon gas to remove air. Carbon dioxide was then loaded in the reactor at 323 K. The reactor was submerged into a molten-salt bath at 573 K for a given reaction time. The reaction temperature was stable within the error of 1 K for all the reactions. Then the reactor was submerged into a water bath for cooling to ambient temperature quickly after the reaction. A mixture of reactant and liquid products was taken out from the reactor with distilled water. A quantitative analysis of liquid products was conducted by gas chromatography with a flame ionization detector (GC−FID) equipped with a DB-WAX capillary column (Agilent Technologies) using 1-propanol (Wako Pure Chemical Industries) as an internal standard material. The products were identified by their retention times of the GC−FID analysis, compared with those for known materials: 3-hydroxytetrahydrofuran (3-HTHF, Wako Pure Chemical Industries), tetrahydrofurfuryl alcohol (THFA, Sigma-Aldrich), tetrahydrofuran (THF, Wako Pure Chemical Industries), 2-methyltetrahydrofuran (2-MTHF, Sigma-Aldrich), and tetrahydropyran (THP, Wako Pure Chemical Industries). 4-Hydroxytetrahydropyran (Aldrich) was used for the quantitative analysis for 3-hydroxytetrahydropyran (3-HTHP). A material balance of all the reactions was more than 95 %.

Results and Discussion

Thermodynamic Equilibrium between 1,4-Butanediol and Tetrahydrofuran in High-Temperature Liquid Water at 573 K. Figure 1 shows yield profiles of 1,4-BDO and THF until thermodynamic equilibrium for the dehydration reaction of 1.0 $mol \cdot dm^{-3}$ 1,4-BDO in water at 573 K (Scheme 1). The yield

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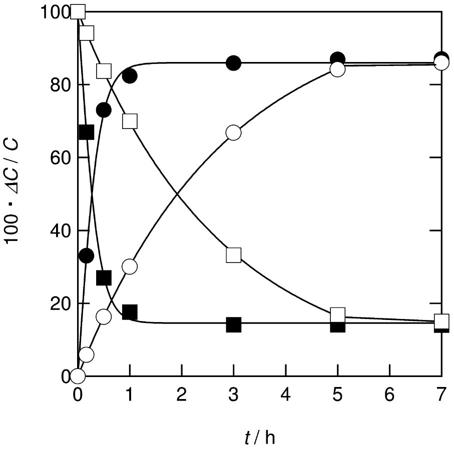
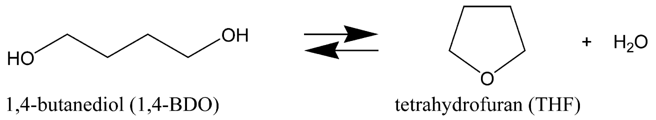
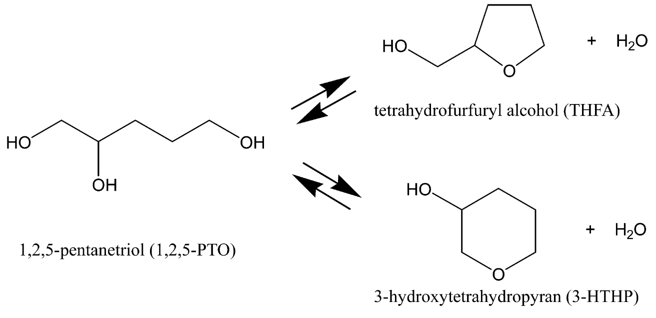


Figure 1. Concentration fraction of tetrahydrofuran (circles) and 1,4-butanediol (1,4-BDO, squares) as a function of elapsed time for the 1,4-BDO dehydration reaction at 573 K in water (initial 1,4-BDO concentration (C), 1.0 mol·dm^{-3}; carbon dioxide partial pressure, 0 MPa (open symbols) and 17.7 MPa (closed symbols)).

Scheme 1. Dehydration Reaction of 1,4-Butanediol



Scheme 2. Dehydration Reaction of 1,2,5-Pentanetriol



of THF from the dehydration reaction of 1,4-BDO without carbon dioxide increased up to 87 % for 5 h and became constant. On the other hand, the THF yield in the presence of 17.7 MPa carbon dioxide increased to 85 % in 1 h and did not change further reaction time. These results indicate that the yield of THF [(87 ± 3) %] would be thermodynamically equilibrated at 573 K. The addition of carbon dioxide enhanced the THF formation rates; however, it did not change the equilibrium yield. The yields of 1,4-BDO and THF at thermodynamic equilibrium were (13 ± 3) % and (87 ± 3) %, respectively. The thermodynamic equilibrium constant between 1,4-BDO and THF ($K_{\text{1,4-BDO,THF}}$) is represented as follows

$$K_{1,4-\text{BDO,THF}} = \frac{[\text{THF}][\text{H}_2\text{O}]}{[\text{1,4-BDO}]} \tag{1}$$

where [THF], [H_2O], and [1,4-BDO] were the concentrations of THF, water, and 1,4-BDO at thermodynamic equilibrium, respectively. $K_{\text{1,4-BDO,THF}}$ was calculated to be (337 ± 120) mol·dm^{-3} from the yields at thermodynamic equilibrium in Figure 1, which was quite consistent with the previous report ($K_{\text{1,4-BDO,THF}}$ = 441 mol·dm^{-3}).[9,10]

The equilibrium yields of 1,4-BDO and THF for the dehydration reaction in water from another concentration (0.30 mol·dm^{-3}) of 1,4-BDO at 573 K were also measured to confirm the thermodynamic equilibrium constant $K_{\text{1,4-BDO,THF}}$. The yields of 1,4-BDO and THF at thermodynamic equilibrium from 0.30 mol·dm^{-3} of 1,4-BDO were (11 ± 3) % and (89 ± 3) %, respectively, leading to the value of $K_{\text{1,4-BDO,THF}}$ to be (437 ± 184) mol·dm^{-3}. The equilibrium constant for 0.30 mol·dm^{-3} of 1,4-BDO dehydration [(437 ± 184) mol·dm^{-3}] was consistent with the value of $K_{\text{1,4-BDO,THF}}$ for 1.0 mol·dm^{-3} of 1,4-BDO dehydration [(337 ± 120) mol·dm^{-3}] within the margin of error.

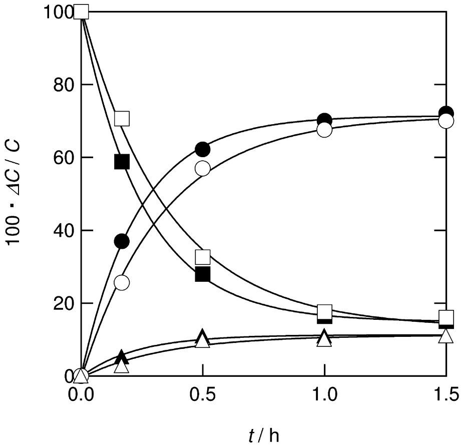


Figure 2. Concentration fraction of tetrahydrofurfuryl alcohol (circles), 3-hydroxytetrahydropyran (triangles), and 1,2,5-pentanetriol (1,2,5-PTO, squares) as a function of elapsed time for the 1,2,5-PTO dehydration reaction at 573 K in water (initial 1,2,5-PTO concentration (C), 1.0 mol·dm^{-3}; carbon dioxide partial pressure, 0 MPa (open symbols) and 17.7 MPa (closed symbols)).

In addition, the thermodynamic equilibrium constant $K_{\text{1,4-BDO,THF}}$ was obtained from the equilibrium yields of the THF hydration reaction (a reverse reaction of 1,4-BDO dehydration, Scheme 1). The reverse reaction was carried out in the same method as the 1,4-BDO dehydration reaction. Briefly, the reactor, in which 3 cm^3 of THF aqueous solution (1.0 mol·dm^{-3}) was loaded, was submerged into a molten-salt bath at 573 K for a given reaction time and then submerged into a water bath for cooling to ambient temperature. The yields of 1,4-BDO and THF at thermodynamic equilibrium from 1.0 mol·dm^{-3} of THF solution were (9 ± 3) % and (91 ± 3) %, respectively, leading to the value of $K_{\text{1,4-BDO,THF}}$ to be (546 ± 300) mol·dm^{-3}. The equilibrium constant for THF hydration was consistent with the value of $K_{\text{1,4-BDO,THF}}$ from the equilibrium yields of (1.0 and 0.30) mol·dm^{-3} 1,4-BDO dehydration within the margin of error, establishing the validity of the thermodynamic equilibrium constants $K_{\text{1,4-BDO,THF}}$.

The thermodynamic equilibrium constant can be calculated from ΔG of the reactants and products under the equilibrium condition. $K_{\text{1,4-BDO,THF}}$ was calculated to be $2.4 \cdot 10^5$ mol·dm^{-3} by the following formula using ΔG in VMGSim code (Virtual Materials Group Inc.), which was much larger than the measured value

$$K = \exp\left(\frac{-\Delta G}{RT}\right) \tag{2}$$

where R and T represent the gas constant and reaction temperature, respectively.

This difference of the thermodynamic equilibrium constant between the measured value and the calculated value would be due to the hydrogen bonding of water with THF and 1,4-BDO.[10] 1,4-BDO is strongly hydrated with two water molecules through hydrogen bonding in water at ambient temperature, and the hydrogen bonding decreases with increasing temperature. It is

Table 1. Thermodynamic Equilibria between Various Polyalcohols and Cyclic Ethers in High-Temperature Liquid Water at 573 K

		Y_E[a]/%		K[b]
polyalcohol	cyclic ether	polyalcohol	cyclic ether	$mol \cdot dm^{-3}$
1,4-butanediol (1,4-BDO)	tetrahydrofuran (THF)	13 ± 3	87 ± 3	337 ± 120
1,2,4-butanetriol (1,2,4-BTO)	3-hydroxytetrahydrofuran (3-HTHF)	28 ± 3	72 ± 3	128 ± 21
1,4-pentanediol (1,4-PDO)	2-methyltetrahydrofuran (2-MTHF)	27 ± 3	73 ± 3	132 ± 23
1,5-pentanediol (1,5-PDO)	tetrahydropyran (THP)	29 ± 3	71 ± 3	125 ± 20
1,2,5-pentanetriol (1,2,5-PTO)	tetrahydrofurfuryl alcohol (THFA)	15 ± 3	73 ± 3	238 ± 71
1,2,5-pentanetriol (1,2,5-PTO)	3-hydroxytetrahydropyran (3-HTHP)	15 ± 3	12 ± 3	39 ± 22

[a] Equilibrium yields (Y_E) were measured with 1.0 $mol \cdot dm^{-3}$ polyalcohols at 573 K. [b] $K_{polyalcohol,cyclic\ ether}$.

difficult at this stage to nonempirically estimate the effect of hydrogen bonding and the thermodynamic equilibrium constant in high-temperature water. Therefore, we determined the thermodynamic equilibrium constants empirically by measuring the concentrations of polyalcohols and cyclic ethers.

Thermodynamic Equilibria among 1,2,5-Pentanetriol, Tetrahydrofurfuryl Alcohol, and 3-Hydroxytetrahydropyran in High-Temperature Liquid Water at 573 K. The dehydration of 1.0 $mol \cdot dm^{-3}$ of 1,2,5-PTO also proceeded in water at 573 K and provided two products: THFA and 3-HTHP (Scheme 2, Figure 2). The yields of 1,2,5-PTO, THFA, and 3-HTHP at thermodynamic equilibrium were [(15 ± 3), (73 ± 3), and (12 ± 3)] %, respectively. The thermodynamic equilibrium constant between 1,2,5-PTO and THFA ($K_{1,2,5\text{-PTO,THFA}}$) and that between 1,2,5-PTO and 3-HTHP ($K_{1,2,5\text{-PTO,3-HTHP}}$) are represented as follows

$$K_{1,2,5\text{-PTO,THFA}} = \frac{[\text{THFA}][\text{H}_2\text{O}]}{[1,2,5\text{-PTO}]} \qquad (3)$$

$$K_{1,2,5\text{-PTO,3-HTHP}} = \frac{[3\text{-HTHP}][\text{H}_2\text{O}]}{[1,2,5\text{-PTO}]} \qquad (4)$$

where [THFA], [3-HTHP], and [1,2,5-PTO] were the concentrations of THFA, 3-HTHP, and 1,2,5-PTO at thermodynamic equilibrium, respectively. THFA and 3-HTHP should be equilibrated via the formation of 1,2,5-PTO, as shown in Scheme 2, and the thermodynamic equilibrium constant between THFA and 3-HTHP ($K_{\text{THFA,3-HTHP}}$) is represented as follows

$$K_{\text{THFA,3-HTHP}} = \frac{[3\text{-HTHP}]}{[\text{THFA}]} = \frac{K_{1,2,5-\text{PTO},3-\text{HTHP}}}{K_{1,2,5-\text{PTO},\text{THFA}}} \qquad (5)$$

$K_{1,2,5\text{-PTO,THFA}}$, $K_{1,2,5\text{-PTO,3-HTHP}}$, and $K_{\text{THFA,3-HTHP}}$ were calculated to be (238 ± 71) $mol \cdot dm^{-3}$, (39 ± 22) $mol \cdot dm^{-3}$, and (0.16 ± 0.05) $mol \cdot dm^{-3}$, respectively, from their yields at thermodynamic equilibrium, indicating that THFA is more stable in high-temperature water than 3-HTHP thermodynamically.

Thermodynamic Equilibria between Various Polyalcohols and Cyclic Ethers in High-Temperature Liquid Water at 573 K. The thermodynamic equilibrium constants between various polyalcohols and cyclic ethers in high-temperature liquid water at 573 K are summarized in Table 1. The thermodynamic equilibrium constants of $K_{1,4\text{-PDO,2-MTHF}}$ [(132 ± 23) $mol \cdot dm^{-3}$] and $K_{1,5\text{-PDO,THP}}$ [(125 ± 20) $mol \cdot dm^{-3}$] were quite similar; in contrast, the dehydration rate of 1,4-PDO to 2-MTHF ($8.6 \cdot 10^{-3}$ $mol \cdot dm^{-3} \cdot s^{-1}$) was ten times larger than that of 1,5-PDO to THP ($0.63 \cdot 10^{-3}$ $mol \cdot dm^{-3} \cdot s^{-1}$).[2] The thermodynamic equilibrium constants between butanepolyols or pentanepolyols and five-membered or six-membered cyclic ethers were within a range from (39 to 337) $mol \cdot dm^{-3}$. We determined the thermodynamic equilibrium values between polyalcohols and cyclic ethers to develop an efficient conversion process of biomass derivatives to useful materials in high-temperature liquid water.

Conclusion

Thermodynamic equilibrium constants between polyalcohols and cyclic ethers in water at 573 K were determined by measuring their concentrations after the long-term reaction in a batch reactor. The thermodynamic equilibrium constants between butanepolyols or pentanepolyols and corresponding cyclic ethers ranged from (39 to 337) $mol \cdot dm^{-3}$.

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