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Cyclization of alkanediols in high-temperature liquid water with high-pressure carbon dioxide

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A R T I C L E I N F O

ABSTRACT

corresponding carbocation species.

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1. Introduction

The chemical transformation techniques of converting biomassderived polyalcohol compounds, such as fructose, sorbitol, and glycerol, to valuable chemicals are indispensable for establishing a sustainable society [1–3]. Dehydration reactions of polyalcohol compounds are important to obtain valuable products with desired boiling points, water solubilities, octane numbers, and viscosities [4]. The chemistry of intramolecular dehydration of polyalcohol compounds provides a key technology for developing an efficient conversion process of biomass derivatives to useful materials [5,6].

High-temperature liquid water has attracted much attention as a promising solvent for acid- or base-catalyzed reactions because self-ionization of water is highly feasible at around 523 K, leading to high concentrations of proton and hydroxide ion. The addition of high-pressure carbon dioxide can enhance the concentration of proton in liquid water because carbon dioxide dissolves in water to form carbonic acid, as shown below,

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}.$$
(1)

The combination of water and carbon dioxide are environmentally benign because the added carbon dioxide can be separated easily by simple depressurization after the reaction. We have demonstrated that intramolecular dehydration of several polyalcohols, which were the chemical blocks of biomass, proceeded in high-temperature liquid water and that the dehydration rates were enhanced by the addition of high-pressure carbon dioxide [7–13].

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Dehydration of 1,4-butanediol (1,4-BDO) to tetrahydrofuran (THF), 2R,5R-hexanediol (2R,5R-HDO)

to 2,5-dimethyltetrahydrofuran (2,5-DMTHF), and 2,5-dimethyl-2,5-hexanediol (2,5-DM-2,5-HDO) to

2,2,5,5-tetramethyltetrahydrofuran (2,2,5,5-TMTHF) proceeded in high-temperature liquid water at

523 K. The formation rates of cyclic ethers were enhanced by high-pressure carbon dioxide (16.2 MPa). The order of dehydration rates in high-temperature water with carbon dioxide was 2,5-DM-2,5-HDO > 2R,5R-HDO > 1,4-BDO (tertiary > secondary > primary alcohols), which was the same order as the stability of

In this paper, we investigated the intramolecular dehydration behavior of alkanediols, such as 1,4-butanediol (1,4-BDO), (2R,5R)-(-)-2,5-hexanediol (2R,5R-HDO), and 2,5-dimethyl-2,5hexanediol (2,5-DM-2,5-HDO), to the corresponding cyclic ethers in high-temperature liquid water with high-pressure carbon dioxide. We compared the dehydration rates of the alkanediols and discussed the reaction mechanism based on the class of alcohols.

2. Experimental

The reactants, 1,4-BDO, 2R,5R-HDO, and 2,5-DM-2,5-HDO, were purchased from Wako Pure Chemical Industries, Ltd. and used without any further purification. The dehydration of alkanediols was carried out in a batch reactor (inner volume: 6 cm³) made of a SUS316 tube [14,15]. Aqueous solution (1,4-HDO and 2R,5R-HDO: 1 mol dm⁻³, 3 cm³; 2,5-DM-2,5-HDO: 0.5 mol dm⁻³, 3 cm³) was loaded in the reactor, which was then purged with argon gas to remove air. Carbon dioxide (10 MPa) was then loaded in the reactor at 323 K. The reactor was submerged into a molten-salt bath or a sand bath at the reaction temperature. The partial pressure values of water and carbon dioxide were 4.0 and 16.2 MPa at 523 K, respectively. After the given reaction time, the reactor was submerged into a water bath for cooling to ambient temperature. A mixture of the reactant and products was taken out from the reactor with distilled water and filtered to remove solid products by a membrane filter (pore size: 200 nm). Amount of organic carbon in the liquid fraction was evaluated



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Fig. 1. Yields of THF (closed symbols) and 1,4-BDO (open symbols) as a function of elapsed time for the 1,4-BDO dehydration reaction at 523 K in water (initial 1,4-BDO concentration: 1.0 mol dm^{-3} , carbon dioxide partial pressure: 0 (circles) and 16.2 MPa (triangles)).

using a total organic carbon analyzer (Shimadzu, TOC-V_{CSN}). The quantitative analysis of the 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 as an internal standard material. The products were identified by their retention times of the GC-FID analysis, compared with those for known materials: tetrahydrofuran (THF, Wako Pure Chemical Industries), 2,5-dimethyltetrahydrofuran (2,5-DMTHF, Aldrich, a mixture of *cis* and *trans* forms), and 2,2,5,5-tetramethyltetrahydrofuran (2,2,5,5-TMTHF, Alfa Aesar). The products, *cis*-2,5-DMTHF and *trans*-2,5-DMTHF, were analyzed by two discriminable peaks of GC-FID and spectra of ¹H and ¹³C NMR. Initial formation rates of the products were estimated from the initial slopes of the fitting curves of their yields.

3. Results and discussion

3.1. Dehydration of 1,4-butanediol (1,4-BDO)

Dehydration behavior of 1,4-BDO (1.0 mol dm⁻³) in water was investigated in the absence and presence of carbon dioxide at 523 K (Scheme 1).

Intermolecular dehydration to THF proceeded slowly in water at 523 K (Fig. 1). The material balance was more than 95% independently of the 1,4-BDO conversion. The dehydration proceeded



Fig. 2. Yields of 2,5-DMTHF (sum of *cis* and *trans* forms, closed symbols) and 2R,5R-HDO (open symbols) as a function of elapsed time for the 2R,5R-HDO dehydration reactions at 523 K in water (initial 2R,5R-HDO concentration: 1.0 mol dm⁻³, carbon dioxide partial pressure: 0 (circles) and 16.2 MPa (triangles)).

with an increase in reaction time. After 5 h, 16% of THF yield was obtained.

The addition of 16.2 MPa of carbon dioxide enhanced the intramolecular dehydration rate. THF was the solo liquid product from the 1,4-BDO dehydration even when high-pressure carbon dioxide was added. The THF yield in water for 30 min was 16% with high-pressure carbon dioxide. After 5 h, the THF yield was 88%. The high dehydration rate could be obtained by the catalysis of protons derived from carbonic acid.

3.2. Dehydration of 2,5-hexanediol (2,5-HDO)

Dehydration behavior of chiral 2R,5R-HDO ($1.0 \text{ mol } dm^{-3}$) in water was also investigated in the absence and presence of carbon dioxide at 523 K (Scheme 2).

Intermolecular dehydration of chiral 2R,5R-HDO also proceeded in water at 523 K (Fig. 2). 2,5-DMTHF (mixture of *cis* and *trans* forms) was the sole liquid product from the intramolecular dehydration of 2R,5R-HDO. The dehydration of 2R,5R-HDO to 2,5-DMTHF was also enhanced by the addition of high-pressure carbon dioxide. It is notable that the dehydration rate of 2R,5R-HDO was larger than that of 1,4-BDO in high-temperature water (523 K) with highpressure carbon dioxide (16.2 MPa) (Figs. 1 and 2).

The selectivities to *cis*-2,5-DMTHF were more than 85% in the total product 2,5-DMTHF independently of both conversion and carbon dioxide pressure. It is reported that the 2R,5R-HDO dehydration proceeded by concentrated sulfuric acid at 293 K to produce a mixture of *cis*- and *trans*-2,5-DMTHF and the selectivities to *cis* and *trans* forms were both 50% [16,17], indicating that the 2,5-HDO dehydration proceeded via S_N1 mechanism by concentrated sulfuric acid. The 85% of *cis*-selectivity was obtained in our reaction conditions, indicating that intramolecular dehydration proceeded mainly via an S_N2 pathway in high-temperature liquid water or high-temperature liquid water with high-pressure carbon dioxide [9].



Scheme 2.

Reactant	Product	Reaction temperature/K	CO ₂ pressure/MPa	Formation rate/mol $dm^{-3} s^{-1}$
1,4-BDO ^a	THF	523	0	3.8×10^{-6}
			16.2	$1.1 imes 10^{-4}$
2R,5R-HDO ^a	2,5-DMTHF	523	0	$3.4 imes 10^{-6}$
			16.2	$2.0 imes 10^{-4}$
2,5-DM-2,5-HDO ^b	2,2,5,5-TMTHF	523	0	>1.2 × 10 ⁻⁴
		473	0	$8.0 imes 10^{-6}$
			14.6	2.3×10^{-4}

Initial formation rates of cyclic ethers for dehydration reactions of 1,4-BDO, 2R,5R-HDO, 2,5-DM-2,5-HDO in water.

^a Initial reactant concentration was $1.0 \text{ mol } \text{dm}^{-3}$.

^b Initial reactant concentration was 0.5 mol dm⁻³.

The material balance, defined as total yield of 2R,5R-HDO and 2,5-DMTHF, decreased with an increase in reaction time for the dehydration with carbon dioxide. The material balance for the dehydration of 2R,5R-HDO in the presence of carbon dioxide for 3 h was 60%, which was almost equivalent to the amount of total organic carbon in the liquid water phase determined by TOC analvsis. These results indicated that the chemicals in the liquid phase after the 2R,5R-HDO dehydration were only 2,5-DMTHF and 2R,5R-HDO and that the solid products, such as solid polymers having more than 200 nm, would be formed at 523 K. We also investigated the stability of 2,5-DMTHF (mixture of cis and trans forms) in water at 523 K in the same procedure as the 2R,5R-HDO dehydration reaction by using $0.3 \text{ mol dm}^{-3} 2.5$ -DMTHF aqueous solution instead of 2R,5R-HDO aqueous solution. The formation of 2,5-HDO (reverse reaction of the 2R,5R-HDO dehydration) was not observed during the high-temperature water treatment of 2,5-DMTHF and the recovery yield of 2,5-DMTHF was 50% for 3 h at 523 K under both conditions with and without carbon dioxide. The total organic carbon (50%) in the liquid phase after the high-temperature water treatment of 2,5-DMTHF was almost the same as the recovery yield of 2,5-DMTHF, indicating that any liquid products were not formed from 2,5-DMTHF and that solid products would be formed by the ring-opening polymerization of 2,5-DMTHF.

3.3. Dehydration of 2,5-dimethyl-2,5-hexanediol (2,5-DM-2,5-HDO)

Dehydration behavior of 2,5-DM-2,5-HDO $(0.5 \text{ mol } dm^{-3})$ in water was also investigated at 523 K (Scheme 3).

Intermolecular dehydration of 2,5-DM-2,5-HDO also proceeded in water at 523 K. The conversion of 2,5-DM-2,5-HDO in water was more than 60% even for 10 min without carbon dioxide. We investigated the 2,5-DM-2,5-HDO dehydration at lower temperature of 473 K (Fig. 3) to evaluate the dehydration rate. The 2,2,5,5-TMTHF yield for 10 min in liquid water at 473 K was 0.9% and increased to 28% by the addition of 14.6 MPa of carbon dioxide. This result supports that proton derived from carbonic acid catalyzed the dehydration of 2,5-DM-2,5-HDO to 2,2,5,5-TMTHF. The material balance, defined as total yield of 2,5-DM-2,5-HDO and 2,2,5,5-TMTHF, in water in the presence of carbon dioxide after 3 h was only 48%, almost equivalent to the amount of total organic carbon estimated as 50% in the liquid phase. These results also indicated that the product in the liquid phase was only 2,2,5,5-TMTHF and that the solid products, such as polymers, were formed during the dehydration of 2,5-DM-2,5-HDO in high-temperature liquid water.



Scheme 3.



Fig. 3. Yields of 2,2,5,5-TMTHF (closed symbols) and 2,5-DM-2,5HDO (open symbols) as a function of elapsed time for the 2,5-DM-2,5HDO dehydration reactions at 473 K in water (initial 2,5-DM-2,5HDO concentration: 0.5 mol dm⁻³, carbon dioxide partial pressure: 0 (circles) and 14.6 MPa (triangles)).

3.4. Comparison of dehydration rates of primary, secondary, and tertiary alkanediols

We compared dehydration rates of three kinds of alkanediols in high-temperature liquid water, estimated from initial slopes of the fitting curves of the amount of cyclic ethers (Table 1). The initial formation rates of cyclic ethers were dramatically increased by the addition of carbon dioxide, indicating that carbonic acid was the catalyst for the intramolecular dehydration. The order of cyclic ether formation rate was 2,5-DM-2,5-HDO to 2,2,5,5-TMTHF>2R,5R-HDO to 2,5-DMTHF>1,4-BDO to THF under the reaction conditions with carbon dioxide. The basicity of the secondary hydroxyl group is higher than that of the primary hydroxyl group [18]; therefore, the intramolecular dehydration of secondary alcohol (2R,5R-HDO) by carbonic acid would be faster than that of primary alcohol (1,4-BDO). The formation rate of cyclic ether from the tertiary alcohol (2,5-DM-2,5-HDO) dehydration was much faster than those from the primary (1,4-BDO) and secondary alcohol (2R,5R-HDO) dehydration. Because carbocation species from protonated tertiary alcohols are stable, the intramolecular dehydration of tertiary alcohols proceed via S_N1 mechanism [18]. Protonated 2,5-DM-2,5-HDO molecules could be easily formed in water with carbon dioxide because of the high concentration of proton derived from carbonic acid, resulting that the highest cyclic ether formation rate was obtained for 2,5-DM-2,5-HDO.

4. Conclusion

We demonstrated the dehydration of 1,4-butanediol (1,4-BDO), 2R,5R-hexanediol (2,5-HDO), and 2,5-dimethyl-2,5-hexanediol (2,5-DM-2,5-HDO) to the corresponding cyclic ethers in

high-temperature liquid water. The enhancement of dehydration rates by the addition of carbon dioxide was obtained because the proton concentration was increased by the carbonic acid formation. The order of dehydration rate was 2,5-DM-2,5-HDO>2R,5R-HDO>1,4-BDO (tertiary>secondary>primary alcohols), which was the same order as the stability of corresponding carbocation species.

This technique could be extended to other acid-catalyzed reactions, which leads to a new technology for conversion of biomass derivatives to useful materials. These reactions are environmentally benign because only water and carbon dioxide are used and the added carbon dioxide can be separated easily after the reaction.

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