# Mechanisms and Kinetics of Noncatalytic Ether Reaction in Supercritical Water. 2. Proton-Transferred Fragmentation of Dimethyl Ether to Formaldehyde in Competition with Hydrolysis

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Noncatalytic reaction pathways and rates of dimethyl ether (DME) in supercritical water are determined in a tube reactor made of quartz according to liquid- and gas-phase $^1$H and $^{13}$C NMR observations. The reaction is studied at two concentrations (0.1 and 0.5 M) in supercritical water at 400 °C and over a water-density range of 0.1−0.6 g/cm$^3$. The supercritical water reaction is compared with the neat one (in the absence of solvent) at 0.1 M and 400 °C. DME is found to decompose through (i) the proton-transferred fragmentation to methane and formaldehyde and (ii) the hydrolysis to methanol. Formaldehyde from reaction (i) is consecutively subjected to four types of redox reactions. Two of them proceed even without solvent: (iii) the unimolecular proton-transferred decarbonylation forming hydrogen and carbon monoxide and (iv) the bimolecular self-disproportionation generating methanol and carbon monoxide. When the solvent water is present, two additional paths are open: (v) the bimolecular self-disproportionation of formaldehyde with reactant water, producing methanol and formic acid, and (vi) the bimolecular cross-disproportionation between formaldehyde and formic acid, yielding methanol and carbonic acid. Methanol is produced through the three types of disproportionations (iv)−(vi) as well as the hydrolysis (ii). The presence of solvent water decelerates the proton-transferred fragmentation of DME; the rate constant is reduced by 40% at 0.5 g/cm$^3$. This is caused by the suppression of low-frequency concerted motion corresponding to the reaction coordinate for the simultaneous C−O bond scission and proton transfer from one methyl carbon to the other. In contrast to the proton-transferred fragmentation, the hydrolysis of DME is markedly accelerated by increasing the water density. The latter becomes more important than the former in supercritical water at densities greater than 0.5 g/cm$^3$.

## I. Introduction

Supercritical water and subcritical water are being recognized as new reaction medium alternatives to hazardous organic solvents for chemical processes of industrial and environmental importance. Hot water is significantly expanded and less packed than ambient water, and the resulting electric field fluctuates strongly and anisotropically at high temperatures. Hot water can induce chemical reactions that are impossible without acidic, basic, or heavy metal catalysts in organic solvents at ambient conditions.[1−17] Thus, it is challenging to investigate noncatalytic hydrothermal reactions in a manner friendly to the earth. To that end, we are systematically examining reaction pathways and kinetics of each functional group.[1,8,12−17] In this series of papers, we pay attention to ether (C−O−C) bonds. Here we focus on dimethyl ether ($CH_3OCH_3$, DME); diethyl ether has been studied in the preceding paper[1] (called part 1 in the present paper). We attempt to elucidate similarities and differences in the mechanism and kinetics of hydrothermal ether reaction between the methyl and ethyl groups.

In part 1, we investigated the reaction pathways and kinetics of diethyl ether in supercritical water at 400 °C using a tube reactor made of quartz that has no catalytic effect.[1] We have found as primary steps that diethyl ether undergoes proton-transferred fragmentation generating acetaldehyde and ethane in competition with the hydrolysis producing ethanol. We should therefore scrutinize whether the aldehyde production is general. When aldehyde is formed, it plays a key role in controlling the reaction pathway of supercritical water reaction of ether, according to the reaction mechanism we established for diethyl ether. In the reaction of diethyl ether, acetaldehyde generated is further subjected to such redox reactions as noncatalytic self- and cross-disproportionations in supercritical water; acetaldehyde is reduced to ethanol and oxidized to acetic acid. The noncatalytic reductive reactions of aldehyde are new paths to alcohol, competing against the hydrolysis of ether. Thus, it is natural to examine whether the simplest ether, DME, can generate formaldehyde. Here we show that the DME hydrolysis in hot water is competing with the aldehyde formation in a way common to other linear aliphatic ethers.

To establish the new reaction mechanism of ether bonds in supercritical water, it is important to use a simple compound like DME. In this work, we focus on the prototype ether, DME, and examine its noncatalytic supercritical water reaction pathways and kinetics through a comparative study with the reaction of diethyl ether. As shown in part 1,[1] the proton-transferred fragmentation is one of the most important pathways in the reaction of ether in supercritical water at high temperatures. For the reaction mechanism of the proton-transferred fragmentation, not homolytic but heterolytic intramolecular proton transfer from the methylene group in one of the ethyl groups to the other surrounding the ether oxygen is considered in part 1. In consequence, it is important to confirm the general feature of the unique fragmentation mechanism. It is of great interest to compare methyl and methylene protons: the fragmentation of

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diethyl ether involves the intramolecular proton transfer between the methylene groups. Here we elucidate the difference in the ability of the proton transfer between the methyl and ethyl groups. For comparison, dipropyl ether is also investigated; in this case, the proton-transferred fragmentation proceeds for the methylene group, in common with diethyl ether.

DME has attracted much attention recently as an alternative to liquid natural gas (mainly $CH_4$) because of the useful range of the liquid and gas phases; volatile DME can be liquefied at −25 °C and 0.1 MPa or at 0.6 MPa and room temperature. Information on the reaction mechanism of DME without oxygen (before the oxygen encounter in combustion) in supercritical water over a wide density range is needed to optimize the combustion efficiency of the DME fuel. This is because the stationary combustion of DME is accompanied by the generation of a large amount of hot water as one of the oxidation products. There has been no report on the supercritical water reaction of the simplest ether despite the above-mentioned importance as a next generation fuel.

To elucidate the reaction pathways and kinetics, we apply the $^1H$ and $^{13}C$ NMR observations to both the liquid and gas phases in the sample vessel after reactions. This is because such gaseous products as methane, hydrogen, and carbon dioxide are distributed among the liquid and gas phases. We have confirmed in the analysis that the mass balance is kept. NMR spectroscopy is hence powerful for the structural, elemental, and quantitative analyses to establish the mechanisms of the supercritical water reaction of DME.

## II. Experimental Section

DME (Tokyo Kasei Kogyo; purity >99%) was used without further purification. Water, used as solvent and reactant, was purified using a Milli-Q Labo (Millipore) filter system. The solution of DME in $H_2O$ was loaded in a quartz tube of 1.5 mm i.d. and 3.0 mm o.d; DME could be handled in the solution state for preparing the samples of the supercritical water reactions because of the solubility of DME in water is ~2 M (M = mol/dm$^3$) at room temperature. The sample was sealed after air in the reactor was replaced by argon. The reaction temperature was fixed at 400 °C. The filling factor, which is defined as the ratio of the solution volume to the vessel volume at room temperature, determines the water density in homogeneous supercritical conditions, and it was varied from 0.1 to 0.6. The minimum and maximum values of the water density for supercritical water are then 0.1 and 0.6 g/cm$^3$, respectively. The detailed analysis of the hydrothermal reaction was performed at 0.5 g/cm$^3$. The solution was prepared in ambient conditions, and the initial concentration of DME is set to 0.1 and 0.5 M in supercritical conditions. In this scheme, the concentration of a sample in ambient conditions is given by the target concentration in the supercritical condition divided by the filling factor; that is respectively 0.2 and 1.0 M for the sample reacted at 0.5 g/cm$^3$. For comparison, the neat reaction was also examined at 400 °C. In this case, no water solvent was added in the sample and the concentration of DME gas was set to 0.1 M before the reaction. Most of the experimental procedures taken here are the same as before.[1] When the samples of the neat gas reactions were prepared, the DME gas was loaded in a quartz tube cooled by liquid nitrogen and was liquefied in the sample vessel. The sample was put into a programmable electric furnace kept at 400 °C; the temperature was controlled within ±1 °C. The sample setup for NMR measurements on the liquid and gas phases was described in detail in a previous paper.[12]

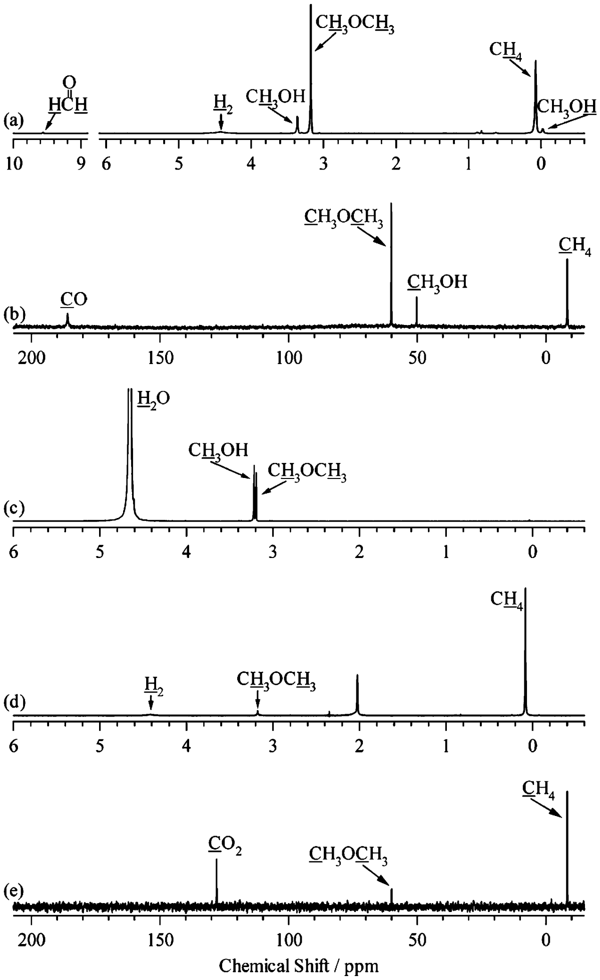

**Figure 1.** NMR spectra for reaction products of DME after treated at 400 °C for 200 h. (a and b) $^1H$ (a) and $^{13}C$ (b) spectra for neat reaction without solvent water at initial concentration of 0.1 M. (c) and (d) $^1H$ spectra for liquid- (c) and gas-phase (d) reactions in supercritical water at 0.5 g/cm$^3$ and initial concentration of 0.1 M. (e) Gas-phase $^{13}C$ spectrum for reaction in supercritical water at 0.5 g/cm$^3$ and initial concentration of 0.5 M. The neat reaction spectra (a) and (b) were obtained by a high-temperature measurement at 150 °C; in this temperature, the sample system is homogeneous.

## III. Results and Discussion

The reaction pathways of DME in supercritical water, here at 400 °C, is established through a comprehensive analysis of products in the neat reaction and supercritical water reaction. For understanding of the reaction mechanisms and kinetics, all species involved in the reaction products, both with and without hydrogens, need to be detected and analyzed quantitatively. For this purpose, $^1H$ and $^{13}C$ NMR measurements are performed both in the gas and liquid phases as functions of time.

**A. Products and Reaction Pathways.** *High-Temperature Neat Reactions.* First let us see what products are generated by the neat DME reaction in the absence of water at a temperature of 400 °C and reaction time of 200 h for the initial concentration of 0.1 M.[18] In this case, DME cannot undergo hydrolysis due to the lack of water as a reactant and solvent. Methane gas is found to be produced dominantly in the neat reaction; see the $^1H$ and $^{13}C$ spectra, respectively, in parts a and b of Figure 1. Methane can be generated from DME as

$$CH_3OCH_3 \rightarrow CH_4 + HCHO \qquad (1)$$

DME (C2 molecule) is thermally fragmented into the two C1 molecules, induced by the proton transfer in the vicinity of the ether oxygen located as a hinge center. We can call this proton-transferred fragmentation a “hinge reaction”. In the new type of fragmentation, one fragment (methane) is more reduced and the other (formaldehyde) is more oxidized. The hinge reaction can be considered as an intramolecular disproportionation and is to be compared with the bimolecular ones discussed below. We consider that the mechanism of the hinge reaction is similar to that of the corresponding reaction shown in part 1. A homolytic bond-breakage process can be a candidate mechanism for the thermal fragmentation (pyrolysis) if such products as ethane and propane are significant. The yields of these minor products are, however, only ~2% at 200 h in the neat reaction studied here. The heterolytic bond-breakage mechanism is therefore to be concluded as referred to above. The fragmentation driven by the simultaneous C−O bond scission and proton transfer is common to the other ethers. It is to be noted, however, that the rate for DME is much slower than that for diethyl ether, as discussed below.[1] The proton transfer between the methyl groups of DME is much more difficult than that beween the methylene groups of diethyl ether.

The proton-transferred fragmentation of DME produces simultaneously formaldehyde in an amount equal to that of methane. Formaldehyde detected is less than methane, however, and it must be subjected to consecutive reactions. This can be demonstrated by a quantitative analysis of the other products, including the species without hydrogens. As shown in Figure 1a,b, some products other than methane and formaldehyde are identified. They are in the order

$$\text{carbon monoxide (0.37)} > \text{hydrogen (0.22)} > \text{methanol (0.14)}$$

where the numbers in parentheses indicate the yields normalized by the initial concentration of diethyl ether. The sum of the carbon monoxide and methanol yields is nearly equal to the difference between the methane (0.58) and formaldehyde (0.01) yields. The balance of the normalized yields between carbon monoxide and the sum of hydrogen and methanol shows thus that these products are generated through the following reactions of formaldehyde:

$$\mathrm{HCHO} \rightarrow \mathrm{H_2} + \mathrm{CO} \tag{2}$$

$$\mathrm{2HCHO} \rightarrow \mathrm{CH_3OH} + \mathrm{CO} \tag{3}$$

Equation 2 is the proton-transferred decarbonylation, and eq 3 is the noncatalytic self-disproportionation in the absence of water.[15,19,20] The proton-transferred decarbonylation is common to other aldehydes.[12,14] In contrast, the self-disproportionation found here in the neat conditions is specific to formaldehyde at high temperatures. The anhydrous self-disproportionation is considered to take place by forming a formaldehyde dimer with their aldehyde group planes in parallel and their dipoles antiparallel. The self-disproportionation mechanism must be unique and different from the ordinary Cannizzaro-type one that requires a base catalyst and solvent to generate the tetrahedral intermediate with a negative charge on the carbonyl oxygen. The intermolecular redox reaction of eq 3 in the neat conditions can be achieved by the following concerted mechanism: the proton is transferred from one formaldehyde to the negatively polarized carbonyl oxygen in the other, accompanied by the simultaneous transfer of the hydride ion from the carboanion to the carbocation generated by the proton transfer. The concerted proton−hydride transfer can occur due to charge fluctuations induced by the thermal excitation of strongly coupled vibrations of H−C═O in the dimer at high temperatures.

Here we discuss the path weights of the proton-transferred decarbonylation (eq 2) and self-disproportionation (eq 3). As shown in eq 3, one molecule of methanol is generated from two molecules of formaldehyde by self-disproportionation. Thus, the yield ratio (0.64) of methanol to hydrogen indicates that the weight of the self-disproportionation is slightly larger than that of the proton-transferred decarbonylation in the present reaction conditions. Here we emphasize that the path weights can be varied significantly by controlling the initial concentration of DME because the self-disproportionation is of second order. Recently, we have confirmed that methanol is generated predominantly with negligible hydrogen in the high-temperature neat reaction of formaldehyde at higher initial concentrations.[15] This shows that the self-disproportionation proceeds essentially as a single pathway for the formaldehyde reaction when the initial concentration in the gas phase is high enough to cause the second-order reaction and suppress the lower order reaction.

*Hydrothermal Reactions.* To examine how the reaction pathways of DME are modified from those in the neat gas reaction by the presence of supercritical water, we compare the products and their distribution with and without hot water. The products generated by the supercritical water reaction of DME (0.1 M) are

$$\text{methanol} > \text{methane} > \text{hydrogen}$$

according to the $^1$H spectra for the liquid and gas phases, respectively, shown in parts c and d of Figure 1. These products are common to those of the neat gas reaction. However, the product distribution in supercritical water is quite different from that of the neat reaction: for both cases, the initial concentration of DME is made equal. Methanol is dominant, instead of methane generated by the proton-transferred fragmentation of DME (eq 1). The amount of methanol is twice as large as that of methane. This clearly indicates that the methanol formation in supercritical water involves some reaction pathways other than eq 3; the yield of methanol produced by the self-disproportionation of formaldehyde cannot exceed the half of methane yield (see eqs 1 and 3). Naturally, hydrolysis is considered as another methanol formation pathway:

$$\mathrm{CH_3OCH_3} + \mathrm{H_2O} \rightarrow \mathrm{2CH_3OH} \tag{4}$$

It is worthwhile to examine whether the contribution of the hydrolysis (eq 4) is larger than that of the proton-transferred fragmentation (eq 1). The yield ratio of methanol to methane indicates that the path weights of the competitive hydrolysis (eq 4) and proton-transferred fragmentation (eq 1) are comparable in supercritical water at 0.5 g/cm$^3$; note that two molecules of methanol are generated from one molecule of DME by the hydrolysis. This is in contrast to the case of diethyl ether:[1] the weight of the proton-transferred fragmentation of diethyl ether is 4 times larger than that of the hydrolysis in the corresponding reaction conditions. The relative acceleration of the hydrolysis of DME is considered to be caused mainly by the slowdown of the proton-transferred fragmentation of DME due to the low stability of the transition state as discussed later, while the hydrolysis is also slowed down. From the gas-phase $^{13}$C spectrum in Figure 1f, carbon dioxide is observed as another product. Formaldehyde and carbon monoxide detected in the neat gas reactions are not observed in the case of supercritical water reactions at 200 h. The absence of these products is

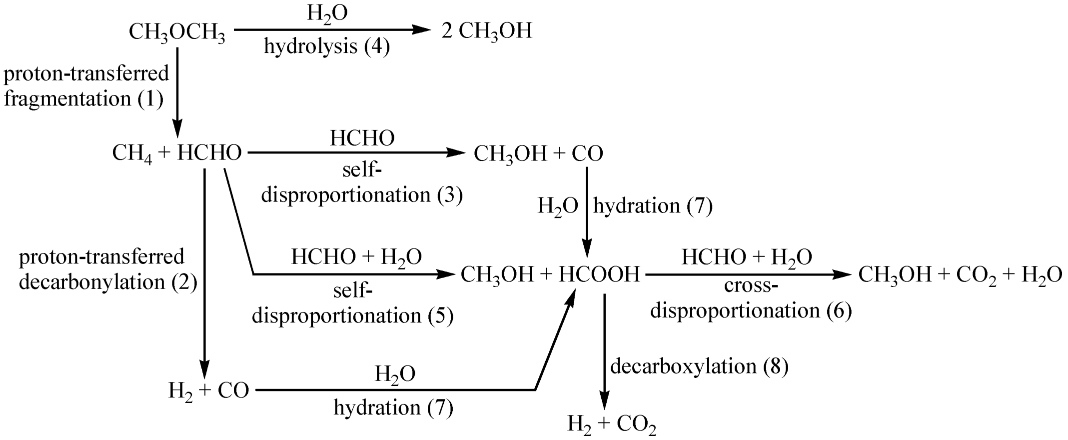

**Figure 2.** Noncatalytic reaction scheme of DME in supercritical water. The numbers in parentheses denote the equation numbers of the reactions in the text.

brought about by the successive transformation into other products through the reactions with water.

An important question is whether methanol is formed by the single pathway of hydrolysis in supercritical water. It is to be noted that the fragmentation of DME leads to the generation of formaldehyde. In the study of diethyl ether,[1] we have found that acetaldehyde produced by the proton-transferred fragmentation of diethyl ether can generate ethanol through the self- and cross-disproportionations in hot water. When we can presume that the reaction scheme of diethyl ether is common to that of DME, the supercritical water reaction of DME involves the following reactions:

$$2HCHO + H_2O \rightarrow CH_3OH + HCOOH \quad \text{(self-disproportionation)} \quad (5)$$

$$HCHO + HCOOH + H_2O \rightarrow CH_3OH + HOCOOH \quad (6)$$

$$\rightarrow CH_3OH + CO_2 + H_2O \quad \text{(cross-disproportionation)} \quad (6')$$

$$CO + H_2O \rightarrow HCOOH \qquad \text{(hydration)} \qquad (7)$$

$$HCOOH \rightarrow CO_2 + H_2 \qquad \text{(decarboxylation)} \qquad (8)$$

The self-disproportionation (eq 5) and cross-disproportionation (eqs 6 and 6′) reactions of formaldehyde can generate methanol. Here, we distinguish the self-disproportionation of eq 5 from that of eq 3 involved in the neat reaction. Note that the self-disproportionation in eq 5 requires a water molecule as a reactant, whereas that in eq 3 does not. In previous studies on a variety of aldehydes,[12−15] we have shown that aldehydes commonly undergo the self-disproportionation that requires water, and have considered that the reaction is induced by the hydrated form of aldehyde (geminal diol) as follows:

$$2RCHO + H_2O \rightarrow [RCH(OH)_2 + RCHO] \rightarrow RCH_2OH + RCOOH \quad (9)$$

Thus, the mechanisms of the hydrous and anhydrous self-disproportionations are different from each other despite the common product of methanol. Thus, we conclude that methanol is produced through the three types of disproportionations of formaldehyde as well as the hydrolysis of DME. The hydrous self-disproportionation (eqs 5 and 9) and cross-disproportionations (eqs 6 and 6′) have been found to proceed even at a lower (subcritical) temperature such as 225 °C.[15] It is also observed that acetaldehyde undergoes these disproportionations in subcritical temperatures.[14]

In the case of diethyl ether, the presence of the self-disproportionation pathway has been confirmed successfully through the detection of the oxidized product, acetic acid.[1] For DME, however, formic acid can be generated but is unstable in supercritical water; it is quickly transformed into some others through the successive reactions.[1,12−15,17] We can demonstrate the presence of the self- and cross-disproportionations later in the discussion based on the mass balance.

All the reaction pathways of DME discussed above can be summarized with the scheme in Figure 2. It is interesting to compare this reaction scheme with that for diethyl ether.[1] Most of the reactions are common to the supercritical water reactions of diethyl ether. Differences are the anhydrous self-disproportionation of formaldehyde (eq 3) and the subsequent hydration reaction of carbon monoxide (eq 7). These differences between DME and diethyl ether make the reaction scheme of DME more complex, as shown in Figure 2. The carboxylic acid, formic acid, generated by the hydration of carbon monoxide and hydrous self-disproportionation of formaldehyde is still a C1 aldehyde, so it can be further involved in the cross-disproportionation with formaldehyde (eq 6) in addition to the decarboxylation (eq 8). Note that the autocatalytic effect of carboxylic acid on the hydrolysis observed in the diethyl ether reactions does not exist in the case of DME.

*Comparison of Different Ethers.* It is important to examine how the reaction rates are modified by the molecular structures of ethers composed symmetrically of linear aliphatic chains. We compare DME, diethyl ether, and dipropyl ether; the comparison of the product yields of alcohol and hydrocarbon (produced from a reaction similar to eq 1) reveals the relative importance of the hydrolysis and proton-transferred fragmentation of the ethers. In this comparative study, the reaction conditions are fixed at 400 °C, water density of 0.5 g/cm$^3$, reaction time of 20 h, and initial ether concentration of 0.1 M. As can be seen in Figure 3, the consumption rate of ether and the fragmentation yield of hydrocarbon are in increasing order

$$\text{DME} \ll \text{diethyl ether} < \text{dipropyl ether}$$

This shows that the proton-transferred fragmentation by the methylene group is faster than that by the methyl group despite the difference (entropy factor) in the number of hydrogen atoms. The acceleration for the methylene proton is especially evident when DME and diethyl ether are compared. This can be explained in terms of a difference in the stability of the transition

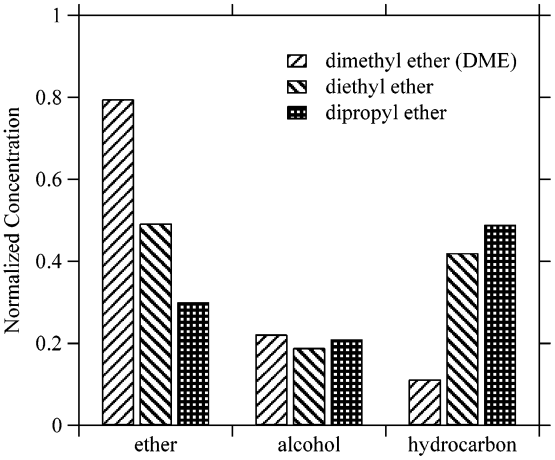

**Figure 3.** Comparison of amounts of alcohol and hydrocarbon produced by proton-transferred fragmentation of dimethyl, diethyl, and dipropyl ethers at 400 °C, water density of 0.5 g/cm$^3$, reaction time of 20 h, and initial concentration of 0.1 M. The hydrocarbons correspond to the ones generated by the proton-transferred fragmentation of ethers through reactions similar to eq 1. The normalized concentration denotes the concentration of the compound of interest divided by the initial concentration of ether.

state between DME and the others. In transition states, a positive partial charge generates on the carbon receiving the transferred proton. The methylene carbon ($C-CH_2-O$) located in the vicinity of oxygen of diethyl and dipropyl ethers can stabilize a positive charge more than the methyl carbon of DME.[21] Hence DME is less reactive in the proton-transferred fragmentation than diethyl and dipropyl ethers. In the case of alcohol, however, the yield is not much different among the three ethers. The similarity is accidental and brought about by the complexity of the alcohol production pathways.

**B. Time Evolution of Products and Kinetic Analysis.** *Effect of Hot Water on Methane Formation.* Let us examine how the reaction pathways and rates are modified by the presence of hot water at the initial DME concentration of 0.1 M; see Figure 4a,b. The consumption rate of DME in the neat reaction is comparable to that in the supercritical water reaction at 0.5 g/cm$^3$ despite the presence of the multiple pathways in the supercritical water reaction; see the scheme in Figure 2. The consumption rates at 200 h are ~60% in both reactions, whereas the methane yields are ~60% and ~25% in the neat and the supercritical water reactions, respectively. The proton-transferred fragmentation is thus decelerated by the presence of hot water. One of the reasons for the slowdown is the suppression of the reactive vibrating mode by solvating water molecules. The slowdown of the proton-transferred fragmentation induced by water is observed also for diethyl ether.[1] The slowdown of the proton-transferred fragmentation of DME can be quantitatively shown by a comparative study of the rate constants with and without water. The first-order rate constant of the proton-transferred fragmentation is found to be $2.0 \times 10^{-6}$ s$^{-1}$ in the neat reaction, while it is $7.6 \times 10^{-7}$ s$^{-1}$ in the supercritical water reaction at 0.5 g/cm$^3$. The rate constant is reduced by a factor of ~0.4 by the presence of water at 0.5 g/cm$^3$.

*Path Weight for Methanol Production.* Here we confirm from the analysis of the mass balance at a higher initial concentration (0.5 M) that methanol can also be produced through the disproportionation reactions of formaldehyde (eqs 3, 5, 6, and 6′) generated by the proton-transferred fragmentation of DME. Furthermore, we determine the weights of the hydrolysis and disproportionation reactions in the methanol formation.

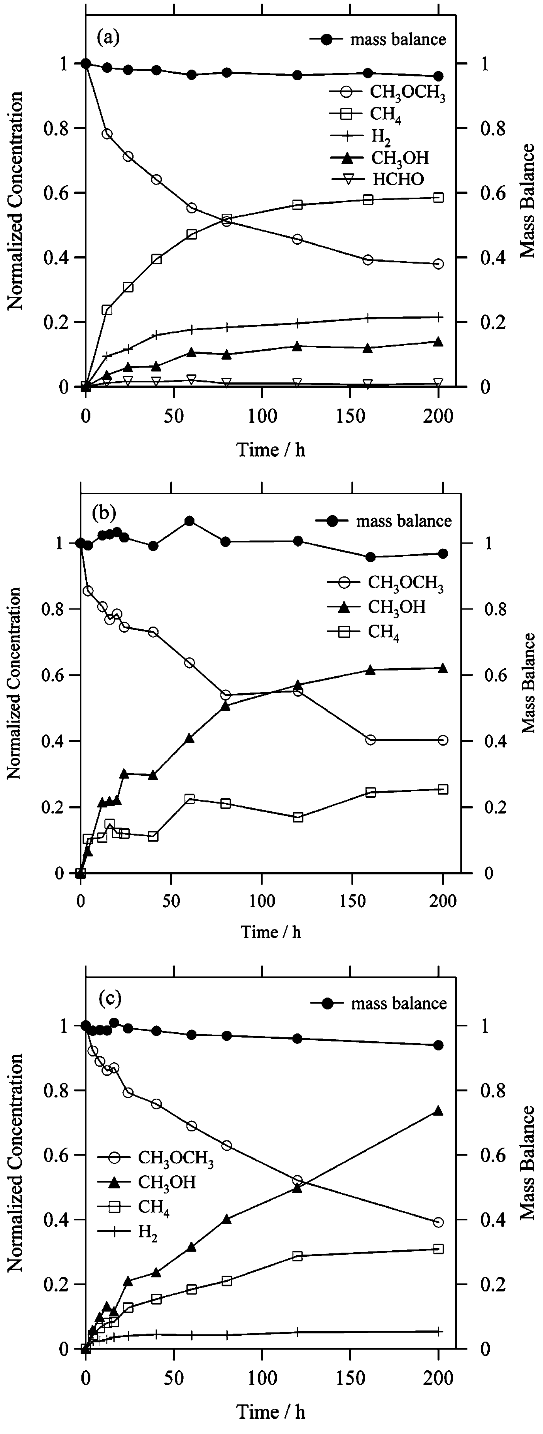

**Figure 4.** Time evolution of concentrations of DME and products treated at 400 °C. (a) Neat reaction at initial concentration of 0.1 M. (b and c) Hydrothermal reactions at water density of 0.5 g/cm$^3$ and initial concentrations of 0.1 (b) and 0.5 (c) M. The normalized concentration denotes the concentration of the compound of interest divided by the initial concentration of DME. The proton mass balance denotes the ratio of the hydrogen amount in DME and the products at a specified reaction time to the initial amount in DME.

According to the reaction scheme in Figure 2, the amount $[\text{methanol}]_{\text{hyd}}$ of methanol produced by the DME hydrolysis can be expressed in terms of the mass balance equation:

$$[\text{methanol}]_{\text{hyd}} = 2([\text{DME}]_0 - [\text{DME}] - [\text{methane}]) \tag{10}$$

where $[\text{DME}]_0$ denotes the initial concentration of DME. If the

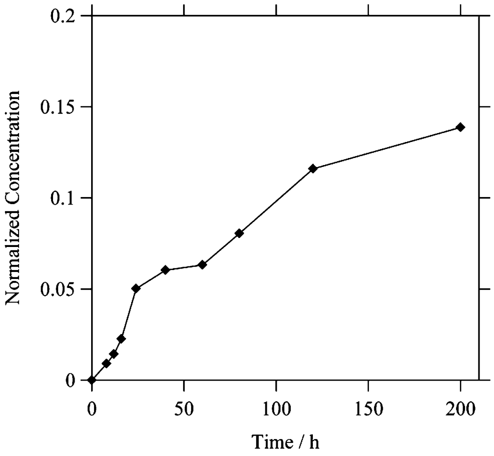

**Figure 5.** Time evolution of concentration of methanol defined by eq 11 ([methanol]$_{disp}$). The initial concentration of DME is 0.5 M in supercritical conditions. The normalized concentration means the concentration of interest divided by the initial concentration of DME.

hydrolysis were the only path to methanol, the concentration of methanol would be equal to [methanol]$_{hyd}$. The methanol concentration actually observed in Figure 4c is, however, larger than [methanol]$_{hyd}$ estimated by eq 10 during the course of the reaction time. The disproportionation reactions of formaldehyde produce the excess methanol, and the amount [methanol]$_{disp}$ of methanol generated by the disproportionations is given by the mass balance equation:

$$[\text{methanol}]_{\text{disp}} = [\text{methanol}] - [\text{methanol}]_{\text{hyd}} \qquad (11)$$

In Figure 5, the amount of methanol generated by the disproportionations is plotted. The concentration of methanol calculated by eq 11 is 0.14 M at 200 h. The value is ~20% of the methanol concentration observed. The relative contributions of the hydrolysis and the disproportionations to the methanol formation are approximately 80% and 20%, respectively.

In part 1 on diethyl ether, we have determined the weights of the self- and cross-disproportionations of acetaldehyde by comparing the ethanol concentration estimated by an equation similar to eq 11 with the acetic acid concentration. In the case of DME, however, formic acid is unstable in supercritical water and is consumed quickly by the reactions of eqs 6 and 8. To establish the weights of the self- and cross-disproportionations of formaldehyde, it is necessary to perform a comprehensive study of the reactions where formaldehyde is used as a starting material. In a subsequent paper, we will present such a detailed study on the reactions of formaldehyde on the basis of the kinetic analysis by NMR.[15]

*Water Density Effect.* The hydrolysis (eq 4) requires water as a reactant as well as a solvent. It is therefore expected to be enhanced by the increase in the supercritical water density, in contrast to the proton-transferred fragmentation (eq 1). We examine the water density dependence of the product yields in the supercritical water reaction at 400 °C, reaction time of 40 h, and initial concentration of 0.1 M. As can be seen in Figure 6, the yield of methanol increases with increasing water density, whereas that of methane shows a decreasing tendency. As mentioned above, formaldehyde generated by the proton-transferred fragmentation of DME can undergo the disproportionations producing methanol even at the low initial concentration of 0.1 M; methanol is indeed observed in the neat reaction (in the absence of water) as shown in Figure 6. The yield of methanol in the supercritical water reactions thus involves methanol generated through both the hydrolysis and disproportionations. The weights of these reactions for methanol formation were not separated here but can be estimated roughly according to the mass balance based on the scheme in Figure 2. According to the reaction scheme, the amount of methanol generated by the disproportionations via formaldehyde should be smaller than that of methane. In the reaction at the water density of 0.6 g/cm$^3$, the yield ratio of methanol to methane is 20. The contribution of the disproportionations to methanol formation is thus reduced to 5% or below from 100% by the density elevation from 0 to 0.6 g/cm$^3$. In other words, the importance of the hydrolysis increases as the water density is elevated. This is considered to be caused by both the deceleration of the proton-transferred fragmentation and the acceleration (transition-state stabilization) of the hydrolysis induced by the increasing water density. These features are common to the case of diethyl ether.[1]

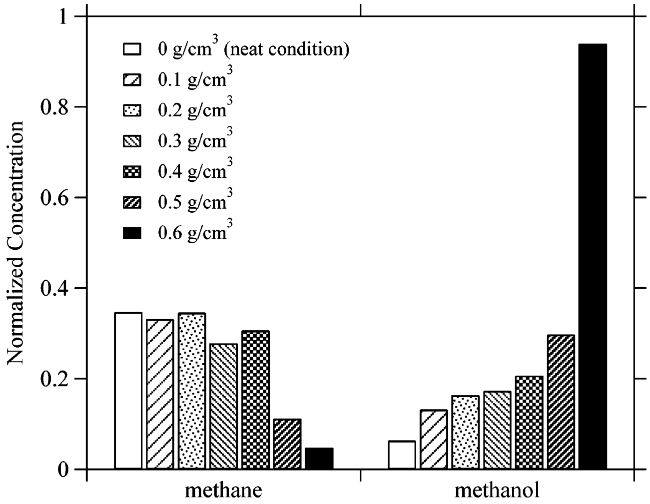

**Figure 6.** Product concentrations in various water densities at the fixed supercritical temperature of 400 °C, reaction time of 40 h, and initial concentration of 0.5 M. The normalized concentration denotes the concentration of the compound of interest divided by the initial concentration of DME.

DME can serve as an alternative to liquefied natural gas (LNG), because it can be easily liquefied and gasified at temperatures not far from room temperature. The combustion of DME is accompanied by the generation of a large amount of hot water; hot water further participates in DME combustion reactions as a reactant and solvent. The present paper has shown how to control the selective production of methane or hydrogen to adjust the combustion efficiency.[22] To generate hydrogen in a higher yield, the concentration of DME should be made low by mixing water. CO produced by the successive reactions, eqs 1 and 2, can be further used to get hydrogen from hot water.[17] At high concentrations, not hydrogen but methanol is produced mainly through the hydrous and anhydrous disproportionations of formaldehyde. These predictions on reaction path control can be made possible by a detailed kinetic study on the supercritical water reaction of fuels at high temperatures.

## IV. Conclusions

We have found that dimethyl ether in supercritical water at 400 °C undergoes as first steps the proton-transferred fragmentation generating formaldehyde and methane in competition with the hydrolysis producing methanol. Formaldehyde is further subjected to such reactions as decarbonylation and the noncatalytic self- and cross-disproportionations, which generate methanol. Self-disproportionation has two types of mechanisms, depending on the participation of water as a reactant. Methanol is thus formed through four types of reactions. Most of the reaction schemes of DME are common to other aliphatic linear ethers. Differences are the self-disproportionation without water and the subsequent hydration of carbon monoxide to formic acid. The differences make the reaction scheme of DME more complex. The formic acid generated is still a C1 aldehyde, so it can be further involved in the cross-disproportionation with formaldehyde. Due to the consumption of formic acid, the autocatalytic effect of carboxylic acid on the hydrolysis observed in the diethyl ether reactions is absent in the case of DME.

The proton-transferred fragmentation of DME and the decarbonylation of formaldehyde can occur even in the neat gas conditions as can the self-disproportionation of formaldehyde. We consider that the mechanisms of these reactions are similar to those of the corresponding reactions of diethyl ether: those are not homolytic but heterolytic. The presence of solvent water decelerates the proton-transferred fragmentation; the rate constant decreases by a factor of 0.4 at the water density of 0.5 g/cm$^3$. This is caused by the suppression of the low-frequency concerted motion corresponding to the reaction coordinate for the simultaneous C−O bond scission and proton transfer from one methyl carbon to the other.

When the structure of ether is varied, the rate of the proton-transferred fragmentation is in the increasing order: DME $\ll$ diethyl ether $<$ dipropyl ether. This order corresponds to the alkyl substituent length. The variation of the reactivity is considered to be induced by the difference in the stability of the transition state. The primary carbon ($C-\mathit{C}H_2-O$) located in the vicinity of oxygen of diethyl and dipropyl ethers can stabilize a positive charge generated on the proton-receptor carbon in the transition states more than the methyl carbon of DME. Hence the reactivities of the proton-transferred fragmentation of diethyl and dipropyl ether are higher than that of DME. When asymmetric ethers such as methyl ethyl ether, methyl propyl ether, ... are subjected to high temperature with or without water, it is predicted that the proton transfer occurs preferentially from the ethylene to methyl groups.

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(20) When the temperature is lowered to 225 °C, neither the proton-transferred decarbonylation (eq 2) nor the self-disproportionation (eq 3) takes place in the neat conditions of formaldehdye.[15] Thus, these reactions are characteristic of high temperatures.

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(22) When the temperature is elevated from the temperature studied here (673 K) to the combustion one (1000 K), the reaction rate can increase by roughly $10^{10}$ times according to the rule of thumb for the rate: a 2-fold rate constant increase with a temperature elevation of 10 K. This indicates that the time scale for the DME reactions is reduced from 200 h (673 K) to on the order of 10 $\mu$s (1000 K) within the same reaction mechanism.