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Mechanisms and Kinetics of Noncatalytic Ether Reaction in Supercritical Water. 1. Proton-Transferred Fragmentation of Diethyl Ether to Acetaldehyde in Competition with Hydrolysis

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Noncatalytic reaction pathways and rates of diethyl ether in supercritical water are determined in a quartz capillary by observing the liquid- and gas-phase ^1H and ^{13}C NMR spectra. The reaction is investigated at two concentrations (0.1 and 0.5 M) in supercritical water at 400 °C and over a water-density range of 0.2−0.6 g/cm^3, and in subcritical water at 300 and 350 °C. The neat reaction (in the absence of solvent) is also studied for comparison at 0.1 M and 400 °C. The ether is found to decompose through (i) the proton-transferred fragmentation to ethane and acetaldehyde and (ii) the hydrolysis to ethanol. Acetaldehyde from reaction (i) is consecutively subjected to the unimolecular and bimolecular redox reactions: (iii) the unimolecular proton-transferred decarbonylation forming methane and carbon monoxide, (iv) the bimolecular self-disproportionation producing ethanol and acetic acid, and (v) the bimolecular cross-disproportionation yielding ethanol and carbonic acid. Reactions (ii), (iv), and (v) proceed only in the presence of hot water. Ethanol is produced through the two types of disproportionations and the hydrolysis. The proton-transferred fragmentation is the characteristic reaction at high temperatures and is much more important than the hydrolysis at densities below 0.5 g/cm^3. The proton-transferred fragmentation of ether and the decarbonylation of aldehyde are slightly suppressed by the presence of water. The hydrolysis is markedly accelerated by increasing the water density: the rate constant at 400 °C is 2.5×10^{-7} s^{-1} at 0.2 g/cm^3 and 1.7×10^{-5} s^{-1} at 0.6 g/cm^3. The hydrolysis becomes more important in the ether reaction than the proton-transferred fragmentation at 0.6 g/cm^3. In subcritical water, the hydrolysis path is dominant at 300 °C (0.71 g/cm^3), whereas it becomes less important at 350 °C (0.57 g/cm^3). Acetic acid generated by the self-disproportionation autocatalyzes the hydrolysis at a higher concentration. Thus, the pathway preference can be controlled by the water density, reaction temperature, and initial concentration of diethyl ether.

I. Introduction

Unlike ambient water, hot water mixes well with nonpolar organic compounds. Due to the strong and anisotropic fluctuations in the local electric field at high temperatures, hot water can induce chemical reactions that are impossible without acidic or basic catalysts under ambient conditions.[1−18] To establish the hydrothermal chemistry for the next generation, systematic studies in a manner friendly to the earth on the reaction of each functional group are necessary. As one of the most important functional groups, ether bonds (C−O−C) are abundantly accumulated in naturally produced organic compounds, in particular, coal, such polysaccharides as cellulose and starch, wood components, etc., that attract much attention for food and energy concerns. Thus, the noncatalyzed reaction mechanism of ether bonds in linear and cyclic forms needs to be revealed in connection with the transformation of natural resources (biomass) into useful organics or renewable fuels.[19] At the present, however, ether reactions in hot water are not well characterized. It is then important to establish the reaction mechanism of ether bonds using a simple compound. In this work, we focus on a chain ether, diethyl ether ($CH_3CH_2{-}O{-}CH_2CH_3$); we focus on dimethyl ether in the following paper (part 2[31]).[20] To elucidate the reaction pathways and kinetics, we apply the powerful NMR spectroscopy to both the liquid and gas phases for the structural and quantitative analyses.

In a previous paper,[7] we investigated the noncatalytic reaction of a simple cyclic ether, tetrahydrofuran, in super- and subcritical water using a quartz tube that has no catalytic effect; metallic vessels can catalyze supercritical water reactions and change their mechanisms.[15−17] We have shown that tetrahydrofuran undergoes the single reaction of hydrolysis and transforms into 1,4-butanediol without byproducts. It turns out that the hydrolysis is reversible in hot water and that the diol becomes less favorable compared to the cyclic ether with the temperature elevation. It is then natural to question whether the single and reversible hydrolysis mechanism found is general or not for open-chain ethers. The point of the present study on a chain ether is that ether is transformed into aldehyde. The reaction is induced by the transfer of an active proximity proton as $R{-}CH_2{-}O{-}CH_2{-}R \rightarrow R{-}CHO + R{-}CH_3$. Alcohol can then be formed easily from the intermediate aldehyde through disproportionations as previously verified for various aldehydes.[11−13] Aldehyde is the key intermediate and can provide an alternative path to alcohol, competing against the hydrolysis of ether. To elucidate how water affects the titled reactions of diethyl ether, we compare the reaction pathways and rates in the neat system (in the absence of solvent) with those in supercritical water; this is essential to elucidate the role of water as shown in the case of acetaldehyde.[12]

Chain ethers may involve phenyl and/or aliphatic groups. Over a decade ago, Townsend and co-workers paid attention to chain ethers involving phenyl rings as model compounds of coal:[8] they studied dibenzyl, phenetyl phenyl, benzyl phenyl ether, etc. using a stainless steel tube reactor. These ethers are

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reported to have two competing reactions—“hydrolysis” and “pyrolysis”—according to the product analysis. Of the six ethers studied, however, only dibenzyl ether is reported to generate aldehyde. Later, Funazukuri et al.[9] confirmed the benzaldehyde formation from dibenzyl ether and reported the complexity of the reaction scheme at a high concentration (1−2 M).

When aldehyde is formed as an intermediate from ether, it is oxidized to carboxylic acid and reduced to alcohol through noncatalytic self-disproportionation, as found for a variety of aldehydes (formaldehyde,[11] acetaldehyde,[12] and benzaldehyde[13]). In previous studies on benzyl ether,[6,8,9] however, benzaldehyde but not benzoic acid was detected. To establish the reaction mechanism of ether in supercritical water, it is of great importance to examine whether both aldehyde and carboxylic acid are generated. Furthermore, the production of carboxylic acid raises a new question about whether it autocatalyzes the ether hydrolysis in supercritical water, although under ambient conditions such a weak acid cannot catalyze the scission of strong ether bonds. It has been communicated that the reverse reaction, dehydration of alcohol, is catalyzed by acetic acid.[18] When attention is paid only to the ethanol formation and its yield, the autocatalytic effect cannot be identified. To confirm the autocatalysis, it is necessary to examine the time evolution of all products at different initial concentrations. Here, we perform a kinetic analysis by varying the initial concentration of diethyl ether.

To elucidate the detailed pathways, kinetics, and mechanisms, it is necessary to analyze quantitatively all products, intermediates, and reactants including the volatile in ambient conditions. After the reaction, such gaseous products as ethane, methane, and carbon dioxide are distributed among the liquid and gas phases in the reaction vessel; the first two are present exclusively in the gas phase. Thus, not only liquid-phase products but also gas-phase ones are observed here by NMR. We confirmed in the analysis that the mass balance is kept. NMR spectroscopy is hence powerful enough for the structural, elemental, and quantitative analyses to establish the mechanisms of the supercritical water reaction of diethyl ether.

The control of competitive reaction pathways is essential for the development of supercritical water chemical engineering. Hot water may exert a strong effect on a chemical process due to the large fluctuations in the local electric field at high temperatures.[7,12,14,21,22] It acts as a medium to modify the reaction pathways and rates, and the role of water in a reaction is strongly dependent on the thermodynamic state. Reaction control by supercritical water thus requires the identification of the pathways and their selectivities as functions of the water density and temperature. A target of the present work is to provide a clearcut and quantitative description of rules for ether reaction path weights in hot water. We will see that the ether reaction is not random in the bond breakings even at high temperatures and that its pathways and rates are subject to well-defined laws.

II. Experimental Section

Diethyl ether (Nacalai; purity >99.5%) was used without further purification. Water employed was purified using a Milli-Q Labo (Millipore) filter system. The solution of diethyl ether in H_2O was loaded into a quartz capillary of 1.5 mm i.d. and 3.0 mm o.d. The sample was sealed after air in the reactor tube was replaced by argon. 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. The filling factor was varied from 0.2 to 0.6. This means that the minimum and maximum values of the water density for the supercritical water are 0.2 and 0.6 g/cm^3, respectively, in the present work. The capillary needs to resist against the high pressure generated, and is sometimes burst. The bursting probability of the capillary at 400 °C is ∼20% at the supercritical water density of 0.5 g/cm^3 (water pressure of 37 MPa) and is ∼50% at 0.6 g/cm^3 (56 MPa). Of course, the analysis after the reaction can be performed only for the surviving samples.

Detailed analysis of the supercritical water reaction was performed at 0.5 g/cm^3. In the batch method applied, the samples were subjected to NMR observations. The initial concentration of diethyl ether was set to 0.1 and 0.5 M ($M = mol/dm^3$) in supercritical conditions. For comparison, the neat reaction was also examined at 400 °C. In this case, no water solvent was added in the sample and the initial concentration of diethyl ether was set to 0.1 M when the system was homogeneous.

The temperature of supercritical water reactions was fixed at 400 °C. The sample was put into a programmable electric furnace kept at 400 °C. The temperature was controlled within ±1 °C. After a reaction time, the reaction tube was removed quickly from the furnace and quenched in a cold water bath. It took less than 30 s for the sample to cool. Actually, the time scales for heating and cooling the sample were shorter than those for the reactions at the thermodynamic states of interest. After the sample was cooled, the liquid and gas phases coexisted in the sample vessel and reaction products were distributed in both phases. The liquid and gas phases were separately subjected to ^1H and ^{13}C NMR measurements at room temperature using ECA400N, ECA500W, and ECA600N (JEOL), and the products and residual reactant were quantified. The sample setup for NMR measurements on the liquid and gas phases was described in detail in a previous paper.[12]

The reaction of diethyl ether in subcritical water was also examined. In this case, the sample was prepared by setting the filling factor to 0.5 and the initial concentration of diethyl ether to 1.0 M under ambient conditions. The reaction was performed at temperatures of 300 and 350 °C on the liquid branch of the saturation curve of water, where the water density is 0.71 and 0.57 g/cm^3, respectively. The procedures for the treatment of the sample and NMR measurements were the same as those for the reaction in supercritical water.

III. Results and Discussion

To establish the reaction pathways, we have examined what kinds of products are generated in the neat and supercritical water reactions of diethyl ether at 400 °C and a reaction time of 20 h. To discuss the reaction mechanisms and the role of supercritical water, all of the reactants and products have been analyzed as a function of time by means of ^1H and ^{13}C NMR spectroscopy.[23]

A. Products and Reaction Pathways. *High-Temperature Neat Reactions.* We first examine the neat reaction in the absence of water at 400 °C and the initial concentration of 0.1 M. In this case, diethyl ether cannot undergo hydrolysis due to the lack of water as a reactant and solvent. We can scrutinize whether the hydrolysis is main or not in supercritical water by comparing the products and their distribution with and without water. As can be seen from the ^{13}C NMR (Figure 1a) taken without proton irradiation, the neat reaction generates the products in the following order:

$$\text{ethane} > \text{methane} \approx \text{carbon monoxide} > \text{acetaldehyde}$$

Since the second and third products arise from the successive

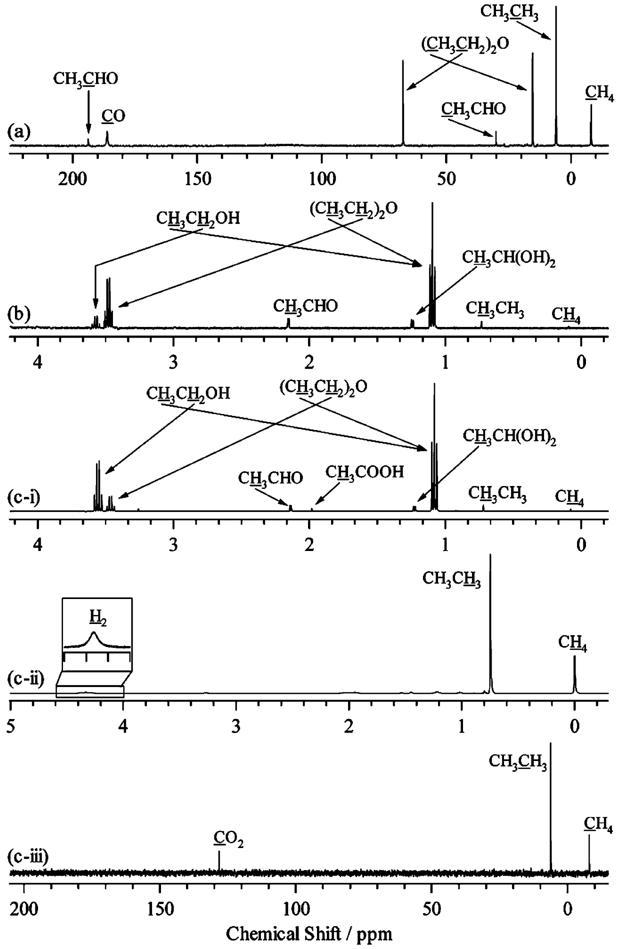

Figure 1. NMR spectra for reaction products of diethyl ether after treatment at 400 °C for 20 h. (a) ^{13}C spectrum for the neat reaction without solvent water at initial concentration of 0.1 M. (b) Liquid-phase ^{1}H spectra for the reaction in supercritical water at 0.5 g/cm^3 and initial concentration of 0.1 M. (c-i, c-ii, and c-iii) Liquid-phase ^{1}H, gas-phase ^{1}H, and gas-phase ^{13}C spectra, respectively, for the reaction in supercritical water at 0.5 g/cm^3 and initial concentration of 0.5 M. The neat reaction spectrum (a) is obtained by a high-temperature measurement at 130 °C; at this temperature, the sample system is homogeneous. In the liquid-phase ^{1}H spectra ((b and c-i)), $CH_3CH(OH)_2$ is the hydrated form of CH_3CHO. The carbonyl proton of CH_3CHO and methine proton of $CH_3CH(OH)_2$ are detected at 9.58 and 5.16 ppm, respectively, and are out of the range of the chemical shift shown.

decarbonylation of acetaldehyde as referred to below, this indicates the initial reaction process is given by

$$CH_3CH_2{-}O{-}CH_2CH_3 \rightarrow CH_3CH_3 + CH_3CHO \qquad (1)$$

This is a new type of C−O bond scission, differing from the homolytic carbon−oxygen bond breakage often assumed in pyrolysis. The C−O bond scission simultaneously accompanies the intramolecular proton transfer from the one methylene group to the other surrounding the ether oxygen as a hinge center. The proton-transferred fragmentation reduces the one aliphatic chain to ethane and oxidizes the other to acetaldehyde; $-CH_2-O-CH_2-$ is fragmented and transformed into $-CH_3$ and $-HC{=}O$. We can regard the high-temperature reaction as an intramolecular disproportionation (redox reaction of the originally equivalent carbons). This can arise from strongly coupled anharmonic stretching and bending vibrations of many degrees of freedom related to a cyclic transition state formed by the C−O−C−H moiety; a key role is played by the electrostatic attractions between the partial charges on the proton and carbon. The vibrations along the reaction coordinate are to be significantly excited due to the high temperatures. Hence the concerted proton transfer and bond scission can take place in neat reactions of molecules involving heteroatoms at high temperatures.

Acetaldehyde is successively transformed into methane and carbon monoxide through a decarbonylation reaction induced by proton transfer.[12] It is given by

$$CH_3CHO \rightarrow CH_4 + CO \qquad (2)$$

This unimolecular disproportionation (redox reaction of the originally similar carbons) plays a key role in controlling the reaction pathway of the supercritical water reaction of diethyl ether. The decarbonylation of acetaldehyde leads us to explain why the yield of acetaldehyde is smaller than that of ethane and why methane and carbon monoxide are generated equally; see Figure 1a. As mentioned above for eq 1, the reaction mechanism is not homolytic but heterolytic and induced by the proton transfer. The homolytic bond-breakage process has been considered for the fragmentation in view of the presence of such products as propane, ethylene, propene, and hydrogen. In the present study, however, the total yield of these products was only ∼3% in the neat reaction for 20 h. Therefore, at temperatures as high as 400 °C, the polar, heterolytic mechanism is overwhelmingly favored over the radical, homolytic one. In other words, the reaction is not “randomized” yet at 400 °C.

Hydrothermal Reactions. Let us examine how the reaction pathways are modified from those in the neat condition by the presence of supercritical water. Here we compare products and their distribution with and without hot water. As shown by the proton spectrum for the liquid phase in Figure 1b, the products generated from diethyl ether at a low initial concentration of 0.1 M in supercritical water are in the decreasing order

$$\text{ethane } (0.82) > \text{methane } (0.44) > \text{ethanol } (0.37) > \text{acetaldehyde } (0.34)$$

where the numbers in parentheses indicate the yield normalized by the amount of diethyl ether consumed; the sum of them is 2. The yield of ethane generated by eq 1 is approximately twice that of ethanol produced by hydrolysis:

$$CH_3CH_2{-}O{-}CH_2CH_3 + H_2O \rightarrow 2CH_3CH_2OH \qquad (3)$$

This clearly indicates that not the hydrolysis but the proton-transferred fragmentation (eq 1) is dominant in supercritical water at 0.5 g/cm^3. The weight of the proton-transferred-fragmentation path is 4 times larger than that of the hydrolysis; note that two molecules of ethanol are generated from one molecule of diethyl ether by the hydrolysis. The second main product, methane, arises from the unimolecular decarbonylation of acetaldehyde (eq 2). This is why aldehyde generated through eq 1 is much smaller in the yield than the fragmentation counterpart. The bimolecular self-disproportionation of acetaldehyde is not observed at the low initial concentration because of the higher reaction order; acetaldehyde undergoes only the unimolecular decarbonylation at the low initial concentration. In consequence, the normalized yield of ethane is equal to the sum of those of methane and acetaldehyde.

When the initial concentration of diethyl ether is increased from 0.1 M to a higher concentration (0.5 M), acetic acid is detected in addition to the products mentioned above; compare the liquid-phase proton spectra in Figure 1b and 1c-i. The presence of acetic acid makes the reaction mechanism more

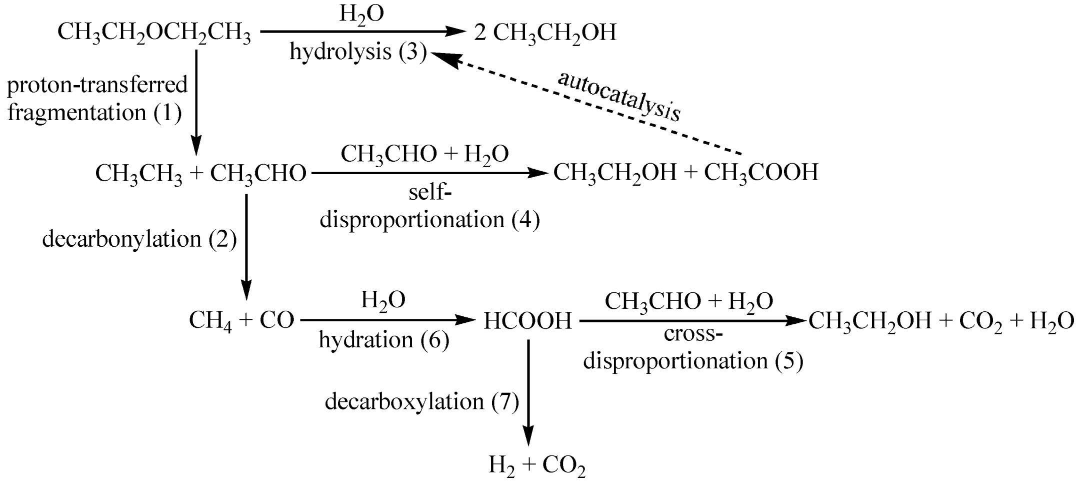

Figure 2. Noncatalytic reaction pathways of diethyl ether in supercritical water. The numbers in parentheses denote the reaction equations in the text. The vertical and horizontal arrows show, respectively, the unimolecular fragmentations induced by proton transfer and the uni- or bimolecular reactions requiring hot water as a reactant as well as solvent. The oblique arrow denotes the autocatalytic effect of acetic acid on the hydrolysis.

complicated by the autocatalytic effect on the hydrolysis, as discussed below. Furthermore, hydrogen and carbon dioxide are observed, respectively, in the gas-phase ^1H (Figure 1c-ii) and ^{13}C (Figure 1c-iii) spectra; hydrogen is detected only at the higher initial concentration of the reactant because its sensitivity to NMR is low due to the broad signal.

The disclosed feature of the supercritical water reaction of ether is that ethanol is not formed by the single pathway, hydrolysis. Ethanol can be produced also from acetaldehyde generated by eq 1 as previously found.[12] Acetaldehyde in supercritical water undergoes the following reactions besides the decarbonylation (eq 2):

$$2CH_3CHO + H_2O \rightarrow CH_3CH_2OH + CH_3COOH \quad \text{(self-disproportionation)} \quad (4)$$

$$CH_3CHO + HCOOH + H_2O \rightarrow CH_3CH_2OH + HOCOOH \quad (5)$$
$$\rightarrow CH_3CH_2OH + CO_2 + H_2O \quad \text{(cross-disproportionation)} \quad (5')$$

$$CO + H_2O \rightarrow HCOOH \qquad \text{(hydration)} \qquad (6)$$

$$HCOOH \rightarrow CO_2 + H_2 \qquad \text{(decarboxylation)} \qquad (7)$$

Acetic acid and carbon dioxide detected clearly indicate that ethanol can be generated through eqs 4 and 5 in the supercritical water reaction of diethyl ether. Attention only to ethanol formation and its yield makes us disregard the essential feature of the ether reaction mechanism simply as the hydrolysis. For a sound understanding of the reaction mechanism, it is necessary to analyze the time evolution of products on the basis of the stoichiometry. Formic acid acts a reducing reagent in the cross-disproportionation (eqs 5 and 5′) and is formed through the hydration of carbon monoxide (eq 6) generated by the decarbonylation of acetaldehyde. Formic acid is also decarboxylated as shown by eq 7.[12,15]

All pathways involved in the supercritical water reaction of diethyl ether can be summarized as the scheme depicted in Figure 2. The vertical and horizontal arrows show, respectively, the unimolecular fragmentations induced by proton transfer and the uni- or bimolecular reactions requiring hot water as a reactant as well as solvent. The oblique arrow denotes the autocatalytic effect of acetic acid on the hydrolysis as discussed below. All reaction pathways except for the hydrolysis (eq 3) and hydration of carbon monoxide (eq 6) are composed of the unimolecular (vertical arrows) and the bimolecular (horizontal arrows) disproportionations. Contrary to the conventional idea, ethanol is produced not only through the single hydrolysis but also through the two types of disproportionation reactions branched horizontally.

It is important to examine whether the reaction scheme determined is common to other ethers in hot water. We have observed a variety of ethers such as dimethyl ether, dipropyl ether, phenetole, and diphenyl ether. The first three were found to generate the corresponding alcohol, aldehyde, and carboxylic acid in supercritical water without any catalysts. Thus, the above competitive and successive scheme is common to the linear ethers. However, diphenyl ether does not undergo the proton-transferred fragmentation because of the absence of hydrogens in the proximity of the hinge-center oxygen. Moreover, diphenyl ether does not give rise to the hydrolysis either, probably due to the C−O bond order higher than the single.

B. Kinetics and Mechanisms. *Effect of Hot Water.* Let us examine how the reaction pathways and rates are modified by the presence of hot water at the initial concentration of diethyl ether of 0.1 M; see Figure 3a,b. The consumption rate of diethyl ether is slower in the supercritical water reaction than that in the neat reaction despite the presence of the multiple pathways in the supercritical water reaction; see the scheme in Figure 2. The consumption ratio at 20 h is ~50% in the supercritical water reaction, whereas it is ~60% in the neat reaction.[24] The proton-transferred fragmentation is slightly decelerated by the presence of hot water. One of the reasons for the slowdown would be the suppression of the reactive vibrating mode by solvating water molecules. Furthermore, it is to be noted that the stationary concentration of acetaldehyde in the supercritical water reaction is higher than that in the neat reaction. This means that the proton-transferred decarbonylation of acetaldehyde (eq 2) is also slowed by the presence of hot water. The extent to which the proton-transferred fragmentation of diethyl ether and decarbonylation of acetaldehyde slow down will be discussed below in terms of the rate constants determined as functions of water density.

Autocatalytic Effect of Acetic Acid on Hydrolysis. Let us show the autocatalytic effect of acetic acid on the hydrolysis (indicated by the inclined, oblique arrow in Figure 2). The acetic acid concentration increases significantly with increasing initial

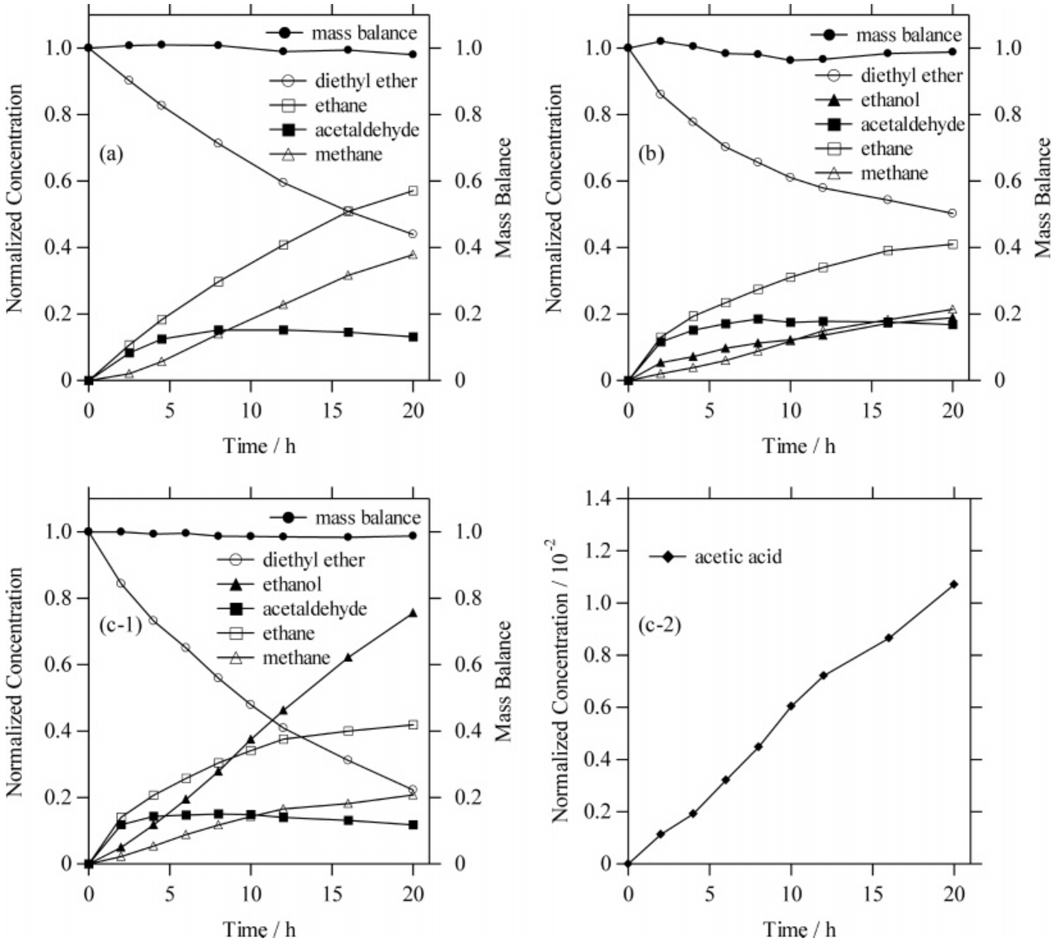

Figure 3. Time evolution of concentrations of diethyl ether and products treated at 400 °C. (a) Neat reaction at initial concentration of 0.1 M. (b and c) Supercritical water reaction at water density of 0.5 g/cm^3 and initial concentrations of 0.1 (b) and 0.5 (c) M. In (c), the products except for acetic acid are plotted in (c-1) and acetic acid is plotted in (c-2). The normalized concentration denotes the concentration of the compound of interest divided by the initial concentration of diethyl ether. The proton mass balance denotes the ratio of the hydrogen amount in diethyl ether and the products except for H_2 at a specified reaction time to the initial amount in diethyl ether; H_2 originates from water as seen in eqs 6 and 7.

concentration because the self-disproportionation is of second order.[12] If the hydrolysis (eq 3) is autocatalyzed by acetic acid, ethanol formation through it is expected to be enhanced markedly by the increase in the initial concentration of diethyl ether. Let us compare the product distributions at the high (0.5 M) and low (0.1 M) initial concentrations. As can be seen in Figure 3b,c, the 5-fold increase of the initial concentration significantly widens the product distribution, and ethanol and acetic acid are produced 4 times more and 1 order of magnitude more, respectively, in terms of the normalized concentration. When the increment of the relative ethanol yield due to the increase in the initial concentration is assumed to be caused only by the self- and cross-disproportionations, the yield increase should not exceed the amount of half of the consumed acetaldehyde as

$$[\text{ethanol}]_H - [\text{ethanol}]_L \leq ([\text{ethane}]_H - [\text{acetaldehyde}]_H)/2 \qquad (8)$$

where the square brackets denote the normalized concentration and the subscripts "H" and "L" mean the high and low initial concentrations, respectively. This relation is, however, contradictory to what is observed for the supercritical water reaction. The failure of the above assumption indicates that the hydrolysis of diethyl ether in supercritical water is actually autocatalyzed by acetic acid generated by the self-disproportionation. Indeed, the production rate of ethanol at the higher initial concentration is notably accelerated in the middle-time region as a result of the accumulation of acetic acid. At a low initial concentration (0.1 M), however, the concentration of acetic acid generated by the self-disproportionation reaction (eq 4) is negligibly low; it is lower than 10^{-3} M even at the longest reaction time (20 h).

The autocatalytic effect of acetic acid on the hydrolysis can be explicitly proved by adding acetic acid to the diethyl ether system (0.1 M). In this case, the concentration of additional acetic acid was set to 11 mM, which was made equal to the concentration at 20 h for the system with the higher initial concentration (0.5 M). Acetic acid does not decompose under these conditions, and the concentration is constant during the reaction. As shown in Figure 4, only ethanol is produced to a large extent by the addition of such a small amount of acetic acid: the yield is found to increase 6 times. The enhancement of the hydrolysis leads to the relative decrease of the yields of ethane, acetaldehyde, and methane (Figures 3b and 4). The autocatalytic effect of the acid generated by the self-disproportionation may be a pitfall to an erroneous conclusion of the dominance of the hydrolysis.

It is interesting to ask whether the catalytic effect of acetic acid is brought about by the neutral state or by the proton ionized from acetic acid. Previously, we have shown that the strong field exerted by the large partial charges of water in the

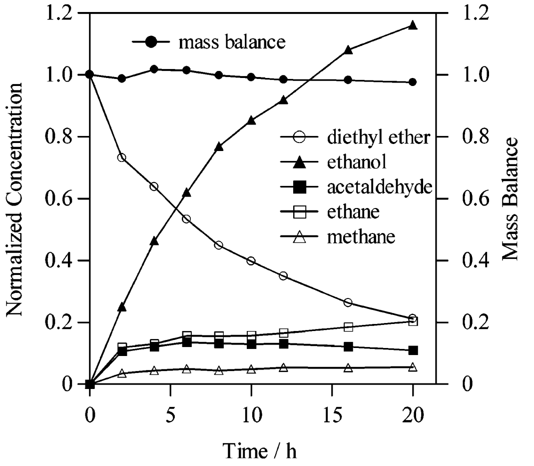

Figure 4. Time evolution of concentrations of diethyl ether and products treated with additional acetic acid of 11 mM at 400 °C and 0.5 g/cm^3. The initial concentration of diethyl ether is 0.1 M in supercritical conditions. The normalized concentration means the concentration of interest divided by the initial concentration of diethyl ether.

undissociated form can accelerate the dehydration reaction process in the transformation of 1,4-butanediol to tetrahydrofuran in hot water including the supercritical. Such a strong polarization effect required for the catalytic action is considered to be realized also by the neutral state of acetic acid. The dielectric constant of supercritical water is less than 10 at 400 °C and densities of 0.1−0.6 g/cm^3, so the ionization constants of acids are expected to be quite low.[25]

Path Weight for Ethanol Production. Here we reconfirm the weights of the hydrolysis (eq 3), self-disproportionation (eq 4), and cross-disproportionation (eq 5) reactions to the ethanol formation on the basis of the mass balance at the higher initial concentration (0.5 M). According to the reaction scheme in Figure 2, the amount of ethanol produced by the hydrolysis of diethyl ether $[\text{ethanol}]_{\text{hyd}}$ can be expressed in terms of the mass balance equation:

$$[\text{ethanol}]_{\text{hyd}} = 2([\text{diethyl ether}]_0 - [\text{diethyl ether}] - [\text{ethane}]) \quad (9)$$

where $[\text{diethyl ether}]_0$ denotes the initial concentration of diethyl ether. The ethanol concentration observed in Figure 3c is larger by ∼10% than $[\text{ethanol}]_{\text{hyd}}$ estimated by eq 9 during the course of the reaction time. This indicates that the relative contributions of the hydrolysis and the disproportionations to the ethanol formation are approximately 90% and 10%, respectively.

On the other hand, the amount of ethanol generated by the self- and cross-disproportionations $[\text{ethanol}]_{\text{disp}}$ is given by the mass balance equation:

$$[\text{ethanol}]_{\text{disp}} = [\text{ethanol}] - [\text{ethanol}]_{\text{hyd}} \quad (10)$$

In Figure 5, the amount of ethanol generated by the disproportionations is plotted against time in comparison with that of acetic acid. The concentration of ethanol calculated by eq 10 is 0.06 M at 20 h.[26] The concentration of ethanol is 4 times as large as that of acetic acid. The large difference in the concentration between ethanol and acetic acid shows the greater contribution of the cross-disproportionation than that of the self-disproportionation.[12] In other words, formic acid (hydroxyl aldehyde) is a stronger reducer than acetaldehyde. The weights

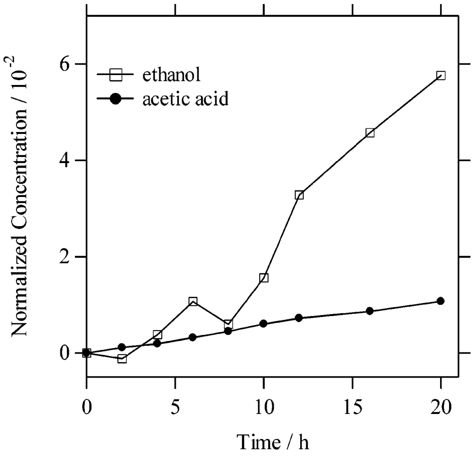

Figure 5. Time evolutions of concentration of ethanol defined by eq 10 ($[\text{ethanol}]_{\text{disp}}$) and acetic acid at 400 °C and 0.5 g/cm^3. The initial concentration of diethyl ether is 0.5 M in supercritical conditions. The normalized concentration means the concentration of interest divided by the initial concentration of diethyl ether. The plot for the ethanol calculated is rather scattered because it is a small difference in eq 10.

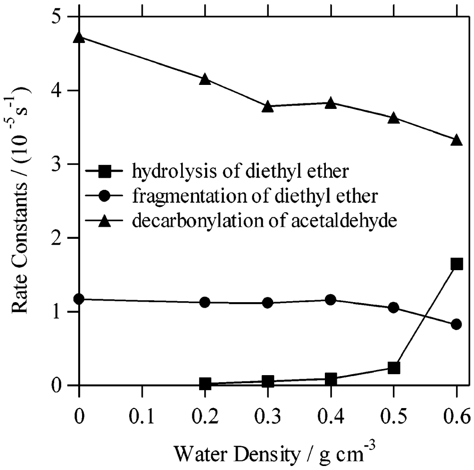

Figure 6. Observed rate constants for proton-transferred fragmentation and hydrolysis of diethyl ether and decarbonylation of the fragmentation intermediate, acetaldehyde, at 400 °C against the density of water.

of the ethanol formation pathways are thus in the decreasing order

$$\text{hydrolysis} > \text{cross-disproportionation} > \text{self-disproportionation}$$

Water Density Effect. The hydrolysis 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) and decarbonylation of acetaldehyde (eq 2). We can determine the rate constants for the noncatalyzed hydrolysis, proton-transferred fragmentation, and decarbonylation as a function of water density when the initial concentration is low enough. This is because the bimolecular self- and cross-disproportionations (eqs 4 and 5) are markedly suppressed and because the catalytic effect of acetic acid on the hydrolysis can be neglected (Figure 3b,c).

The first-order rate constant for the hydrolysis increases steeply with increasing water density: the value is 2.5×10^{-7} s^{-1} at 0.2 g/cm^3 and 1.7×10^{-5} s^{-1} at 0.6 g/cm^3 (see Figure 6). A 2-order-of-magnitude increase in the rate constant is caused by the density increase of water by a factor of 3. The increasing tendency is not linear against the water density (concentration). This indicates that hot water plays a key role not only as the reactant but also as the solvent in driving the hydrolysis; hot water dipoles with a more naked and less screened charge fluctuation[27−29] can stabilize an ionic or polar transition state through the hydration effect.[7] In contrast, the rates of the proton-transferred fragmentation of ether and the decarbonylation of aldehyde are decreased by the increase of the water density. The rate constant of the proton-transferred fragmentation is 1.1×10^{-5} s^{-1} at 0.2 g/cm^3 and 8.2×10^{-6} s^{-1} at 0.6 g/cm^3. As seen in Figure 6, the rate constants for the competing fragmentation and hydrolysis cross at a medium density between 0.5 and 0.6 g/cm^3; no singularity is observed in the region of the critical density of water (0.32 g/cm^3), as previously noted for other supercritical water reactions.[7,14,30] In consequence, the weight of the hydrolysis becomes larger than that of the proton-transferred fragmentation at 0.6 g/cm^3, whereas the latter is much more important than the former below 0.5 g/cm^3.

Subcritical Water Reaction. In the supercritical water reaction of diethyl ether at 400 °C, the proton-transferred fragmentation competes against the hydrolysis. In contrast, in subcritical water at 300 °C where the water density is 0.71 g/cm^3, only the hydrolysis proceeds. The proton-transferred fragmentation is dramatically suppressed to disappear at such a high density of hot water and a low temperature. The rate constant of the hydrolysis is found to be 5.8×10^{-7} s^{-1}. This is comparable to the value for the supercritical reaction at 400 °C and 0.3 g/cm^3. The acceleration by the 230% increase in the water density (from 0.3 to 0.7 g/cm^3) is almost compensated by the deceleration due to the 20% drop in the temperature (from 673 to 573 K). The response coefficient of the rate to the temperature is much larger than that to the density, while both effects are nonlinear.

When the temperature is elevated to 350 °C and the water density is lowered to 0.57 g/cm^3 along the water saturation curve, both the hydrolysis and the proton-transferred fragmentation proceed at almost the same rate: the former and latter rate constants are 1.8×10^{-6} and 1.6×10^{-6} s^{-1}, respectively. It is to be noted that the proton-transferred fragmentation begins to be observable at such a medium density of hot water and a high temperature. The dominance of the hydrolysis is a valid picture at temperatures below 300 °C. We saw, however, that the validity is not simply transferred when the temperature is further raised. The dominant reaction pathway varies with the density and temperature, and can be identified only through a reaction study keeping the mass balance, as performed here.

IV. Conclusions

We have found that diethyl ether in supercritical water at 400 °C undergoes competitively proton-transferred fragmentation and hydrolysis as primary steps. The former path generates acetaldehyde and ethane and is dominant over the wide water density range up to 0.5 g/cm^3. The acetaldehyde is further subjected to such reactions as decarbonylation and noncatalytic self- and cross-disproportionations, which generate ethanol. Contrary to the conventional idea of the single hydrolysis path, ethanol is formed through three types of reactions. These reaction pathways are common to open-chain ethers, such as dimethyl ether, dipropyl ether, and phenetole. Diphenyl ether is an exception to this rule, because it cannot undergo the proton-transferred fragmentation due to the absence of hydrogens on the ether-bonding carbon.

For the reaction mechanism of the proton-transferred fragmentation, not homolytic but heterolytic intramolecular proton transfer from the one methylene group to the other surrounding the ether oxygen is concluded here. This is considered to proceed through a cyclic transition state formed by the C−O−C−H group. The reaction is decelerated with increasing solvent water density; the rate constant decreases from 1.2×10^{-5} s^{-1} at neat condition to 8.2×10^{-6} s^{-1} at 0.6 g/cm^3. This is caused by the suppression of the low-frequency concerted proton transfer by solvating water molecules. In a similar way, the decarbonylation of acetaldehyde into methane and carbon monoxide induced by the proton transfer slows down with increasing water density.

The hydrolysis is accelerated steeply with an increase in the supercritical water density in contrast to the proton-transferred fragmentation: the rate constant increases from 2.5×10^{-7} s^{-1} at 0.2 g/cm^3 to 1.7×10^{-5} s^{-1} at 0.6 g/cm^3. The increasing tendency is not linear against the water density (concentration). This indicates clearly that hot water plays a key role in the hydrolysis not only as the reactant but also as the solvent that stabilizes polar transition states with the large partial charges exerting a strong field. The hydrolysis is autocatalyzed by acetic acid generated by the self-disproportionation. The catalytic action can be realized by the neutral state of acetic acid. This catalytic mechanism is in sharp contrast to the conventional notion that the hydrolysis is catalyzed only by the ionized proton.

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(20) The following are reasons why we selected here diethyl ether rather than the prototype, dimethyl ether. First, the reaction pathways of acetaldehyde are well studied in the previous paper.[12] Second, dimethyl ether generates formaldehyde. There are more reaction pathways for formaldehyde because its disproportionation product, formic acid, is decomposable in two pathways.[11,12,15] Thus, the supercritical water reaction of dimethyl ether is most complicated in those of ethers.

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(23) Carbon dioxide is the only compound that is not addressed quantitatively in supercritical water reactions. To determine the carbon dioxide concentration precisely, it is necessary to use a ^{13}C-enriched sample, rather than a natural-abundance one, as shown in our previous work.[12] As clearly shown here, the features of reactions targeted here can be elucidated through the analysis of products with hydrogens.

(24) The reactions of dimethyl ether with and without water are much slower than those of diethyl ether. Actually, we have found that the consumption ratio of diethyl ether is ~0.6 at 400 °C and 20 h of the neat reaction, whereas that of dimethyl ether is ~0.3 under the same reaction condition.

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