Noncatalytic Cannizzaro-type Reaction of Acetaldehyde in Supercritical Water

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(Received January 6, 2003; CL-030001)

In supercritical water at 400 °C and 0.5 g/cm^3 (37 MPa), acetaldehyde was found to be transformed without catalysts into ethanol and acetic acid through a Cannizzaro-type disproportionation reaction. No aldol-type condensation products were detected, and the disproportionation competed with the decomposition into methane. Ethanol was generated in excess to acetic acid, and carbon dioxide appeared as a product only in the presence of supercritical water. This reaction behavior is explained by considering that carbon monoxide is provided by the acetaldehyde decomposition and leads to the formation of formic acid as a reducing intermediate for acetaldehyde.

Hot water including supercritical attracts much attention as a novel solvent for chemical processes and as a green and earth-friendly alternative to harmful organic solvents. Water in hydrothermal conditions mixes well with organic compounds, and often induces noncatalytic chemical reactions that proceed only in the presence of acidic or basic catalysts at ambient conditions.[1–7] In a previous paper, we showed a simple chemical reaction that the undissociated form of solvent water involved an effective acid character under hydrothermal conditions.[8] To understand and control new and diverse types of hydrothermal reactions, a systematic investigation about the behaviors of functional groups is necessary. Aldehydes are important in laboratorial and industrial processes as solvent and synthetic starting materials, and are abundant in chemical products. In a series of papers, we focus on the noncatalytic reaction behavior of aldehydes in hot water including supercritical.

At ambient conditions, it is well-known that aldehydes without α-hydrogen exhibit a disproportionation reaction in the presence of a large amount of base catalyst like OH^-.[9] In this reaction, one molecule of aldehyde activated by OH^- reduces another to primary alcohol and the former is oxidized to carboxylic acid; the yields of the alcohol and acid are equal and cannot exceed 50%. In contrast, Tsujino et al. found that a Cannizzaro-type disproportionation of formaldehyde, which does not have an α-hydrogen, proceeds in hydrothermal conditions without any base catalyst.[6] In this communication, we report a reaction of acetaldehyde in supercritical water. At ambient conditions, an aldehyde with α-hydrogen is not accompanied by the Cannizzaro reaction because the aldol reaction is dominant in the presence of base catalyst.[9] The purpose of this work is to clarify whether the dominant noncatalytic reaction of acetaldehyde having α-hydrogen is disproportionation or aldol condensation, or other reactions in supercritical water.

Acetaldehyde was used as received from Nacalai. Water was distilled 3 times after ion-exchange. The solution of acetaldehyde in H_2O at 0.5 M (M = mol/dm^3) filled a quartz tube of 1.5 mm i.d. The sample was sealed after the air in the reactor was replaced by argon. It was then put into an electric furnace kept at 400 °C; the temperature was controlled within ±1 °C. In the sample vessel, the reaction system was homogeneous in supercritical water whose density was adjusted to 0.5 g/cm^3 by controlling the ratio of the sample volume to the vessel volume at room temperature. At the reaction condition, the initial concentration of acetaldehyde corresponds to 0.25 M. After 4 h of reaction the sample was removed from the furnace quickly and quenched in a cold water bath; it took less than 30 s for the sample to cool down. At this stage, the liquid and gas phases coexist in the sample vessel. The liquid and gas phases were separately subjected to ^{1}H and ^{13}C NMR measurements at room temperature (JEOL ECA-400); a solution of 1,3,5-trioxane in D_2O was sealed in a capillary and used as an external reference. The mass balance was confirmed to be maintained from the total peak areas of both the liquid- and gas-phase spectra. For comparison, the neat pyrolysis was also examined at 400 °C. In this case, no solvent was added and the density of acetaldehyde was set to 0.25 M at the initial reaction condition.

Figure 1 shows the proton spectra in the liquid phase before and after the reaction. Before the reaction, both acetaldehyde and its hydrated form 1,1-ethanediol were detected.[9] After the reaction, three new peaks emerged and those of aldehyde and diol disappeared; one peak at 2.0 ppm represents acetic acid, and the others ethanol. This reaction corresponds to the disproportionation of acetaldehyde. According to the classical Cannizzaro reaction, the disproportionation reaction proceeds in the presence of a large amount of base catalyst.[9] In supercritical water, on the other hand, the disproportionation of acetaldehyde is seen to take place without catalysts. No products of an aldol-type condensation reaction were observed. Thus, a Cannizzaro-type reaction, rather than an aldol-type, is induced under our experimental condition. This observation is in marked contrast to the well-known Cannizzaro disproportionation at ambient conditions

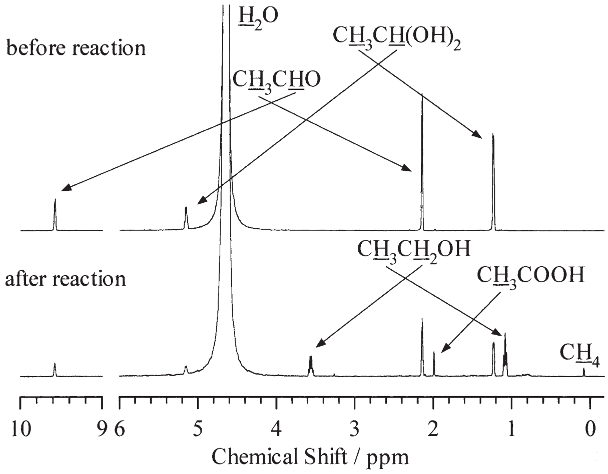

Figure 1. The liquid-phase ^{1}H-NMR spectra of acetaldehyde in H_2O. The reaction was performed for 4 h at 400 °C and a water density of 0.5 g/cm^3.

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which generally needs a large amount of base catalyst and is overwhelmed by the aldol condensation for aldehyde with α-hydrogen. The conversion of acetaldehyde after 4 h of the reaction was 78%. The peak area of methyl proton of ethanol is ~2.5 times as large as that of acetic acid as shown in Figure 1, although the acid/alcohol ratio by the classical Cannizzaro reaction is 1:1. The excess production of ethanol is discussed below.

In Figures 2(a) and (b), are shown the proton and carbon spectra for the gas phase of the sample system, respectively, after the reaction. Figure 2(c) shows the carbon spectrum for the neat pyrolysis of acetaldehyde at 400 °C. When no solvent water is added, methane and CO were detected. It was substantiated, furthermore, by the carbon NMR measurement without proton irradiation that the yields of the two products are equal. This means that methane and CO are produced through the thermal decarbonylation of acetaldehyde.[9] In supercritical water, in contrast, methane and CO_2 were detected as shown in Figures 2(a) and (b) and CO and H_2 were not. Methane was also seen in the liquid-phase spectrum in Figure 1. In a separate experiment, we confirmed that acetic acid was stable under the present experimental condition. In other words, methane and carbon dioxide are not the products of decarboxylation of acetic acid. The methane production thus shows that decarbonylation of acetaldehyde proceeds in the present supercritical condition. It is then expected that carbon monoxide generated by decarbonylation is further converted through a reaction with water to such a hydration product as formic acid.[10] According to Tsujino et al., formic acid reduces formaldehyde to methanol and the former is oxidized to carbon dioxide and H_2O.[6] The production of carbon dioxide and the absence of carbon monoxide can thus explain that formic acid is a reaction intermediate and reduces acetaldehyde to ethanol. Moreover, H_2 was not detected. This shows that CO_2 is not produced through the water gas shift reaction of CO. In consequence, Figure 3 is presumed to be the noncatalytic reaction pathway of acetaldehyde in supercritical water. This scheme is also consistent with the excess ethanol formation in Figure 1. The disproportionation reaction competes with the decarbonylation, and ethanol is generated through two pathways.

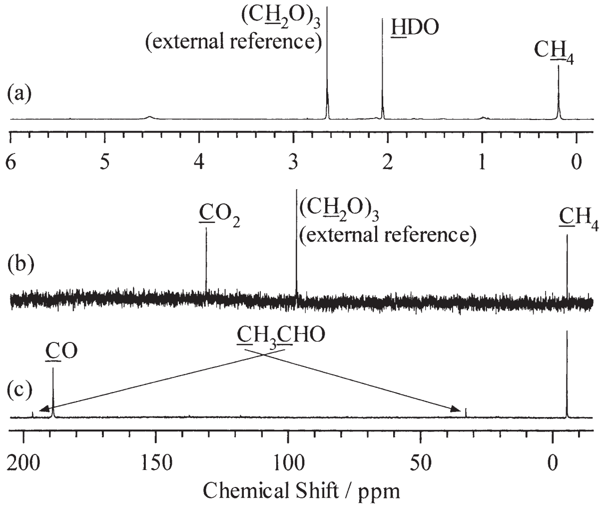

Figure 2. The gas-phase spectra at a reaction time of 4 h for acetaldehyde. (a) and (b) represent the ^1H and ^{13}C spectra, respectively, for the reaction in water at 400 °C and 0.5 g/cm^3, and (c) stands for the ^{13}C spectrum for the pyrolysis at 400 °C without solvent. The external reference employed is 1,3,5-trioxane in D_2O, and the magnetic susceptibility correction is made.

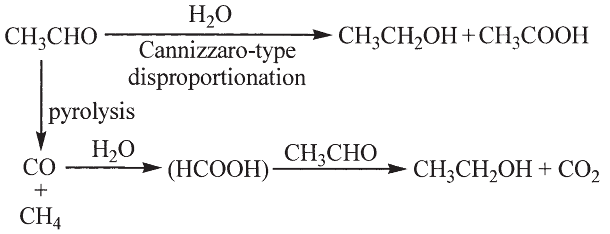

Figure 3. Noncatalytic reaction pathway of acetaldehyde in supercritical water.

In this communication, we demonstrated that acetaldehyde, which is a representative aldehyde with α-hydrogen, exhibits a Cannizzaro-type disproportionation in supercritical water. Furthermore, we observed that the disproportionation reaction proceeds in supercritical water for the aldehydes with longer hydrocarbon chain, such as propion-, butyr-, and valeraldehyde. This shows that the noncatalytic Cannizzaro-type disproportionation is common to aldehyde in hydrothermal conditions. In subcritical water, on the other hand, we found that acetaldehyde exhibits only an aldol-type reaction at temperature below 250 °C. The crossover temperature at which the Cannizzaro-type reaction becomes more important than the aldol-type was seen to be about 350 °C. In subsequent papers, using in situ NMR measurements, we present detailed kinetic analysis of Cannizzaro, decarbonylation, and aldol reaction of acetaldehyde and other aldehydes in hot water.

This work is supported by the Research Grant-in-Aid from the Ministry of Education, Culture, Sports, Science, and Technology (No. 10304047, 13440179, and 13640509) and by the CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST).

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