Noncatalytic Cannizzaro-type Reaction of Formaldehyde in Hot Water

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(Received December 7, 1998; CL-980908)

In hot water heated up to 250 °C and 4 MPa, methanol and formic acid are produced from the Cannizzaro-type reaction of formaldehyde without a catalyst, although this disproportionation reaction is well-known to occur in the presence of a large amount of base catalysts in ambient conditions. Formic acid further undergoes the hydride transfer reaction with formaldehyde, and the final yield of methanol exceeds 50%.

Recently, water in the high-temperature and high-pressure (HTHP) conditions receives much attention as a novel and clean medium for chemical reactions of environmental and industrial importance.[1-7] In the HTHP conditions, organic compounds come to dissolve well into water; HTHP water serves as a good solvent for a variety of organic chemical reactions.[8,9] Thus, HTHP water can be a safe alternative to hazardous organic solvents, so far extensively used.[10-12] In order to understand and control a wide variety of organic reactions in HTHP water, first of all, we need to establish physical organic chemistry of aqueous solutions at high temperatures and high pressures.

Formaldehyde is one of the most important reaction intermediates in C_1 chemistry. For example, it is expected to be an intermediate in the hydrothermal recycling of such a hazardous organic solvent as dichloromethane into the useful compounds, methanol and formic acid.[12] Thus, it is natural to focus on the reaction of formaldehyde in HTHP water. In addition, formaldehyde is a strongly reduced form of CO_2 and its reaction is of interest from the viewpoint of CO_2 cycle.

In order to generate formaldehyde in HTHP water, 1.5 M (mol/dm^3) of *s*-trioxane is dissolved into heavy water at room temperature. The sample solution was sealed into a quartz capillary with inner diameter of 2.5 mm. The sample tube was placed in the furnace and the temperature was raised from room temperature to 250 °C at the rate of 5 °C/min in order to keep the homogeneity of the system; the temperature was homogeneous whitin ±2°C. Since the high temperature is achieved in a sealed capillary, our reaction system is on the saturation curve; vapor pressure is about 4 MPa at 250 °C. The time 0 of the reaction was then set to be the time at which 250 °C was reached. After a reaction finished, the capillary was removed from the furnace quickly and cooled down to room temperature. The solution was subjected to NMR measurements (JEOL, EX-270 wide-bore) and the gas components were analyzed with gas chromatography (Shimadzu GC-14B) equipped with a thermal conductivity detector.

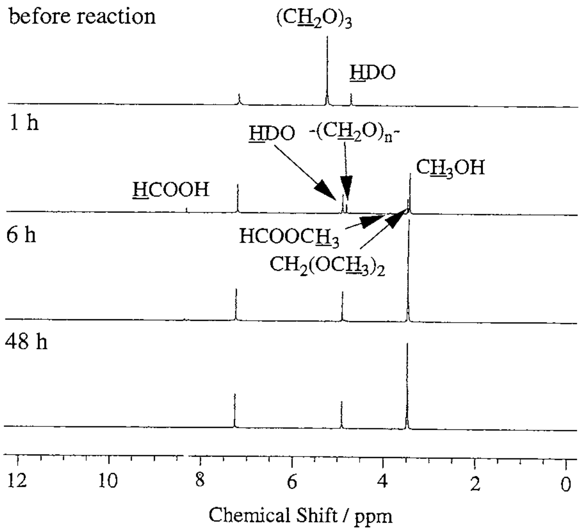

Figure 1. The ^{1}H-NMR spectrum of *s*-trioxane in D_2O reacted at 250 °C as a function of time. External reference; C_6H_6, 7.27 ppm.

Figure 1 shows how the ^{1}H-NMR spectrum of the solution reacted at 250 °C varies with time. At the time of 1 h, two peaks emerge with disappearance of the *s*-trioxane peak; one is methanol and the other formic acid. In HTHP water, formaldehyde is formed from *s*-trioxane by ring-opening. While it is reported that without water, the pyrolytic opening of the *s*-trioxane ring proceeds at temperatures higher than 272 °C,[13] the interaction of the water hydrogen and the ether oxygen of *s*-trioxane is considered to promote the ring opening. After the formation of formaldehyde, the disproportionation reaction of formaldehyde occurs without catalysts in the present HTHP condition. According to the classical Cannizzaro reaction, the disproportionation reaction proceeds under the presence of a large amount of catalysts.[14] Although the autoprotolysis constant of water at 250 °C and 4 MPa is larger than that at ambient conditions,[15] this does not cause the occurrence of disproportionation reaction since the OH^- concentration is still much smaller than that required for the classical Cannizzaro reaction. In the HTHP state studied here, therefore, the fact that the reaction occurs without catalysts suggests the possibility that water takes part in the HTHP Cannizzaro-type reaction. In addition, oligomers of formladehyde and dimethoxymethane persist, as seen in the spectra of formaline studied elsewhere. This shows that formaldehyde existed during the reaction. Formaldehyde which did not participate in disproportionation reaction oligomerized when sample was cooled down to room temperature. As the reaction time passed, the methanol peak grew with disappearance of the formic acid and the oligomers. Disappearance of the formic acid peak is discussed below. As a side reaction, methyl formate was produced.

The yield of a compound is defined as the ratio of the concentration of the compound to the total concentration of the starting material, formaldehyde at the time 0 of the reaction, where *s*-trioxane is counted as a trimerized state of formaldehyde. The final yields of the organic compounds involved in the reaction are shown in Table 1.

It is of interest to note in Table 1 that the final yield of methanol is larger than that of formic acid in the disproportionation reaction in HTHP water, whereas the ratio

Table 1. Yields of methanol and formic acid produced from formaldehyde reacted in water at 250 °C and 4 MPa

Reaction time (h)	Methanol[a]	Formic acid
0	0	0
1	0.35	0.10
6	0.59	0.03
48	0.67	0.00

The errors in the above values are within ±0.05. [a] Dimethyl ether is counted as a dimeric form of methanol.

between methanol and formic acid produced from formaldehyde will be 1:1 if the disproportionation reaction is the classical Cannizzaro reaction. In addition, although the yields of alcohol and acid do not exceed 50% in the classical Cannizzaro reaction, the yield of methanol is found to reach about 70% in our reaction. In Figure 2, we show ^{13}C spectra for the reaction system. The spectrum at each time in Figure 2 represents the same system as the corresponding spectrum in Figure 1. Figure 2 provides a possible mechanism for excessive methanol formation. Notably, CO_2 is detected in Figure 2. In fact, the production of CO_2 in the gas phase is also confirmed from gas chromatography. This indicates that the oxidized aldehyde, formic acid, participates in the methanol formation in HTHP water. Thus, the less reactive aldehyde, formic acid is considered to undergo a hydride transfer reaction with formaldehyde expressed as

$$HCHO + HCOOH + H_2O \xrightarrow[250\ ^\circ C\ water]{no\ catalyst} CH_3OH + CO_2 + H_2O$$

This reaction causes further formation of methanol. In addition, CO was not detected in the gas phase of our reaction, in agreement with quantum-chemical calculations.[16] The apparent disagreement with the recent suggestion that formic acid converts into CO_2 and H_2[17-19] will be discussed in a subsequent paper.[20] Thus, the hydride transfer reaction shown above is considered to occur when both formic acid and formaldehyde exist in HTHP water. With the reaction time, methanol peak and CO_2 peak in Figure 2 grew, accompanied with the decrease of the peak intensities of the oligomers and formic acid. This mechanism also accounts for the disappearance of the formic acid peak in Figure 1. Finally, it is seen from Figure 2 that in HTHP water, methanol dehydrates to form dimethyl ether. In subsequent papers, using *in-situ* NMR measurements, we present detailed mechanisms of hydrothermal reactions of formaldehyde and other aldehydes and characterize not only products but also reaction intermediates.

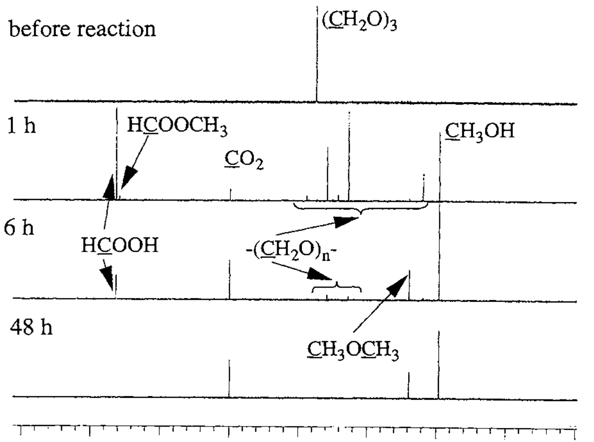

Figure 2. The ^{13}C-NMR spectrum of *s*-trioxane in D_2O reacted at 250 °C as a function of time. Internal reference; CH_3OH, 49.0 ppm.

This work has been supported by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST) and from Kansai Research Foundation for Technology Promotion. We are also grateful to the Research Grant-in-Aid from the Ministry of Education, Science and Culture (No.10304047).

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