

Noncatalytic Cannizzaro-type Reaction of Formaldehyde in Hot Water

Yasuo Tsujino, Chihiro Wakai, Nobuyuki Matubayasi, and Masaru Nakahara

In water at 250 °C and 4 MPa, methanol and formic acid are produced from the disproportionation reaction of formaldehyde without a catalyst, although at mild conditions, this reaction usually occurs in the presence of a large amount of base catalyst. Formic acid further undergoes the hydride transfer reaction with formaldehyde, and the final yield of methanol exceeds 50%.

Keywords : Hydrothermal reaction / NMR / C₁ chemistry / Formaldehyde / Cannizzaro reaction

Water in the high-temperature and high-pressure (HTHP) conditions receives much attention recently as a novel and clean medium for chemical reactions of environmental and industrial importance. In order to understand and control a wide variety of organic reactions in HTHP water, it is important to establish physical organic chemistry of aqueous solutions at high temperatures and high pressures.

Formaldehyde is one of the most important reaction intermediates in C₁ chemistry. For example, it is expected to be an intermediate of decomposition of dichloromethane in HTHP water, and dichloromethane is transformed through formaldehyde into methanol and formic acid. Thus, it is natural to focus on the reaction

of formaldehyde in HTHP water. In addition, formaldehyde is a strongly reduced form of CO₂ and its reaction is of interest from the viewpoint of CO₂ cycle.

In order to form formaldehyde in HTHP water, 1.5 M (mol/dm³) 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. 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 the room temperature. The solution was

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Scope of research
Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biological interests are systematically studied by NMR under extreme conditions. High pressures and high temperatures are employed to shed light on microscopic controlling factors for the structure and dynamics of solutions. Vibrational spectroscopic studies are carried out to elucidate structure and orientations of organic and water molecules in ultra-thin films. Crystallization of protein monolayers, advanced dispersion systems at liquid-liquid interfaces, and biomembranes are also investigated.



Prof
NAKAHARA, Masaru
(D Sc)



Assoc Prof
UMEMURA, Junzo
(D Sc)



Instr
MATSUMOTO, Mutsuo
(D Sc)



Instr
MATUBAYASI, Nobuyuki
(Ph D)



Assoc Instr
OKAMURA, Emiko
(D Pharm Sci)



Assoc Instr
WAKAI, Chihiro
(D Sc)

Research

Assistants(pt)

KIMURA,
Noriyuki (D Sc)

TANO,
Takanori (D Sc)

Students

BOSSEV,
Dobrin (DC)

KONISHI,
Hirofumi (DC)

KIMURA,
Tomohiro (DC)

MCNAMEE,
Cathy (DC)

TOYA, Hiroshi (MC)

IMADA,
Tomokatsu (MC)

KAWAI,
Kunichika (MC)

TSUJINO,
Yasuo (MC)

KAKITSUBO,
Ryou (MC)

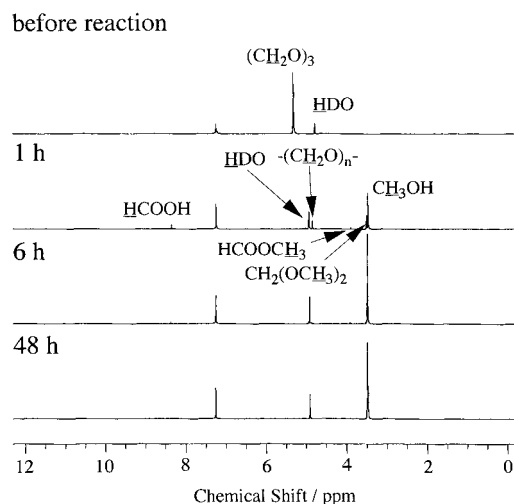
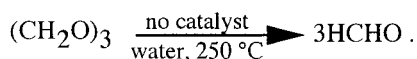


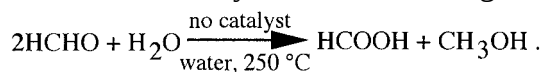
Figure 1. The ^1H -NMR spectra of *s*-troxane in D_2O reacted at $250\text{ }^\circ\text{C}$ as a function of time. (external reference; C_6H_6 , 7.27 ppm)

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 shows how the ^1H -NMR spectrum of the solution reacted at $250\text{ }^\circ\text{C}$ 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 as follows,



After the formation of formaldehyde, the disproportionation reaction of formaldehyde occurs without catalysts in the following,



According to the classical Cannizzaro reaction, the disproportionation reaction proceeds under the presence of a large amount of catalysts. Although the autoprotolysis constant of water at $250\text{ }^\circ\text{C}$ and 4 MPa is larger than that at ambient condition, 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. As the

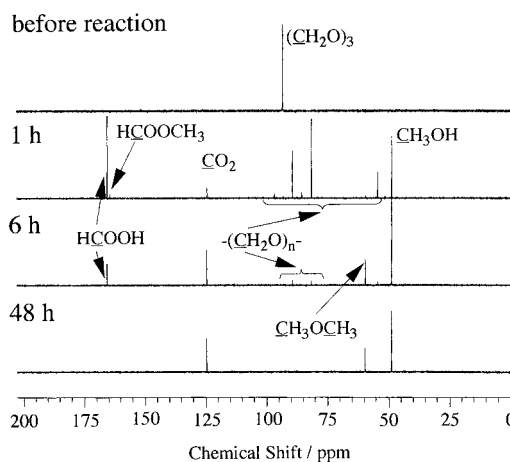
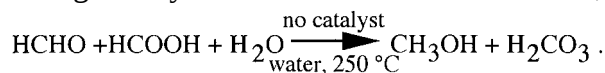


Figure 2. The ^{13}C -NMR spectra of *s*-troxane in D_2O reacted at $250\text{ }^\circ\text{C}$ as a function of time. (reference; CH_3OH , 49.0 ppm)

reaction time varied, the methanol peak grew with disappearance of formic acid and oligomers of formaldehyde.

It is of interest to note that the yield of methanol is found to reach about 70% in our reaction, exceeding the predicted value from the classical Cannizzaro-type reaction (50%). 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, formic acid is considered to undergo the hydride transfer and react as follows,



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. 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 oligomers and formic acid. This mechanism also accounts for the disappearance of the formic acid peak in Figure 1.