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**In-situ NMR Study of Hydrothermal Reactions of Hazardous Chlorinated Organic Compounds: CH$_2$Cl$_2$**

Chihiro Wakai, Masaru Nakahara, Yasuo Tsujino and Nobuyuki Matubayasi

Hydrothermal decomposition of a hazardous chlorinated organic compound, dichloromethane, has been investigated using in-situ NMR spectroscopy. It is found that the hydrolysis of dichloromethane yields methanediol as an intermediate. Methanediol is a hydrated form of formaldehyde and easily transformed into methanol and formic acid under basic conditions. In the temperature range of 70-140 °C, the Cannizzaro-type reaction occurs: methanediol produces the reduced form, methanol and the oxidized form, formic acid. At higher temperatures between 200 and 250 °C, on the other hand, two methanediol molecules form glycolic acid which has a new C-C bond. The reaction rate constants and activation energies for the dechlorination and the Cannizzaro-type reactions have been obtained.

**Keywords**: Hydrothermal reaction / in-situ NMR spectroscopy / dichloromethane / dechlorination / Cannizzaro reaction

Recently we are alerted that many useful chlorinated organic compounds are biologically and environmentally hazardous. It is thus a main goal of environmental chemistry to establish a reaction scheme which provides nontoxic and recyclable organic compounds from chlorinated organic compounds by reducing the C-Cl bonds as shown in Fig. 1. To achieve this goal, high-temperature and high-pressure water is a desirable medium since it is clean and safe and able to dissolve organic compounds. In order to convert hazardous chlorinated compounds to recyclable compounds, the reduction process in supercritical water (SCWR) is more preferable than the oxidation process (SCWO), as shown in Fig. 1. By the SCWO method, organic compounds are oxidized completely and any useful compounds are not recovered. In contrast, the hydrothermal dechlorination enables one to recycle hazardous chlorinated compounds under milder conditions. In order to develop an optimal process for recycling hazardous chlorinated compounds, it is essential to understand the dechlorination mechanism. The purpose of this report is to show the power of in-situ NMR spectroscopy for gaining insights into the reaction mechanism. By this method, the formation and breakage of chemical bonds can be observed in real time and it is possible to simultaneously characterize not only products but also reaction intermediates. Here we focus on the in-situ NMR observation of the hydrothermal reactions of CH$_2$Cl$_2$.

CH$_2$Cl$_2$ supplied by Nacalai was used after the stabilizer and impurity were removed. NaOH of guaranteed reagent grade obtained from Nacalai was used without further purification. Water was purified using a Milli-Q Labo. filter system (Milli-Q Pore). Aqueous NaOH solution was prepared by weight; the concentration...
new product is glycolic acid (CH$_2$(OH)COOH), and the used as reference materials for the 1H and 13C chemical shifts measurements. The free induction decay signal was accumulated 8-16 times for 1H and 25000 times for 13C.

At higher temperatures (200 and 250 °C), we measured 1H and 13C spectra as functions of temperature and NaOH concentration; it took ~10 min to heat the system up to 250 °C. CH$_2$Cl$_2$ and CH$_2$OH were used as reference materials for the 1H and 13C chemical shift measurements. The free induction decay signal was accumulated 8-16 times for 1H and 25000 times for 13C.

The main reaction of methanediol in the temperature range of 70-140 °C is:

$$2\text{CH}_2\text{(OH)}_2 + \text{OH}^- \rightarrow \text{HCOO}^- + \text{CH}_3\text{OH} + 2\text{H}_2\text{O}.$$  

At higher temperatures (200 and 250 °C), on the other hand, we have found another reaction path of methanediol. From the chemical shifts of 1H and 13C, it is clear that the new product is glycolic acid (CH$_2$(OH)COOH), and the reaction path of the formation of glycolic acid is considered as follows:

$$2\text{CH}_2\text{(OH)}_2 \rightarrow \text{CH}_2\text{(OH)}\text{CHO} \rightarrow \text{CH}_2\text{(OH)}\text{COOH}.$$  

According to the time dependence of the concentrations of the reactant and products of the hydrothermal reaction of CH$_2$Cl$_2$ (0.8 M) in aqueous NaOH solution (1.6 M) at 140 °C.

It is depicted in Fig. 2 how the concentrations of the reactant and products vary with time at 140 °C: at 120 and 130 °C, the time dependences are very similar to that at 140 °C. As expected, the dechlorination at 140 °C is much faster than that at 80 °C. The plateau values for the concentrations of the products indicate that the Cannizzaro reaction is quickly finished. The stationary concentrations of methanol and formic acid produced are almost the same (~170 mM) at 120, 130, and 140 °C. Methanediol increases monotonously with time. When more than 300 min has passed, the concentration of methanol is larger than that of formic acid. This is caused by the cross Cannizzaro-type reaction between methanediol and formic acid, which produces methanol and carbon dioxide as clarified in the previous work on the hydrothermal decomposition of s-trioxane.

We also determined the rate constants as functions of the [OH$^-$] concentration at 80 °C according to the following reaction scheme:

$$\text{CH}_2\text{Cl}_2 + 2\text{OH}^- \rightarrow k_1 \rightarrow \text{CH}_2\text{(OH)}_2 + 2\text{Cl}^-,$$

$$2\text{CH}_2\text{(OH)}_2 + \text{OH}^- \rightarrow k_2 \rightarrow \text{HCOO}^- + \text{CH}_3\text{OH} + 2\text{H}_2\text{O}.$$  

In the low concentration range, the rate constant for the Cannizzaro reaction is almost independent of [OH$^-$]; $k_2 = 5.6 \times 10^{-3}$ and $6.2 \times 10^{-3}$ M$^{-2}$ s$^{-1}$ at 0.5 and 1.0 M, respectively. In 2.0 M solution, on the other hand, $k_2$ is $15 \times 10^{-3}$ M$^{-2}$ s$^{-1}$ and ~3 times larger than those in 0.5 and 1.0 M solutions. It has been reported that the rate constant is proportional not to [OH$^-$] but to [OH$^-$]$^2$ at high concentrations due to the existence of the second ionized state, CH$_2$(O)$^-$. of methanediol: the ability to make the hydride ion H$^-$ is much higher for CH$_2$(O)$^-$. than for CH$_2$(OH)$^-$.  

It is therefore concluded that the hydrothermal dechlorination of dichloromethane can be achieved efficiently at 250 °C in the presence of a base (NaOH). Such a high temperature is required to compensate for the solubility drop due to the base and to accelerate the rate of the transformation to useful compounds.