Carbon–Carbon Bond Formation in Glycolic Acid Generated Spontaneously from Dichloromethane in Hot Water

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Hydrothermal reaction of dichloromethane (CH_2Cl_2) at $1\,mol/dm^3$ leads to the formation of glycolic acid without metal catalysts at temperatures of 200–250 °C. The reaction consists of three steps. First CH_2Cl_2 is converted into methanediol through hydrolysis. The disproportionation of methanediol then produces methanol and formic acid. Finally, glycolic acid is formed from methanediol and formic acid catalyzed by the acid (HCl) generated by the dechlorination of CH_2Cl_2. The yield of glycolic acid exceeds 50% at 225 and 250 °C.

Water in hydrothermal conditions can serve as an alternative to widely used organic solvents. It is thus of interest to establish reaction mechanisms by which carbon–carbon, carbon–oxygen, and carbon–hydrogen bonds can be produced without any added catalysts.[1–7] In the present work, we report a new C–C bond formation from the popular organic solvent, CH_2Cl_2, leading to the generation of glycolic acid.

Glycolic acid is the first and simplest member of the series of hydroxy-carboxylic acids. It is contained in sugar beets, unripe grapes, and spent sulfite liquor from pulp processing[8] and is used widely as a precursor of medicine.[9] We show a new synthesis pathway of glycolic acid from CH_2Cl_2 without any additives or metal catalysts. The supercritical water decomposition of CH_2Cl_2 has been studied at very dilute solutions of 1 mM by several authors[4] and the main decomposition products were found to be methanol, water, and carbon dioxide. Here, we focus on rather concentrated solutions of CH_2Cl_2 to find a bimolecular carbon–carbon bond formation. Our key finding is the hydrothermal synthesis beyond the decomposition. A formation of a C2 compound from C1 compounds is achieved in hot water without any added catalysts.

CH_2Cl_2 was obtained from Nacalai and used after removing impurity and stabilizer species. ^{13}C-enriched CH_2Cl_2 (>99%) was also obtained from CEA. Water was purified to a specific conductivity of $5.6 \times 10^{-6}\,S\,m^{-1}$. We used a JEOL NMR spectrometer (JNM-ECA500W) equipped with a JASTEC superconductor magnet (11.7 T).

CH_2Cl_2 and water were sealed in a quartz NMR tube (2.2-mm i.d. and 3.0-mm o.d.) with volume filling factors of 90, 85, and 80% for the reaction temperatures of 200, 225, and 250 °C, respectively. To optimize the yield of glycolic acid, the gas phase volume must be made negligible at each temperature. The concentration of CH_2Cl_2 is 1 M ($M = mol/dm^3$) in ambient conditions; the concentrations at high temperatures are equal to the ambient concentration multiplied by the filling factors (0.90, 0.85, and 0.80 M). The sample tube was heated in a furnace for 10–370 min and quenched by air. After the reaction, the tube was put in a Pyrex NMR tube (5.0-mm o.d.). Not only the liquid phase but also the gas one was measured since gaseous
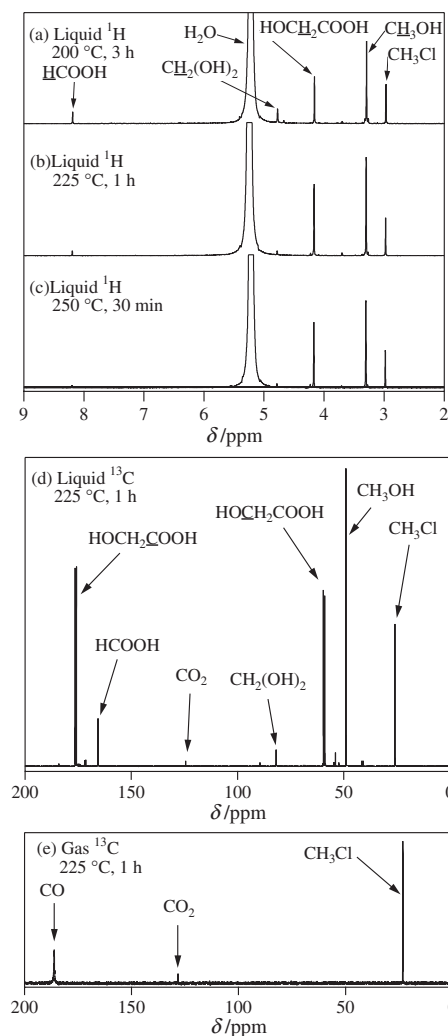

Figure 1. The liquid-phase ^1H (a)–(c) spectra and the liquid- and gas-phase ^{13}C (d)–(e) spectra; see the text for the conditions.

products were formed. The ^1H spectra for the liquid and gas phases are accumulated 8 times for the reaction systems from natural CH_2Cl_2. The ^{13}C spectra for the liquid and gas phases of aqueous solutions of ^{13}C-enriched CH_2Cl_2 are accumulated 300 and 3000 times, respectively, with gated ^1H decoupling. A delay time between radiofrequency pulses is long enough to relax the magnetization and to enable us to determine concentrations.

Figures 1a–c show the ^1H spectra of aqueous solutions of CH_2Cl_2 after the treatments (a) at 200 °C for 3 h, (b) at 225 °C for 1 h, and (c) at 250 °C for 30 min. These spectra were obtained under the conditions where the reactions were almost completed.
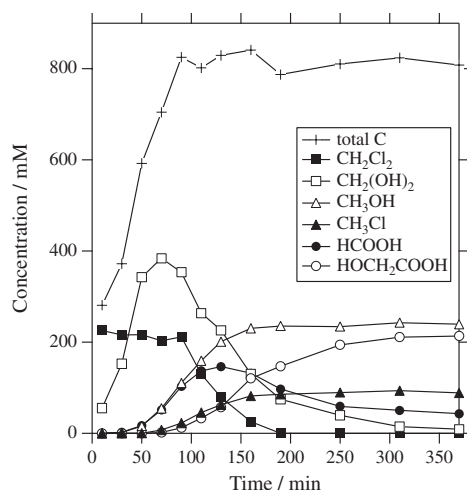
Figure 2. Time evolution of the concentrations of reactant and products treated at 200 °C and quenched to room temperature.

From the ^{1}H spectra, hydrogen-containing products were identified. The peak of reactant CH_2Cl_2 is observed at 5.4 ppm. The peak at 4.8 ppm is assigned to methanediol, $CH_2(OH)_2$, which is a hydrated form of formaldehyde. The two peaks at 3.3 and 8.2 ppm are assigned to methanol (CH_3OH) and formic acid (HCOOH), respectively. The peak at 3.0 ppm is assigned to methyl chloride (CH_3Cl). The signal at 4.2 ppm is assigned to the methylene proton of glycolic acid.

To confirm the peak assignments, we measured ^{13}C spectra for aqueous solution of ^{13}C-enriched CH_2Cl_2 after the treatment at 225 °C for 1 h. Glycolic acid is confirmed by the ^{13}C spectrum shown in Figure 1d; the doublet peaks at 59 and 176 ppm stand for the methylene and carboxylic carbons in glycolic acid, respectively. The peaks at 26, 49, and 166 ppm are assigned to CH_3Cl, CH_3OH, and HCOOH, respectively. Glycolic acid was also confirmed from the ^{1}H and ^{13}C chemical shifts of the authentic compound.

Figure 2 shows the time evolution of the reactant and products at 200 °C. It indicates that the hydrothermal reaction of CH_2Cl_2 is composed of the three steps. The concentration of CH_2Cl_2 is kept constant at the saturated concentration of 220 mM up to 90 min; the total amount of CH_2Cl_2 added corresponds to 1 M. The concentration of $CH_2(OH)_2$ increases with time up to 70 min through the dechlorination of CH_2Cl_2 as follows:[5,6]

$$CH_2Cl_2 + 2H_2O \rightarrow CH_2(OH)_2 + 2HCl. \qquad (1)$$
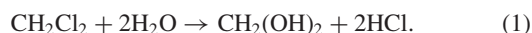
With increasing $CH_2(OH)_2$, the total carbon concentration also increases because the reactant is initially added in excess of the ambient solubility. Methanediol is active in hot water and reacts with itself even in the neutral or acidic condition through[2,3,5,6]

$$2CH_2(OH)_2 \rightarrow CH_3OH + HCOOH + H_2O. \qquad (2)$$
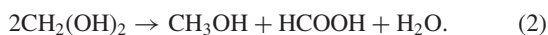
Methanol and formic acid were observed at 30 min and over. The concentrations of CH_3OH and HCOOH are almost the same up to 70 min according to the stoichiometry of Eq. 2. After that, CH_3Cl was observed. As seen in Figure 2, the time dependence of CH_3Cl is very similar to that of CH_3OH. CH_3OH becomes at equilibrium with CH_3Cl under acidic condition by

$$CH_3OH + HCl \rightleftharpoons CH_3Cl + H_2O. \qquad (3)$$

The concentrations of CH_3OH and CH_3Cl reach a plateau at 190 min. At 70 min, glycolic acid emerges. With increasing time, the concentration of glycolic acid increases as can be seen in Figure 2. It is thus considered that the glycolic acid formation occurs bimolecularly through

$$CH_2(OH)_2 + HCOOH \rightarrow HOCH_2COOH + H_2O. \qquad (4)$$

This reaction proceeds under acidic condition since dechlorination generates HCl and is enhanced by the concentration effect. The concentration of HCOOH gets smaller than that of CH_3OH and decreases with time over 130 min because of the formation of glycolic acid.

At the end of the reaction (CH_2Cl_2, 1 M), the yield of the main product glycolic acid exceeds 50% at 225 and 250 °C. The yields (carbon atom %) at 225 °C for 1 h are as follows: 53, 19, 16, 2, 3, and 1% for $HOCH_2COOH$, CH_3OH, CH_3Cl, HCOOH, CO_2, and CO, respectively.

In previous works,[2,3,6] we have shown that HCOOH decomposes to CO and CO_2 under hydrothermal conditions. To estimate the concentrations of these gaseous products, we measured ^{1}H and ^{13}C spectra for the gas phase of the aqueous solution of ^{13}C-enriched CH_2Cl_2 after the treatment at 225 °C for 1 h. For ^{1}H, the peak of CH_3Cl was observed; the concentration was only 10 mM. For the ^{13}C spectrum in Figure 1e, furthermore, the peaks at 186 and 128 ppm are assigned to CO and CO_2, respectively. Their concentrations are 32 and 1 mM, respectively. We consider that CO_2 is a product of the cross disproportionation reaction of formaldehyde (HCHO or $CH_2(OH)_2$) and formic acid. In a previous work,[2] we studied the reaction of 1,3,5-trioxane, which is a trimer of HCHO, under hydrothermal condition without catalysts. At 250 °C, HCHO formed from trioxane yields CH_3OH and HCOOH through the disproportionation (reaction scheme (2)). HCOOH further reacts with HCHO and yields CH_3OH and CO_2 through the cross disproportionation reaction of

$$HCHO + HCOOH \rightarrow CH_3OH + CO_2. \qquad (5)$$

With respect to the CO formation, we reported that the dehydration of HCOOH occurs under hydrothermal conditions.[2,3,6] In the reaction studied here, however, this reaction path is minor.

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