Methanol Formation from Dichloromethane under Hydrothermal Conditions

Yuki Yamasaki,# Heiji Enomoto, Nakamichi Yamasaki,† and Masaru Nakahara††
Resource Engineering, Faculty of Engineering, Tohoku University, Aoba-ku, Sendai 980-8579
†*Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, Akebonocho, Kochi 780-8520*
††*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011*

(Received October 9, 1998; CL-980777)

CH_2Cl_2 (1 mole) mixed with NaOH (2 moles) was treated under hydrothermal conditions at 250 °C. The chlorinated methane was completely hydrolyzed to form methanol and the formate by the Cannizzaro reaction. The reactant and products were analyzed by ^1H-, ^2H-, and ^{13}C-NMR. Solvent isotope effect on the transformation was also investigated. The hazardous and environmentally troublesome organic solvent was safely converted into the useful compounds.

Dichloromethane is one of the most widely used chlorinated organic solvents that can dissolve a variety of chemicals. Recently, it is wanted to make innovations for recycling thermally stable chlorinated compounds to protect our environment and ozone layer. Such hazardous compounds as dioxin and PCBs (polychlorinated biphenyls) have been target compounds.[1-3] The purpose of this work is to examine a possibility of applying hydrothermal reactions to the chlorinated compounds in order to transform the used materials into some useful forms without carbon dioxide emission.[4] Tester and coworkers studied the decomposition of CH_2Cl_2 by the supercritical water oxidation reaction[5] and the main products were carbon monoxide and dioxide. Here we attempt to find suitable conditions by which we can avoid the drastic and complete oxidation of CH_2Cl_2 for saving energy on the earth by recycling. In the temperature range 80-150 °C, Moelwyn-Hughes et al. first have studied the reaction kinetics of CH_2Cl_2 in aqueous alkaline solution at a low concentration due to the solubility limit.[6,7] CH_2Cl_2 becomes completely miscible with water when heated up. Concentrated solution at ~1 M (1 M = 1 mol dm^{-3}) is therefore studied here by means of ^1H-, ^2H-, and ^{13}C-NMR which is sensitive and rich in structural information.

A mixture of CH_2Cl_2 (7.8 mmol) and 8 cm^3 of 2 M NaOH (NaOD) in H_2O (D_2O; 99.9% D) were pored into an autoclave which was made of stainless steel and lined with Teflon (inner volume, 28 cm^3). The mole ratio of the alkali to chlorine atoms, [OH]/[Cl], was 1.02. In ambient conditions, the mixture has two liquid phases because of the low solubility (0.23 M) of CH_2Cl_2 in water. In a sealed glass tube, it was observed that the mixture becomes homogeneous at about 165 °C; the concentration was about 0.92 M. The autoclave was placed in an oven kept at 250 ± 1 °C. After a reaction time, the autoclave was cooled down to room temperature in 10-20 min in order to stop the hydrothermal reaction. The reaction products were analyzed by taking ^1H-, ^2H-, and ^{13}C-NMR spectra with a NMR spectrometer (JEOL, EX270) as a function of the reaction time; a sample tube of 10 mm in o.d. was used. The reaction time was regarded as being approximately equal to the time during which the hydrothermal solution was kept in the oven. For the peak assignment and the quantitative analysis of the proton intensities, benzene C_6H_6 contained in a capillary was used as an external reference. The concentration of the chloride ion was also measured by means of ionchromatography (Hitachi, Ion-chromatoanalyzer). The decomposition ratio of CH_2Cl_2 thus obtained agreed well with that due to the ^1H-NMR analysis.

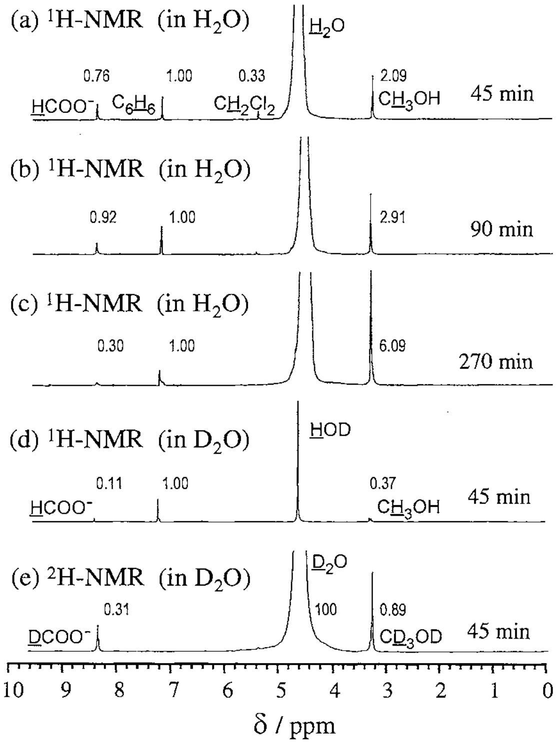

Figure 1. ^1H-NMR spectra for the solution hydrothermally treated with NaOH in H_2O at 250 ℃ for (a) 45 min, (b) 90 min, (c) 270 min, and (d) ^1H- and (e) ^2H-NMR spectrum with NaOD in D_2O (99.9% D) for 45 min. Chemical shifts (δ/ppm) were determined relative to C_6H_6 at 7.28 ppm. The number near the peak represents the relative intensity.

Figure 1 shows the chemical species determined by ^1H- and ^2H-NMR analysis of the solution after the hydro-thermal reaction of CH_2Cl_2 with NaOH or NaOD at 250 °C. The signal assigned to water is vertically expanded to such an extent that the product signals become discernible. Comparison of the time-dependent spectra (a) to (c) allows us to see that the gradual consumption of the reactant CH_2Cl_2 is accompanied by the production of methanol and the formate ion. The transformation of this hazardous compound to the safe and useful ones is completed in 270 min under the alkaline hydrothermal conditions. While the amount of methanol is gradually increased, the increase of the formate ion is suppressed by its gradual decomposition, as mentioned below.

How are the products dueterated during the transformation process in D_2O solvent? It can be seen from the ^1H- and ^2H- spectra in Figure 1. In an independent run, we have confirmed that CH_3OH and $HCOO^-$ cannot be transformed into CD_3OD and $DCOO^-$ in D_2O under the same hydrothermal conditions. Only a weak signal of the deuterated reactant CD_2Cl_2 is recognized at ~5.5 ppm. In contrast, the yield of CD_3OD at 270 min was calculated to be ~40%. These therefore indicate that the H/D exchange reaction takes place not for CH_2Cl_2 but *via* such a reactive intermediate as $CH_2(OD)_2$ or HCHO in D_2O.[6]

Since no other products except formic acid and methanol were detected in this study, this hydrothermal reaction is similar to the Cannizzaro reaction,[8,9] in which disproportionation of formaldehyde or its hydrate yield gives rise to $HCOO^-$ and CH_3OH. In this disproportionation reaction, formaldehyde or its hydrated form is reduced to CH_3OH and oxidized to $HCOO^-$ through bimolecular hydride transfer. In contrast to the usual Cannizzaro reaction, however, the alkali is not added in excess. The products of the usual Cannizzaro reaction in D_2O with alkali are known not to be subjected to the H/D exchange. In this study, the deuterated products was formed as shown in spectrum (e).

The yields (%) of $HCOO^-$ and CH_3OH are shown in Figure 2 as a function of reaction time. At early reaction time, both products are increased with time. There are no products during 0-15 min probably due to the dead time caused by inefficient heat transfer in the autoclave. The yields of $HCOO^-$ (○) and CH_3OH (●) are almost the same at the early stage. Before the yield of CH_3OH becomes saturated, that of $HCOO^-$ begins to decrease and then disappear due to decomposition. The yield of CH_3OH reaches ~50% just as predicted from the bimolecular hydride transfer reaction. After ~400 min, such sparingly water-soluble gases as CO (dominant), CO_2, and H_2 were detected by means of gas chromatography (Hewlett Packard GC5890). The total amount of the gases can be explained by considering the difference in the yield between methanol and the formate. The formate ion is considered to be decomposed to CO + H_2O. In words, the total mass balance for carbon is kept during the reaction. The solution hydrothermally treated for 270 min was also analyzed by ionchromatography in order to determine the Cl^- concentration. The dechlorination ratio is estimated to be more than 99%, which corresponds to the almost complete decomposition of CH_2Cl_2. In the ^{13}C-NMR analysis of the same reaction solution, the Cannizzaro reaction products were observed at 171 ppm (H<u>C</u>OO$^-$) and at 49.5 ppm (<u>C</u>H_3OH). The present NMR study of the hydrothermal reaction clearly shows that CH_2Cl_2 can be completely transformed or recycled to safe and useful compounds without hazardous ones.

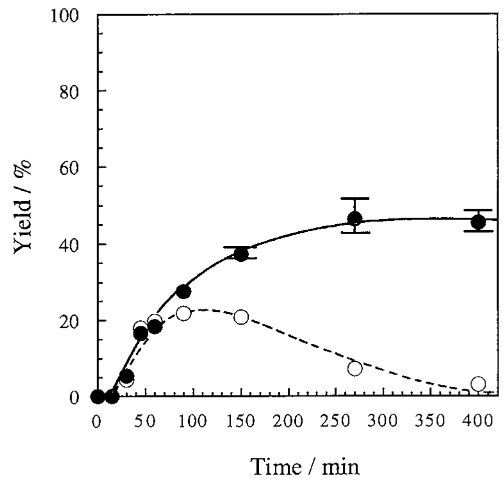

Figure 2. Time dependence of the yields of $HCOO^-$ (○) and CH_3OH (●), which were calculated from the molal ratio of the product to the reactant CH_2Cl_2.

References and Notes

Present address: Osaka Prefectural College of Technology, Depart. Indust. Chem., 26-12 Saiwai-cho, Neyagawa, Osaka 572-8572

1 N. Yamasaki, T. Yasui, and K. Matsuoka, *Environ. Sci. Technol.*, **14**, 550 (1980).

2 N. Yamasaki, K. Yanagisawa, and M. Fujita, *Organohalogen Compd.*, **19**(Dioxin '94), 343 (1994).

3 K. Hatakeda, Y. Ikushima, S. Ito, N. Saito, and O. Sato, *Chem. Lett.*, **1997**, 245.

4 M. Nakahara, T. Tennoh, C. Wakai, and H. Enomoto, *Chem. Lett.*, **1997**, 163.

5 A. Marrone, R. P. Lacance, J. L.DiNaro, B. D. Phenix, J. C. Meyer, J. W. Tester, W. A. Peters, and K. C. Swallow, "Innovations in supercritical fluids", American Chemical Society, Washington, D.C.(1995), Chap. 13, p.197.

6 I. Fells and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, **1958**, 1326.

7 I. Fells and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, **1959**, 398.

8 S. Cannizzaro, *Justus Liebigs Ann. Chem.*, **88**, 129(1853).

9 C. G. Swain, A. L. Powel, W. A. Sheppard, and C. R. Morgan, *J. Am. Chem. Soc.*, **101**, 3576(1979).