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NMR Study of Hydrothermal Reactions of Dichloromethane with and without Alkali

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Hydrothermal reactions of considerably concentrated (ca. 1 M; M = mol dm^{-3}) dichloromethane, CH_2Cl_2, were investigated with and without alkali in the temperature range of 150—300 °C by using batch reactors, such as an autoclave and sealed glass tubes. ^1H, ^2H, and ^{13}C NMR spectra were taken at room temperature as a function of reaction time to analyze the quenched reactants, intermediates, and products. In the presence of NaOH at 2 M, the complete dechlorination was achieved in 270 min at 250 °C and in 60 min at 300 °C. Such gaseous by-products as CO, CO_2, and H_2 were generated by the decomposition of the disproportionation product, $HCOO^-$. Without alkali, $CH_2(OH)_2$ could be detected by ^1H and ^{13}C NMR as an intermediate in the hydrolysis of CH_2Cl_2, before such Cannizzaro products as methanol and formate ion were formed. The mechanism of the hydrothermal reactions of CH_2Cl_2 is discussed in terms of the hydrolysis intermediate, $CH_2(OH)_2$.

Chlorinated organic compounds have been widely used for the past several decades because of their excellent physical and chemical properties as electric and thermal insulators and solvents. The large-scale consumption of chlorinated organics has brought about serious problems of wastes and environmental contaminants, such as halomethanes and dioxins; dioxins, endocrine disrupters, can be formed during their incineration at too-low temperatures.[1] Their toxicity due to the affinity for hydrophobic membranes in water is dependent on the molecular dipole moment, which is determined by the number and geometrical arrangement of the dipolar carbon–chlorine bonds within the hazardous molecule. To destroy halogenated organic wastes, various processes have been proposed, such as biodegradation,[2,3] metal-promoted dehalogenation,[4] electrolytic reduction,[5,6] and direct photolysis.[7] Here we attempt to make an innovation in recycling the hazardous chlorine-containing wastes by complete dechlorination in hot water containing the alkali, NaOH. Hydrothermal reactions of hazardous halogenated aliphatic wastes in the subcritical region of water need to be developed as a friendly-to-environment method for the recycle. A previous letter[8] on this subject has been extended here to discuss the mechanism of hydrothermal reactions of CH_2Cl_2 according to the detailed NMR information.

To decompose hazardous chlorinated organics, supercritical water oxidation (SCWO) reaction has been proposed in the presence of an oxidant like O_2.[9] Tester and coworkers[10—12] attempted a continuous SCWO treatment of CH_2Cl_2 at a very low concentration of 0.2—0.6 mM using a flow tube reactor at high temperatures up to 600 °C and 25 MPa, as shown in Table 1. The relative amount of the SCWO decomposition at 6 s reactor residence time was 40% at 451 °C, 70% at 550 °C, and 100% at 600 °C. At the highest temperature, the SCWO decomposition was reported to be almost complete, with the major products CO_2 and HCl. In contrast, we use a much more concentrated (ca. 1 M) mixture of CH_2Cl_2 and H_2O to completely dechlorinate and transform CH_2Cl_2 with NaOH *but without any oxidant* into nontoxic NaCl and useful CH_3OH and $HCOO^-$ under milder conditions in the temperature range of 150—300 °C.

As seen in Table 1, the present work is somewhat related to the first kinetic study on the chlorinated methanes by Fells and Moelwyn-Hughes.[13—15] They studied the rate of the hydrolysis of CH_2Cl_2 at a concentration lower than the solubility, 0.23 M at room temperature, in the temperature range of 80—150 °C, according to the assumption that the main path was the Cannizzaro reaction of formaldehyde. The conventional Cannizzaro reaction is given by

$$2-\mathrm{HC{=}O} \xrightarrow{\text{strong base}} -\mathrm{COO^-} + -\mathrm{CH_2OH}. \tag{1}$$

This disproportionation reaction can proceed in hot water even without alkali, as previously demonstrated.[16] Instead of the classical analytical method, here we have applied NMR spectroscopy in order to elucidate the general features of the subcritical hydrothermal reactions of CH_2Cl_2. A better

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Table 1. Experimental Conditions of Previous Studies on CH_2Cl_2 Decomposition

Method	Temp	Concn./mM		Time	Reactor
	°C	$[CH_2Cl_2]_0$	$[OH^-]_0$	min	
Hydrothermal[a)]	80—150	25	109	< 19800	Pyrex tube
SCWO[b,c)]	25—600	0.2—0.6	—	< 0.15	Hastelloy tube
Hydrothermal[d)]	250	920	2000	< 400	Teflon & glass tube

a) I. Fells and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, **1958**, 1326. b) P. A. Marrone, T. A. Arias, W. A. Peters, and J. W. Tester, *J. Phys. Chem. A*, **102**, 7013 (1998). c) D. Salvatierra, J. D. Taylor, P. A. Marrone, and J. W. Tester, *Ind. Eng. Chem. Res.*, **38**, 4169 (1999). d) Y. Yamasaki, H. Enomoto, N. Yamasaki, and M. Nakahara, *Chem. Lett.*, **1999**, 83.

understanding of the hydrothermal reaction mechanism is required for the development of green chemistry and for its successful application to environmental problems. We have carried out NMR analyses of the reactants, intermediates, and products with and without alkali. NMR spectroscopy is very sensitive and rich in structural information, as shown in the previous investigations of sub- and supercritical hydrothermal reactions of rubber[17] and *s*-trioxane (cyclic trimer of formaldehyde),[16] and it is a powerful means for the mechanistic study. It allows us to directly monitor how the C–Cl bonds are transformed into C–H or C–OH in the hydrothermal reactions of chlorinated organic compounds. In particular, the total mass balance for the reaction can be checked from the quantitative analysis of proton signals.

Experimental

CH_2Cl_2 of reagent grade was obtained from Aldrich. It was shaken with concentrated sulfuric acid to extract water-soluble impurities and was then dried with molecular sieves 5A (Wako) for more than 1 day. Although CH_2Cl_2 is not completely miscible in water at ambient conditions, it becomes soluble at high temperatures; its solubility is 1.33 g/100 g H_2O, 0.23 M (M = mol dm^{-3}), at 25 °C. Aqueous mixtures of CH_2Cl_2 at 0.92 M were used for the hydrothermal experiment. Distilled and deionized H_2O was used as solvent, whereas D_2O (99.9% D) supplied by Aldrich was employed without further purification. For the alkaline hydrothermal reaction, NaOH (Wako) or NaOD (99.9%D, Aldrich) was added to H_2O or D_2O, respectively, to adjust the concentration at 2 M; $[OH^-]/[Cl]$ = ca. 1. Solvent D_2O was utilized to examine the H/D exchange during the hydrothermal reaction. Formalin supplied by Wako was used for the detection of the hydrolysis form of formaldehyde. The formalin was 37%(w/w) (= ca. 13 M) aqueous solution of HCHO, containing 10%(w/w) CH_3OH as an inhibitor for polymerization. The formalin solution in D_2O at 2.2 M was prepared by diluting the commercially available solution with D_2O.

A mixture of CH_2Cl_2 and solvent was introduced into an autoclave with a volume filling factor of 30%. The design of an autoclave which can withstand acidic or basic hydrothermal conditions is illustrated in Fig. 1a. We took an NMR glass tube of 5 mm o.d. (Kusano or Wilmad) as a nonmetallic reactor under acidic conditions, as shown in Fig. 1b. Sealed glass tubes with a larger diameter, e.g., 10 mm, were often exploded by a high pressure due to steam and generated gases; the vapor pressure of water is 4 MPa at 250 °C. The hydrolysis reaction without NaOH makes the solution acidic. Glass tubes are advantageous for the direct observation with eyes and structural analysis by NMR. They were not used, however, under alkaline conditions because of the corrosion at high temperatures. The hydrothermal reaction of formalin in D_2O was carried out in the sealed NMR tube reactor.

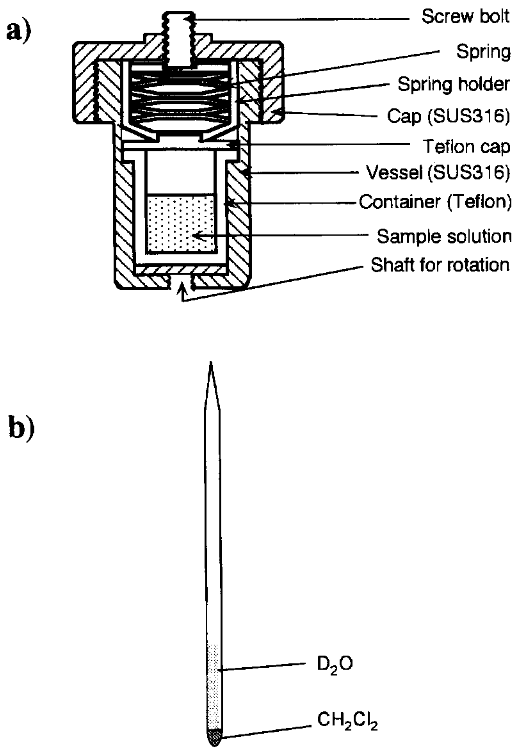

Fig. 1. a) The autoclave employed for the alkaline hydrothermal reaction of CH_2Cl_2. The Teflon inner container (ca. 28 cm^3) was set in the vessel made of SUS 316 from 150—250 °C. At higher temperatures, the autoclave equipped with a liner made of Hastelloy-C was used to prevent the thermal destruction (melting). The high pressure was sealed with the Teflon–Teflon contact supported by the spring and the screw bolt. b) The glass tube reactor used for the hydrothermal reaction without alkali.

The autoclave or the sealed glass tube containing the reaction solution was placed in an oven already heated up to the reaction temperature; the temperature was controlled within ±1 °C. The reactors were quickly cooled down to room temperature in order to stop the reaction by using an electric fan for the autoclave and iced water for the sealed glass tube. The reaction time was more accurate in the case of the glass tube reactor. As depicted in Fig. 1b, CH_2Cl_2 was phase-separated at the bottom of the tube at room temperature. When the sealed glass tube containing CH_2Cl_2 and D_2O was heated from room temperature in an oven to which a glass door was attached for direct observation, the mixture contained became homogeneous above 165 °C. The homogenization was accomplished by the distribution of CH_2Cl_2 to the liquid and gas phases by dissolution and vaporization, respectively. The liquid and gas phases of the reaction mixture coexist during the hydrothermal reaction. In the direct heating of the sample at 250 °C, it took about 1.5 min for the mixture to be homogeneous. Thus the dissolution rate was greatly accelerated in the hot water. We defined the time of the homogeneity as the zero reaction time.

^1H, ^2H, and ^{13}C spectra were taken by means of an NMR spectrometer (JEOL, EX270) equipped with a superconductor magnet whose magnetic field was 6.35 T. In the alkaline treatment of CH_2Cl_2, the reaction solution was transferred from the autoclave to a large-sized tube of 10 mm o.d. for the product analysis by ^1H NMR. The chemical shifts and intensities of the chemical species involved in the reaction solution were determined by using benzene ($C_6\underline{H}_6$) (7.28 ppm) contained in a capillary as an external reference. The reference compound was chosen so that it might not interfere with the signals of interest. In the case of hydrothermal reactions of CH_2Cl_2 without alkali, the sealed reactor tube of 5 mm o.d. was directly analyzed with solvent as an internal reference. A gas chromatographic (GC)/mass spectrometer (MS) instrument (Hewlett Packard 5890/MS5972) equipped with a PoraPLOT Q capillary column was used for detecting residual CH_2Cl_2. Such gaseous by-products as CO, CO_2, and H_2 were analyzed by GC with a flamed ionization detector (FID) and a thermal conductivity detector (TCD) with a column (Porapak Q or Molecular Sieve 5A). The concentration of the chloride ion in the reaction solution was measured by ion-chromatographic and Mohr's methods. Yields of all the species in the solution and/or the gas phase are given in the mole percentage to the reactant (CH_2Cl_2). Polymer by-products were analyzed by FT-IR (Perkin Elmer) and SEM (Scanning Electron Microscope; Hitachi, S-530).

Results and Discussion

Product Analysis and Mechanism. Figure 2 illustrates the ^1H and ^{13}C NMR spectra of the products in the alkaline hydrothermal reaction of CH_2Cl_2 in H_2O at 250 °C; lock solvent D_2O was not used here to avoid H/D exchanges. In these spectra for the reaction solutions quenched at different reaction times, we can identify methanol (CH_3OH) and the formate ion ($HCOO^-$) as main products. These products appear in the same yield, keeping the mass balance during the reaction as long as the reaction is at an early stage within 50 min; the ratio of the proton intensity of methanol to that of the formate ion is ca. 3 as expected; note that the precision is not so high because of the weakness of the signals relative to the over-scaled one for H_2O. These products are suggested by the Cannizzaro reaction; in the presence of concentrated alkali, aldehydes containing no α-hydrogens undergo self-oxidation-and-reduction to yield a mixture of an alcohol and a salt of a carboxylic acid.[18] Thus we have the following reaction steps:

$$CH_2Cl_2 + 2OH^- \longrightarrow CH_2(OH)_2 + 2Cl^-, \tag{2}$$

$$2CH_2(OH)_2 + OH^- \longrightarrow CH_3OH + HCOO^- + 2H_2O. \tag{3a}$$

Equation 3a is the usual Cannizzaro reaction explained in textbooks; it takes place in the presence of a large excess amount of a strong base. On the other hand, the hydrothermal disproportionation reaction without alkali is suggested[16] as

$$2CH_2(OH)_2 \rightleftharpoons CH_3OH + HCOOH + H_2O. \tag{3b}$$

Thus Eq. 3b can be the case when an equivalent amount of NaOH added as a neutralizer. This possibility will be discussed later for the case of the hydrothermal disproportionation reaction of formaline without alklai.

Without direct identification of the products, Fells and Moelwyn-Hughes speculated that the reaction took place by the Cannizzaro[19] mechanism via "formaldehyde". They investigated the reaction rate at a much lower temperature, as shown in Table 1, by analyzing the chloride ion, hydrogen ion, and "formaldehyde" by Mohr's method, acid-base titration, and the chromotropic acid and polarographic methods,

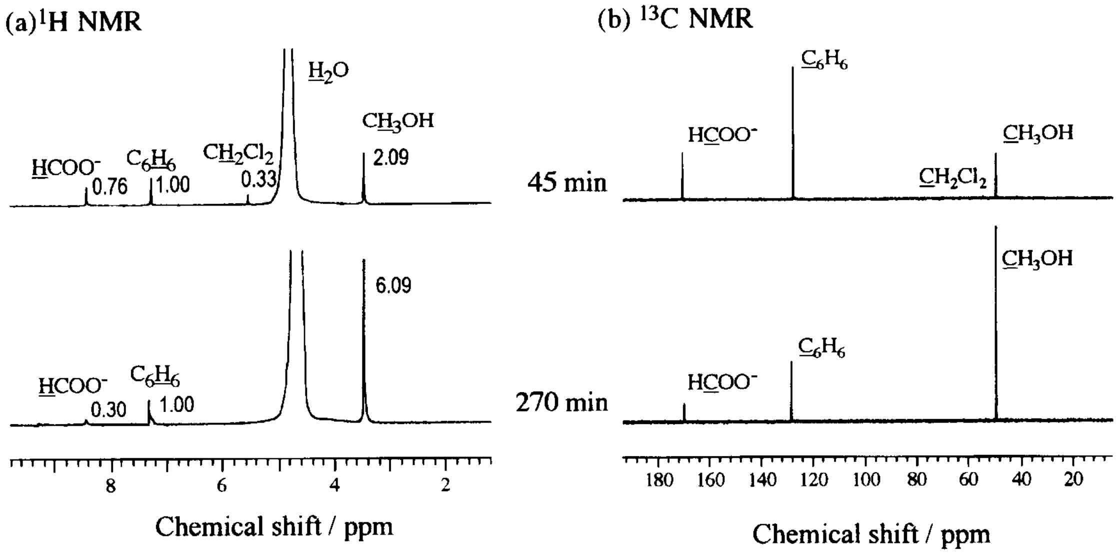

Fig. 2. ^1H and ^{13}C spectra of the products in the alkaline (2 M NaOH) hydrothermal reaction of CH_2Cl_2 in H_2O at 250 °C for 45 (a) and 270 min (b). Intensities of the ^1H signals are expressed relative to benzene (reference). The spectral ordinate axis is substantially expanded so that the weak signals may be observed.

respectively.[13] Gas chromatography as well as these analytical methods were used by Tester and co-workers.[10—12] These methods, however, lack structural information required for the mechanistic study. The yields of CH_3OH, $HCOO^-$, and Cl^- produced in the alkaline hydrothermal reaction are shown as a function of reaction time in Fig. 3. While the yield of CH_3OH reaches ca. 50% as the saturated value, the concentration of $HCOO^-$ decreases after the maximum and finally disappears. The formate ion or formic acid decomposes under the hydrothermal conditions as reported elsewhere.[8,16] The hydrothermal decomposition pathways of formic acid,

$$HCOOH \longrightarrow CO + H_2O \tag{4}$$

$$HCOOH \longrightarrow CO_2 + H_2 \tag{5}$$

have been examined by analyzing the gaseous decomposition products from the same alkaline hydrothermal reaction. As summarized in Table 2, the CO production path is dominant under the conditions studied here; the reaction 5 is stated to be predominant at higher temperatures by Brill[20] and Savage.[21] The sum of the final yields of CO, CO_2, and H_2 corresponds to the total amount of decomposed $HCOO^-$, in favor of the Cannizzaro reaction.

The increment of the chloride ion agrees with the consumption of the chlorinated methane. The final dechlorination ratio thus determined at 250 °C is 100 ± 1% at 400 min, which is the time required for the complete disappearance of CH_2Cl_2. This verifies that the chlorinated methane can be easily dechlorinated and transformed into useful methanol in the presence of the alkali under the hydrothermal conditions. Thus the strong alkali plays a key role not only in transforming the chlorinated methane into useful compounds but also in neutralizing the reactive and dangerous hydrochloric acid formed by the hydrolysis of C–Cl bonds. The dechlorination process is of great importance to prevent the chlorine atom from being involved in some further chlorination reactions; e.g., as Cl sources in the dioxin formation.[1] As shown later in the next section, such undesirable chlorination reactions can successively take place under the hydrothermal conditions without alkali. For the actual application of this hydrothermal dechlorination treatment, it is indispensable to examine how the hydrothermal temperature varies the reaction time required for the complete dechlorination of CH_2Cl_2 in hot water at ca. 1 M. As seen in Fig. 4, the required dechlorination time becomes shorter as the temperature is raised. At 300 °C the complete dechlorination is finished for less than 60 min. Thus, the efficiency of the hydrothermal dechlorination can be controlled by tuning the high temperature and the amount of the neutralizer.

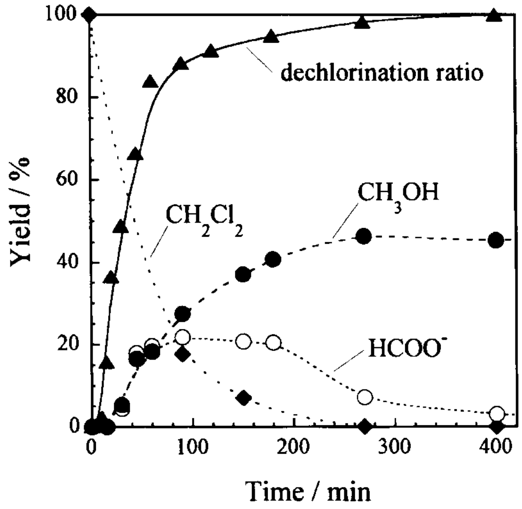

Fig. 3. Time dependence of the yields of products for the alkaline reaction at 250 °C. Dechlorination ratio (▲) was $[Cl^-]/[CH_2Cl_2]_0$; $[CH_2Cl_2]_0 = 2\times0.92$ M. The yields of $HCOO^-$ (○) and CH_3OH (●) were calculated from the integrated intensities of the ^1H signals. Residual CH_2Cl_2 after 90 min (◆) was measured by GC/MS.

Table 2. Final Yields of the Gases Produced in the Alkaline Hydrothermal Reaction of CH_2Cl_2 at 250 °C for 270 min

Gas	Yield[a)]/%
CO	30
CO_2	10
H_2	5

a) They were calculated relative to the starting mole of CH_2Cl_2.

When an aldehyde is subjected to the Cannizzaro reaction in D_2O, the C–H bond in HCOOH is not to be deuterated.[22] This is another important criterion for the Cannizzaro reaction. In order to scrutinize whether the main products are deuterated or not, the alkaline hydrothermal reaction of CH_2Cl_2 has been carried out in D_2O instead of H_2O. The resultant ^1H and ^2H NMR spectra are given in Figs. 5a and 5b, respectively. Both deuterated and non-deuterated products are observed. It is to be noted that the reactant CH_2Cl_2 is already subjected to the H/D exchange under the alkaline hydrothermal conditions. At 45 min the impurity HDO in D_2O increases to a considerable extent as a result of the H transfer from CH_2Cl_2 to D_2O, and correspondingly, a very weak ^2H

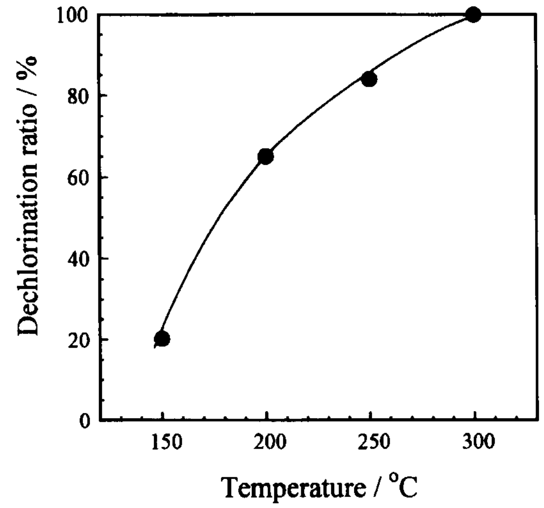

Fig. 4. Temperature dependence of the dechlorination ratio in the hydrothermal reaction of CH_2Cl_2 with alkali (2 M NaOH) for 60 min.

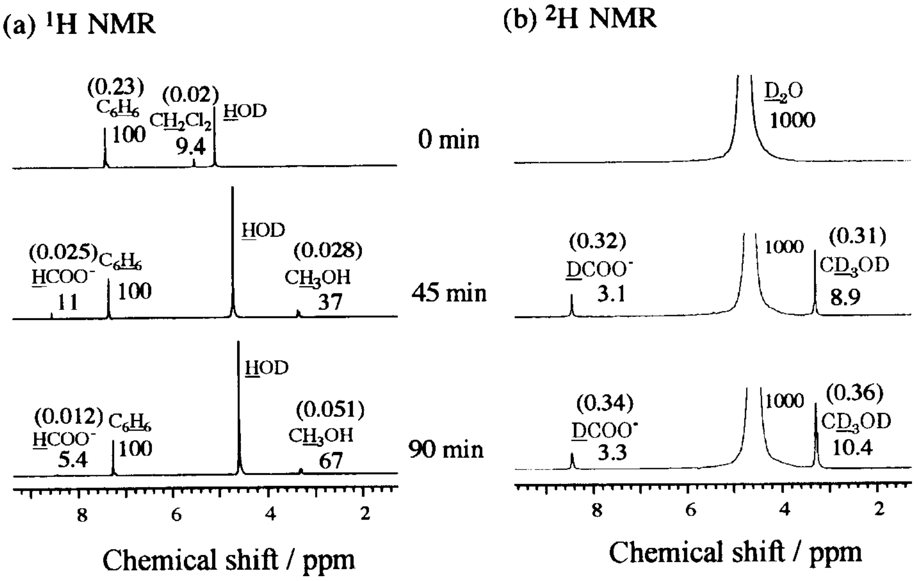

Fig. 5. ¹H (a) and ²H (b) spectra of the solution subjected to the alkaline (2 M NaOD) hydrothermal reaction of CH_2Cl_2 at 250 °C. The unparenthesized and parenthesized numerical values indicate the integrated intensity and the molar concentration, respectively.

signal of CD_2Cl_2 is discernible at ca. 5.4 ppm. This is simply because the parent molecule CH_2Cl_2 is already deuterated in part under the alkaline hydrothermal conditions; the H retention is advantaged in the acidic solution, as can be seen in Fig. 6. Thus the product deuteration in the alkaline hydrothermal reaction is not contradictory to the Cannizzaro reaction mechanism.

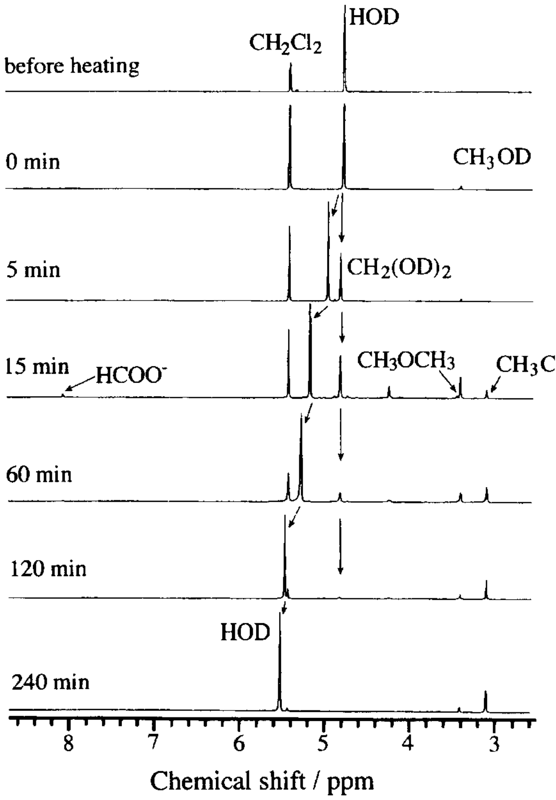

Fig. 6. ¹H spectra of the acidic hydrothermal solution of CH_2Cl_2 in D_2O at 250 °C for the detection of the intermediate.

Intermediate Detection. What is the most important in the present NMR study is to detect formaldehyde or its hydrolyzed form at an early stage of the hydrothermal reaction of CH_2Cl_2. To increase the chance of finding the intermediate species in solution, we need to slow down the reaction rate in a suitable way. We can achieve this in the absence of alkali. When no alkali was added, the pH value of the solution was markedly decreased, even lower than 0, as an indication of the HCl formation due to the hydrolysis. Without NaOH added, hence we can hope to identify formaldehyde or its more stable, hydrolyzed form $CH_2(OH)_2$ at an early reaction stage.

The chemical species generated by the hydrothermal reaction without any strong base in a sealed NMR tube have been analyzed by means of ¹H and ¹³C NMR. The ¹H NMR spectra taken in D_2O are shown in Fig. 6; D_2O can be used for the intermediate detection because of the slower H/D exchange rate in the absence of alkali. Compared with the spectra for the alkaline reaction in Fig. 2, the spectral time resolution is "increased", and more signals are observed. Noticeably, a new signal appears at 4.8 ppm at 5 min; at the same time, the impurity water HDO, the reactant CH_2Cl_2 and the Cannizzaro reaction product CH_3OD are observed as well. We can assign this to the wanted species, methanediol $CH_2(OD)_2$, for the reasons discussed below in more detail. The decrease of the methanediol signal in intensity after 60 min indicates the gradual consumption of the reaction intermediate. Unfortunately, the signal of $CH_2(OD)_2$ overlaps with that of HDO at early reaction stage, say, at ca. 0 min because the solution is almost neutral; cf., only a trace amount of CH_3OD is produced. At 5 min, more $CH_2(OD)_2$ is produced by the hydrolysis of CH_2Cl_2 and the solution becomes more acidic. In consequence, the solvent proton peak moves downfield.[23,24] The pH-controlled shift makes the reaction intermediate detectable in the hydrothermal reaction of CH_2Cl_2 without alkali. The intermediate has been ex-

Table 3. ^1H and ^{13}C Chemical Shifts δ of the Products of Hydrothermal Reactions of CH_2Cl_2

Detected species (^1H, δ / ^{13}C, δ)				
CH_3O	$HCOO^-$	$CH_2(OH)_2$	CH_3Cl	CH_3OCH_3
(3.34/49.5)	(8.26/171.0)	(4.80/82.4)	(3.02/40.4)	(3.24/60.1)

pected but never been confirmed in the previous works.[10—15] The methylene group of the intermediate was detected by ^{13}C NMR at 82.4 ppm; see Table 3. This assignment has been supported by an in situ NMR study of this reaction in hot water under alkaline conditions.[25] When water is heated up to sub- and supercritical temperatures, the proton signal dramatically moves to a higher magnetic field from the overlapping position due to the temperature-induced breakdown of the hydrogen bonds.[26] Thus the intermediate signal can be isolated from the solvent signal in hot water.

The reactive intermediate $CH_2(OH)_2$ has been identified here for the first time, and we need to justify the assignment of the ^1H and ^{13}C NMR signals. For this purpose we have carried out an independent experiment on the hydrothermal reaction of formalin solution in D_2O. We expect to observe the intermediate in the formalin reaction without NaOH because formalin is one of the most popular sources of formaldehyde as well as *s*-trioxane.[16] Methanediol is expected to be formed in a diluted aqueous solution of formalin because of the shift of the hydrolysis equilibria expressed as follows:

$$HCHO + H_2O \rightleftharpoons CH_2(OH)_2, \qquad (6a)$$

$$nCH_2(OH)_2 \rightleftharpoons -(CH_2O)_n- + nH_2O. \qquad (6b)$$

High temperature shifts the equilibrium Eq. 6b towards the monomers, $CH_2(OH)_2$ to favor the intermediate detection at high temperature. Formic acid generated by the hydrothermal Cannizzaro-type reaction makes the aqueous solution more or less acidic in the absence of a strong base; see Eq. 3b. Consequently, the overlapping of the ^1H peaks of HDO and $CH_2(OD)_2$ can be avoided.

Figure 7 shows the ^1H NMR spectra for the quenched solution after the neutral hydrothermal reaction of the diluted formalin solution at ca. 2 M; note the large expansion of the chemical shift compared with Fig. 6. It is found that the proton signals of water (HOD) and methanediol overlap at around 4.8 ppm and that some signals of the oligomers distribute around the water signal before the hydrothermal treatment. The progress of the Cannizzaro-type reaction without alkali is recognized by the growth of the signal of methanol at ca. 3.3 ppm; recall Eq. 3b. The small downfield shift of the signal of water between 0 and 30 min is brought about by the formation of formic acid by the Cannizzaro-type reaction. As a result, methanediol is successfully detected here in the hydrothermally reacted formalin solution. In this case, however, the signal of water after 60 min comes back to the original chemical shift at around 4.8 ppm, because the solution returns to neutral again due to the consumption of the formate by the decomposition and polymer formation.

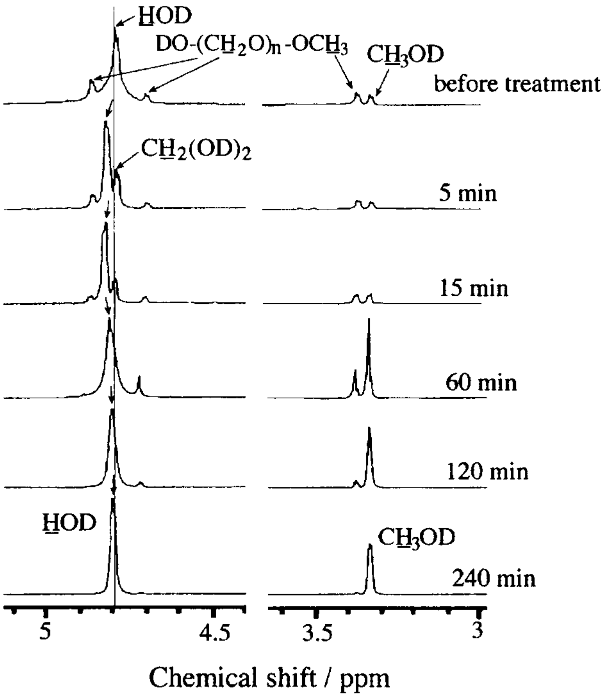

Fig. 7. ^1H spectra of the hydrothermal reaction of formalin in D_2O at 2.2 M without NaOH at 250 °C. The horizontal axis for the chemical shift is largely expanded in order to discernibly separate the signals around water and methanol. Note that methanol is originally contained in the diluted formalin to an extent.

Finally, we mention the relative stability of formaldehyde on the left-hand side of Eq. 6a. Although formaldehyde was not observed in the formalin solution before or after the hydrothermal reaction, it was observed at ca. 10 ppm in the in situ ^1H spectrum of aqueous solution of *s*-trioxane at ca. 200 °C before the hydrothermal Cannizzaro-type reaction.[25] Thus it turns out that the equilibrium of the reaction given by Eq. 6a is shifted to the left-hand side at such a high temperature.

Products of Reaction without Alkali. In the hydrothermal reaction of CH_2Cl_2 without NaOH, after the main products of the Cannizzaro reaction appeared at 15 min CH_3Cl and $(CH_3)_2O$ were observed; see Fig. 6. CH_3Cl is considered to be formed by the conversion of CH_3OH through the OH/Cl substitution under the hydrothermal conditions. $(CH_3)_2O$ is supposed to be generated by the acid-catalyzed bimolecular dehydration of CH_3OH.[18] The species observed at 4.2 ppm is identified as glycolic acid elsewhere.[25]

A brownish polymer precipitated as a by-product after 60 min. Since the intermediate, $CH_2(OH)_2$, is stable for a long time in the absence of alkali, it can participate in some pathway other than the Cannizzaro reaction. One of the most possible reaction pathways is the polymerization as expressed by Eq. 6b ($n \gg 1$). The brownish precipitate can be attributed to such a polymer or a polymerization product of glycolic acid. Actually, formalin is used as a starting material for the formalin-resin formation.[27] The FT-IR spectra obtained from the hydrothermal reactions of formalin and

CH_2Cl_2 were almost identical. The two polymers were morphologically similar, being spherical with a μm size.

Conclusions

Concentrated CH_2Cl_2 in water at ca. 1 M can be completely dechlorinated and converted into useful methanol at a yield of 50% by the Cannizzaro reaction under the alkaline (NaOH) hydrothermal conditions. The comparison of the hydrothermal reactions with and without alkali tells us that the alkali plays a key role in the first step of the following reaction processes:

$$CH_2Cl_2 + 2OH^- \longrightarrow CH_2(OH)_2 + 2Cl^-,$$

$$2CH_2(OH)_2 + OH^- \longrightarrow CH_3OH + HCOO^- + 2H_2O.$$

We have succeeded in detecting the hydrolysis intermediate of the hydrothermal reaction of CH_2Cl_2 without alkali; the ^1H and ^{13}C signals are observed at 4.8 and 82 ppm, respectively.

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