Improvement of Thermal Hydrolysis Rate of Dichloroacetic Acid (DCAA) using Alcohol

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Abstract

Dichloroacetic acid (DCAA) is produced during the oxidation of Trichloroethylene (TCE). It is also produced in drinking water treatment as a disinfection by-product. DCAA is a problem material, because of its toxicity. The objective of this research is to find the final products and the reaction pathway of the DCAA decomposition by hydrolysis, and to increase the hydrolysis rate. The removal of both chlorine atoms in DCAA structure was achieved with hydrolysis at around 75 °C, and the final products were oxalic acid and glycolic acid. The reaction pathway was the production of oxalic acid and glycolic acid from two glyoxylic acid molecules by Cannizzaro reaction after the glyoxylic acid production from dechlorination of DCAA with hydrolysis. The hydrolysis rate of DCAA was increased with the use of 90% ethanol solution as solvent. The activation energy of DCAA was about 80 kJ/mol in it, while it was around 105 kJ/mol in water.

Keywords: Base catalyst; Cannizzaro reaction; Dichloroacetic Acid; Ethanol; Hydrothermal Dechlorination; Insolubilization

1. Introduction

Many groundwater sources are still contaminated by TCE (Trichloroethylene) with a higher concentration than the environmental quality standard in the world (Lopes and Bender, 1998; Stager and Perram, 1999; Wang et al., 2000). One of the basic treatment technologies for TCE is "aeration" (air stripping), which is very simple and effective for the removal of volatile organic compounds (VOC). However, because the vaporized TCE should be treated, the adsorption of the vaporized TCE onto activated carbon is used with "aeration" in order to prevent air pollution (secondary pollution). In addition, the adsorption treatment of vaporized TCE by activated carbon is necessary for soil remediations since one of the major remediation technologies is "soil vapor extraction" (Braida and Ong, 2001). However TCE cannot be decomposed into harmless substances in this adsorption treatment. Therefore, the development of a vaporized TCE purification method is important. Some researchers have reported high efficiencies of ultraviolet (UV) photooxidation in air for the decomposition of TCE (Bhowmick and Semmens, 1994; Hirvonen et al., 1996; Shen and Ku, 1997). The UV photooxidation method only needs quartz tubes and UV lamps. Moreover, the operation and maintenance are easy, and the establishment and operation costs are cheap. However, even with the gas-phase photooxidation, the mineralization of TCE needs a long reaction time because the mineralization of intermediates is 5~10 times slower than the first TCE degradation step (Okamura et al., 1994; Shen and Ku, 1998). The main intermediate in the first TCE degradation step is dichloroacetic chloride (DCAC) and the limiting stage of TCE mineralization is the degradation of DCAC or its hydrolyzed product; dichloroacetic acid (DCAA) (Catoire et al., 1997; Prager and Hartmann, 2001; Manouge and Pigford, 1960). In addition, DCAA is also produced through other oxidation methods (Okamura et al., 1994; Prager and Hartmann, 2001) and DCAA is a problem as a disinfection-byproduct in drinking water because of its toxicity.

In general, the toxicity of halogenated organic compounds is caused by halogen atoms on the structure, it is chlorine atoms in the case of TCE. It is assumed that dechlorination may be effective for the detoxification of DCAA. An effective dehalogenation method is hydrolysis reaction. Hydrolysis can remove chlorine groups (-Cl) from the organic structure and install a hydrolysis group (-OH), and it can be enhanced by heating, acid-catalyst and base-catalyst. DCAA can be decomposed into other materials by hydrolysis that can be enhanced by heating or alkaline conditions, but a lot of energy and tough apparatus are necessary for the thermal enhancement at highly temperature or high alkaline conditions. The hydrolysis of DCAA is also not rapid under relatively mild conditions, e.g. at a temperature below 100 ^{o}C with 1 M NaOH (Haag and Johnson, 1996). The decomposition in such mild conditions contributes to reduce cost and the evaporation amount of DCAA, if the hydrolysis of DCAA can be enhanced by other technique, e.g. improvements of solvent.

Investigations of the reaction pathway are necessary to improve solvents or others in reactions. Haag and Johnson (1996) expected that the hydrolyzed product of DCAA was glyoxal, but that were not confirmed in their paper.

The objective of this study is to investigate the increase of the DCAA decomposition rate at around 75 ^{o}C in the base-catalyzed thermal hydrolysis by the improvement of solvent. For the improvement, isolation of the final products and investigation of the reaction pathway of the DCAA decomposition were first studied.

2. Materials and Methods

2.1. Base-catalyzed thermal hydrolysis of DCAA

Batch experiments were conducted to evaluate the hydrolysis rate of DCAA. Hydrolysis was conducted in a polypropylene bottle. Initially, the alkaline concentration was adjusted to 1.0 N sodium hydroxide and 100 ml of the solution was placed a 250 ml polypropylene bottle. The bottle was heated and kept the solution temperature at certain temperature in a water bath within ±1 ^{o}C. The bottle was closed with a polypropylene cap, with a condenser was installed to the cap in order to balance the pressure and the solution volume. Then, a certain amount of DCAA was added into the bottle and the hydrolysis of DCAA was started.

2.2. Analytical method and Reagents

DCAA was determined by ion chromatograph (Dionex, IC-1400) (Funaishi and Seki, 1998). Sodium bicarbonate buffer, 1.8 mM Na_2CO_3 +1.7 mM $NaHCO_3$, was used as elutant. The detection limit of DCAA was approximately 100 mg/l (0.5 mM) in this quantitative analysis. Anion chromatography was used to determined chloride ion and for the isolation of other products (glyoxylic acid, glycolic acid and oxalic acid). Dissolved organic carbon (DOC) was determined by an organic carbon analyzer (Rosemount Dohrmann, DC-180).

Dichloroacetic acid (DCAA), glyoxylic acid and glycolic acid were obtained from Aldrich Chemical Company. Extra pure grade sodium hydroxide (NaOH), oxalic acid, special grade of ethanol and other chemicals were also used for this research.

3. **Results and Discussion**

3.1. Reaction pathway of DCAA hydrolysis

The activation energy is calculated by Arrhenius plot using the base-normalized hydrolysis rate constant (k_B) and reaction time. The activation energy of DCAA was reported as 109-149 kJ/mol by Haag and Johnson (1996) with sodium hydroxide base-catalyst. Figure 1 shows the Arrhenius plot from our data obtained at different temperatures and sodium hydroxide concentration. The data of the present study were compared with the reported data. The calculated activation energy was 105 kJ/mol within 60-100 ^{o}C and is almost similar to the reported result.

The degradation of DCAA and the production of chloride ion were conducted to check dechlorinations and the results are shown in Fig. 2. If dechlorination is perfectly done, two moles of chloride ion are produced from one mole of dechlorinated DCAA. "Cl^- Calculated" in Fig. 2 corresponds to chloride ion concentration, calculated on the hypothesis; both chlorine atoms are dechlorinated from the DCAA's structure by hydrolysis. Around 3 mM of DCAA was decomposed after 6 hours at 74 ^{o}C, and the chloride ion concentration produced was well fitted by the "Cl^- Calculated" in Fig. 2. The result indicates that the dechlorination of both chlorine atoms from DCAA was achieved well even at around 75 ^{o}C. The DOC concentration was also examined during the study, but no difference was observed indicating that mineralization of dechlorinated DCAA does not happen at this temperature.

During the anion chromatograph analysis, however, some peaks appeared in the reacted solution. Isolation of these peaks was tried using some compounds with anion chromatography. Glyoxylic acid, glycolic acid and oxalic acid were isolated. Thus, the final products expected are the glycolic acid, oxalic acid and sodium chloride.

The proposed reaction pathway is described in Fig. 3 considering the increase and decrease of isolated peaks (exact concentrations were not investigated in this research). Glyoxylic acid is initially produced by the dechlorination of DCAA during hydrolysis and from the hydrolysis of glyoxylic acid oxalic acid and glycolic acid are produced. The reaction transferring the two glyoxylic acids to glycolic acid and oxalic acid, is a famous reaction called Cannizzaro reaction (Varma et al., 1853; Yoshizawa et al., 2001).

3.2. Improvement of product recovery and increase in hydrolysis rate of DCAA

Since the products could not be mineralized during a few hours under the experimental conditions, the concentration of oxalic acid and glycolic acid may increase until a saturated concentration in the system. However, the solubility of intermediate, glyoxylic acid, is very low in alcohol. Similarly, the solubility of sodium chloride and oxalic acid in alcohol is also low. If alcohol can be used as a solvent for the base-catalyzed thermal hydrolysis of DCAA, intermediate is precipitated with its low solubility. This may increase the hydrolysis rate because the intermediates and products are maintained at low concentration. This implies that the improvement of solvent may decrease the activation energy of DCAA hydrolysis.

Figure 4 shows the hydrolysis rate constant under several ethanol concentrations during 5 hours at 74 ^{o}C. The k_B was almost the same between 0 and 55% ethanol concentration but it increased beyond 55% resulting to a value of 6.3μ x 10^{-5} (1/s) at 90%. This improvement can decrease the reaction time or temperature to achieve the same efficiency.

The effect of temperature on the hydrolysis constant was studied in 90% ethanol at a temperature range from 45 to 75 ^{o}C to calculate the activation energy by Arrhenius plot (data not shown). The activation energy of DCAA was 80 kJ/mol in 90% ethanol solution, it indicate that the solvent improvement decreased the activation energy of DCAA hydrolysis by 25%.

Insoluble materials appeared in the reaction with 90% ethanol as expected. The products were also isolated by anion chromatogram after redissolution with water and were the same as the ones contained in the water system. These results indicate that the reaction pathway in 90% ethanol is the same as that in water and the hydrolysis rate was accelerated only by the existence of ethanol. It seems that the acceleration in ethanol solution is due to the removal of product from the reaction liquid layer although it is not clear. Further studies are necessary to confirm this result.

4. Conclusions

The decomposition of DCAA with base-catalyzed thermal hydrolysis was studied and the following specific conclusions were obtained from this study;

1. Dechlorination of DCAA occurred during the base-catalyzed thermal hydrolysis. Glyoxylic acid was produced by the dechlorination of DCAA during hydrolysis, and oxalic acid and glycolic acid were produced from two molecules of glyoxylic acid through the Cannizzaro reaction.
2. The hydrolysis rate of DCAA increased when 90% ethanol solution was used as solvent.

The solvent improvement decreased the activation energy of DCAA hydrolysis by 25%, it was 80 kJ/mol in 90% ethanol solution.

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Figures

Figure 1. Arrhenius plot of our data with present study and data of Hagg and Johnson.
<Bold line, the data of Hagg and Johnson; ×, present study data; "k_B" is base-normalized hydrolysis rate constant>

Figure 2. Decrease of DCAA and increase of chloride ion.
< Initial sodium hydroxide, 1.0 M; reaction temperature, 74±1 °C>

Figure 3. Expected reaction pathway of the DCAA decomposition with hydrolysis.

Figure 4. Relationship between hydrolysis rate and ethanol concentration in solution.
<Initial sodium hydroxide, 1.0 M; initial DCAA, 10 mM; reaction temperature, 74±1 °C>

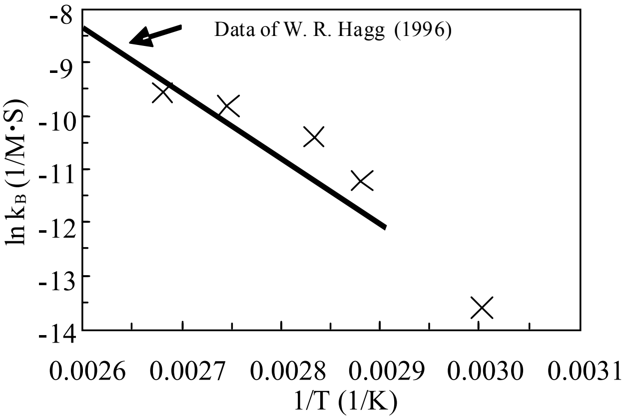

Figure 1

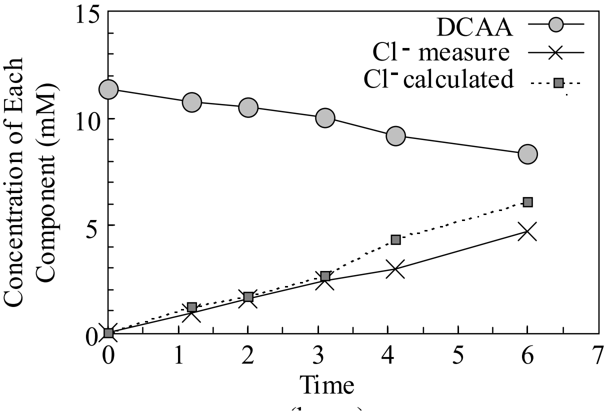

Figure 2.

$CCl_2H\text{-}COOH + 2\,NaOH \rightarrow COH\text{-}COOH + 2\,NaCl + H_2O$

DCAA *Glyoxylic Acid* *Sodium Chloride*

$2\,COH\text{-}COOH + NaOH \rightarrow COOH\text{-}CH_2OH + COOH\text{-}COONa$

Glycolic Acid *Oxalic Acid*

Figure 3.

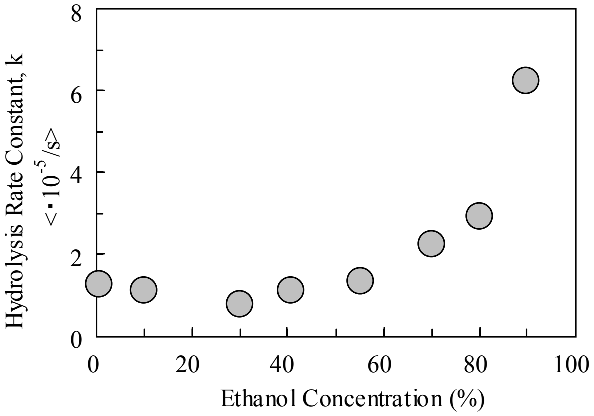

Figure 4.