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# Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

## Status Report

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September 2009



**Pacific Northwest**  
NATIONAL LABORATORY

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Pacific Northwest National Laboratory  
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(a) State University of New York at Cortland

## Summary

Hydrolysis is a ubiquitous abiotic degradation reaction for organic compounds, driven by reaction of the compound with water and other nucleophiles, that generally yields innocuous degradation products. If the rate of hydrolysis for a given compound is known, it can be incorporated into remediation planning, and, if significantly large, can be used to minimize the expense of active-remediation. At the Hanford Site in eastern Washington, two common organic contaminants, chloroform (CF) and carbon tetrachloride (CT), have been measured in groundwater plumes. Because their rates of hydrolysis are very slow, the only data available in the literature were from experiments conducted at temperatures of 70°C and above. Extrapolation of these rates to groundwater temperatures yielded unacceptable margins of error. This project, therefore, was initiated in FY 2006 to help address these uncertainties and to explore the possible effects of contact with minerals and sediment (i.e., heterogeneous hydrolysis) on the overall rates of hydrolysis. It was funded by the U.S. Department of Energy (DOE) through the Office of Environmental Management (EM-22) Columbia River Protection Supplemental Technologies (CRPST) project and complements work initiated by the Hanford Groundwater Project in FY 2006 that focused primarily on CT in homogenous solution. Work was performed by staff at the Pacific Northwest National Laboratory (PNNL) and the State University of New York at Cortland (SUNY–Cortland).

Thirteen long-term experiments were initiated at PNNL involving CF or CT. These involved sealed glass ampules that were approximately two-thirds full of liquid or suspension; the remaining volume was air-filled headspace. Experiments were conducted at incubation temperatures of 20°C to 70°C and designed for a total of about 10 sampling periods. Reaction progress was followed by measuring chloride-ion concentrations using ion chromatography. Four experiments with CF (two at pH 3 and one each at pH 8 and pH 12 in a phosphate buffer) were conducted in homogeneous solution to obtain rate constants for neutral and base-catalyzed hydrolysis. Five experiments with CF were started in Hanford groundwater containing Hanford sediment, montmorillonite, muscovite, albite, or kaolinite in suspension. An analogous set of four experiments with CT in Hanford groundwater containing each of the four minerals was also started. At SUNY–Cortland, several experiments were conducted with CF at pH 12 in sodium hydroxide to complement the PNNL base-catalyzed hydrolysis experiments in phosphate buffered solutions.

About 60% of the ampules were sampled and analyzed during the period of project funding, and 32 provisional rate constants were determined. These were chiefly the high-pH and/or high-temperature treatments, for which hydrolysis rates are relatively fast. An additional 31 provisional rate constants remain to be determined as data from the lower-pH and lower-temperature experiments become available in the future.

Provisional activation energies were calculated for the homogeneous base-catalyzed experiments with CF. These were 123 kJ mol<sup>-1</sup> for 0.01 m NaOH (pH 12), 140 kJ mol<sup>-1</sup> for 0.1 m Na<sub>3</sub>PO<sub>4</sub> (pH 12), and 167 kJ mol<sup>-1</sup> for 0.1 m phosphate buffer (pH 8). These results were substantially higher than the previously reported value of 105 kJ mol<sup>-1</sup> obtained in NaOH. The higher value in NaOH is attributed to the corrections for liquid-vapor partitioning incorporated into the study. The even higher results obtained in phosphate buffers are attributed to parallel hydrolysis reactions caused by the nucleophilic character of the phosphate anions, particularly HPO<sub>4</sub><sup>-</sup>. Although the activation energies in the phosphate buffers are higher than in NaOH, the rates observed are similar at groundwater temperatures. It is surmised that

neither phosphate nor  $\text{HCO}_3^-$ , which is common in groundwaters and has a nucleophilic character comparable to  $\text{HPO}_4^-$ , significantly increases the rates of hydrolysis for CF over those observed in waters where they are absent.

A twenty-fold range in hydrolysis rate constants was obtained for CF in contact with various solid phases at 50°C. This high sensitivity to type of solid is likely due to the different pH values maintained by the solid surface in contact with the aqueous phase. Further work to clarify this is planned. In contrast, very little effect of mineral type on CT hydrolysis rates was noted. This is consistent with the pH hypothesis for CF because CT hydrolyzes only by a neutral, pH-independent mechanism.

At SUNY–Cortland, liquid-vapor partition coefficients ( $K_{lv}$ ) for CF were measured at the temperatures and CF concentrations used in our homogeneous hydrolysis experiments. These coefficients differed from the values for the Henry's law constant ( $K_h$ ) reported in the literature; in general, the  $K_{lv}$  values were lower, and the size of the difference from  $K_h$  increased with temperature.

It is noted that the ultimate impact of this project will depend on the degree and accuracy to which activation energies can be calculated at temperatures relevant to groundwater. These calculations, which use the Arrhenius expression, require determination of rate constants for similar systems across a range of temperatures. Once the activation energy is known, the Arrhenius expression can be used in reverse to estimate rate constants accurately for any temperature within or near the experimental range originally used to determine the activation energy. It is emphasized that completion of the lower-temperature experiments to allow accurate calculation of activation energies is critical to produce a scientifically robust predictive capability. This temperature-sensitive capability, coupled with knowledge gained about the impacts of the solid phase on hydrolysis rates, will provide an excellent platform on which to base remediation decisions for the Hanford Site and other groundwater sites where CT and CF contamination is present.

## **Acknowledgments**

Funding for this project was provided by the U.S. Department of Energy Office of Environmental Management (EM-22) Columbia River Protection Supplemental Technologies Project. We thank R. Blaine Rowley (DOE Headquarters, EM-22), K. Mike Thompson, DOE Richland Operations Office, and Jonathan S. Fruchter, PNNL, for overall management of the EM-22 project and support of this project. We also thank Andrea Currie for editorial assistance and Mike Parker for formatting the report.

## Acronyms and Abbreviations

CF	chloroform
CT	carbon tetrachloride
CRPST	Columbia River Protection Supplemental Technologies
EM-22	DOE Office of Environmental Management
GC	gas chromatography
HEIS	Hanford Environmental Information System (database)
HPLC	high-performance liquid chromatography
IC	ion chromatography
PCE	perchloroethene
PFO	pseudo-first-order
PNNL	Pacific Northwest National Laboratory
PRA	pesticide residue analysis
PTFE	polytetrafluoroethylene
SUNY-Cortland	State University of New York at Cortland
XRD	x-ray diffraction
ZHR	zero-headspace reactor

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# 1.0 Introduction

This report documents a project initiated in FY 2006 to help address uncertainties related to the rates of hydrolysis in groundwater for carbon tetrachloride (CT) and chloroform (CF). The study sought also to explore the possible effects of contact with minerals and sediment (i.e., heterogeneous hydrolysis) on these rates. It was funded by the U.S. Department of Energy (DOE) through the Office of Environmental Management Columbia River Protection Supplemental Technologies (CRPST) project and complements work initiated by the Hanford Groundwater Project in FY 2006 that focused primarily on CT in homogenous solution. Work was performed by staff at the Pacific Northwest National Laboratory (PNNL) and the State University of New York at Cortland (SUNY–Cortland).

## 1.1 Rationale

Between 1955 and 1973, an estimated 920,000 kg of carbon tetrachloride (CT) were discharged to the soil in the 200 West Area of the Hanford Site as part of the plutonium production process (Oostrom et al. 2007). Of this amount, some CT reached the groundwater more than 70 m below the ground surface and formed a plume of 10 km<sup>2</sup> extent. Recent data show that the CT plume extends to a depth of at least 60 m below the water table. Some CT has been degraded either by the original process or subsequent transformations in the subsurface to form a co-existing chloroform (CF) plume.

Although current characterization efforts are improving the conceptual model of the source area, more information is needed to effectively assess the fate and transport of CT/CF to support upcoming remediation decisions for the plume. As noted in a simulation study by Truex et al. (2001), parameters describing porosity, sorption, and abiotic degradation have the largest influence on predicted plume behavior. The work conducted in this study of heterogeneous hydrolytic reactions improves the ability to predict future plume movement by better quantifying abiotic degradation mechanisms and rates. With this information, it is easier to define how much active remediation may be needed and to estimate where the plume will eventually stabilize—key factors in determining the most appropriate remedy for the plume. A preliminary evaluation of remediation alternatives for the plume (Siegel et al. 2003) drew the following conclusions:

*The conditions present at the 200 West Area appear favorable to the successful implementation of the MNA [Monitored Natural Attenuation] approach. Application of this technique in conjunction with source-term removal or containment and control in both the vadose zone and the ground water could be a potentially cost-effective strategy. The most significant requirement is to identify and quantify the natural attenuation mechanisms in both the soil and ground water at Hanford.*

Truex et al. (2001) concluded that of the possible natural attenuation mechanisms, biodegradation is not likely to contribute significantly. They also noted that abiotic degradation processes such as hydrolysis and reduction would be significant factors and therefore important to understand in the context of selecting how active remedies will be applied to the CT/CF plume at Hanford. Previous field and modeling efforts have focused on determining the impacts of other attenuation mechanisms including dispersion and dilution processes and CT sorption to Hanford sediments (Riley et al. 2005). The abiotic degradation processes, however, are not well understood.

Previous determinations of the hydrolysis rate for CT in water (i.e., homogeneous hydrolysis) have been made, but they involved experiments at high temperature (>70°C). Arrhenius parameters developed from these data were used to extrapolate the hydrolysis rate to ambient groundwater temperatures. However, the uncertainty in these values is so large that the current information is not sufficient to distinguish whether the attenuation rate by hydrolysis will have a significant impact on the plume. To decrease this uncertainty, in FY 2006 the Hanford Groundwater Project initiated a study to determine the homogeneous hydrolysis rate of CT at temperatures closer to ambient groundwater temperatures. The homogeneous hydrolysis study also provides initial observations of possible sediment effects on the CT degradation rate. These heterogeneous effects may involve both hydrolysis and electron-transfer pathways, although the generally oxidizing nature of the Hanford subsurface suggests that electron-transfer may not contribute significantly.

The CT homogeneous hydrolysis study initiated by the Hanford Groundwater Project<sup>1</sup> does not address two relevant topics that may be important in quantifying the overall attenuation capacity for the CT/CF plume. First, it does not investigate the hydrolysis rate for CF, a prominent co-contaminant with CT. Under homogeneous conditions, CF degrades by both neutral and base-catalyzed hydrolysis. As with CT, extrapolation of high-temperature data has been made and suggests a half-life under Hanford groundwater conditions that is several times slower than that for CT but with comparable uncertainty. Again, as with CT, the overall abiotic degradation rate of CF at ambient temperatures may be a combination of homogeneous and heterogeneous hydrolysis reactions as well as other redox-related heterogeneous reactions. Second, the CT homogeneous-hydrolysis study does not include an experimental approach that would allow anything to be said about the mechanism of a possible heterogeneous effect. In particular, experiments with a variety of mineral surfaces such as clays, zeolites, feldspars, and iron oxides are needed if a robust predictive capability is to be developed for heterogeneous effects on CT or CF hydrolysis in the Hanford subsurface. Unfortunately, the already sparse literature on the hydrolysis of CT and CF is completely silent on the question of heterogeneous effects for these two compounds.

To fill these knowledge gaps and to leverage the work started in the CT homogeneous hydrolysis project, a second project was initiated as part of the Columbia River Protection Supplemental Technologies (CRPST) project in FY 2006 and is the subject of this report. This project addresses the uncertainty in the homogeneous hydrolysis rate for CF using an approach similar to that in the CT homogeneous hydrolysis project. We also are conducting thorough investigations of the possible impacts of mineral surfaces on the hydrolysis rates of both CT and CF. Although the final results of this work will require several years because of the slow hydrolysis rates expected at near-ambient temperatures, the major cost associated with the work was in the experimental setup during FY 2007. We anticipate that funding beyond the mandate of the current opportunity will be made available to continue sampling and analysis in the out years. Even if such funding is not available, the additional information gathered in a roughly 2-year time span will be of great value in selecting the appropriate application of active remediation in conjunction with natural plume attenuation. Ultimately, the results of this work will help provide a scientific basis for predicting the contribution of abiotic degradation processes to remediation of CT and CF at the Hanford Site.

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<sup>1</sup> Amonette JE, PM Jeffers, O Qafoku, CK Russell, TW Wietsma, and MJ Truex. *Abiotic Degradation Rates for Carbon Tetrachloride: Progress in FY2008*. 2008 Draft Report, Pacific Northwest National Laboratory, Richland, Washington.

In this report, we provide a summary of the project objectives and organization, the technical approaches taken, the status and results of the hydrolysis-rate experiments at the end of the 2 years of funding by the CRPST project, and a brief discussion of how these results add to scientific understanding of the behavior of the CT/CF plume at the Hanford Site. Because the hydrolysis rate experiments are continuing at least through FY 2009, albeit with a different funding source, we will refer to the project in the present tense.

## **1.2 Project Objectives**

The major objectives of this project are to

1. Determine the neutral and base-catalyzed homogeneous hydrolysis rates for CF under near-ambient temperatures.
2. Determine the impact and mechanisms of representative Hanford mineral surfaces on the hydrolysis of CT at near-ambient temperatures.
3. Determine the impact and mechanisms of representative Hanford mineral surfaces on the neutral and base-catalyzed hydrolysis of CF at near-ambient temperatures.

## **1.3 Project Organization**

The project manager is Jim Amonette (PNNL), who also serves as co-principal investigator with Peter Jeffers (SUNY–Cortland) and Mike Truex (PNNL). Work on the project is being conducted in two laboratories: the Environmental Molecular Sciences Laboratory at PNNL and the Chemistry Department at SUNY–Cortland. At PNNL, work focuses on determinations of hydrolysis rates in deionized water, Hanford groundwater, and suspensions of Hanford sediment or mineral phases in groundwater using ampules with a headspace-to-liquid ratio of 1:2. At SUNY–Cortland, work focuses on hydrolysis-rate determinations in deionized water and groundwater using minimal-headspace ampules (headspace-to-liquid ratio of about 1:50) and a home-built zero-headspace reactor. Work at SUNY–Cortland also includes direct determinations of aqueous:vapor partition coefficients for CF using a home-built reactor.

## 2.0 Technical Approach and Method Development

Technical work is organized under three major tasks. Task 1 focuses on the neutral and base-catalyzed homogeneous rates of CF, Task 2 focuses on the heterogeneous rate of CT, and Task 3 focuses on the neutral and base-catalyzed heterogeneous rates of CF. Our approach is designed to succeed in the shortest time possible while producing robust data that will withstand the critical scrutiny of scientists, decision-makers, and stakeholders. Detailed descriptions of each task follow.

### 2.1 Task Descriptions and Experimental Design

#### 2.1.1 Task 1 – Neutral and Base-Catalyzed Homogeneous Hydrolysis of Chloroform

The overall experimental design involves collection of data at six temperatures covering the range of 20°–70°C. Samples are incubated in sterile deionized (DI) water adjusted to one of three initial pH values (3, 8, or 12) with H<sub>2</sub>SO<sub>4</sub> or a 0.1 M sodium phosphate buffer, at one concentration (400 ppm), for periods of up to 5 years. We conduct five replicate analyses for each treatment combination at each of ten times during the experiment, with an additional two replicates reserved for verification of reaction mechanism and 14 vials reserved for determination of initial and total concentrations. Thus, the total number of experimental units is  $6 \times 3 \times 1 \times (7 \times 10 + 14) = 1512$ .

#### 2.1.2 Task 2 – Heterogeneous Hydrolysis of Carbon Tetrachloride

The experimental approach for determination of heterogeneous hydrolysis of CT differs in some respects from that of Task 1 because of logistical constraints. Data are collected at four temperatures (20°, 30°, 40°, and 50°C) and at one concentration (400 ppm). Samples are incubated in one of four environments consisting of sterile Hanford groundwater in the presence of fine-grained mineral powder. As in Task 1, we conduct five replicate analyses for each treatment combination at each of ten times during the experiment, with an additional two replicates reserved for verification of reaction mechanism and 14 vials reserved for determination of initial and total concentrations. Thus, the total number of experimental units is  $4 \times 1 \times 4 \times (7 \times 10 + 14) = 1344$ .

#### 2.1.3 Task 3 – Neutral and Base-Catalyzed Heterogeneous Hydrolysis of Chloroform

The experimental approach for heterogeneous hydrolysis of CF closely follows that of Task 2 except that experiments with Hanford groundwater and sediment suspended in groundwater are included with the four mineral experiments. The total number of experimental units is  $4 \times 1 \times 6 \times (7 \times 10 + 14) = 2016$ .

### 2.2 Groundwater, Sediment, and Minerals

Uncontaminated Hanford groundwater was obtained from Well 699-49-100C located near the Yakima barricade west and up-gradient of the 200-West Area at the Hanford Site. The sample # B1JX90 (SAF# X06-043) was collected on 12 July 2006. Water from this well has been used by the Hanford groundwater monitoring project for background values for a number of years. Although not measured

specifically for the samples in this project (aside from chloride) the composition of the water from this well is summarized from Hanford Environmental Information System (HEIS) data in Table 2.1.

**Table 2.1.** Typical Composition and Chemical Properties of Hanford Groundwater from Well 699-49-100C

Constituent/Property	Value ( $\mu\text{g L}^{-1}$ unless otherwise indicated)
$\text{SO}_4^{2-}$	75000
$\text{NO}_3^-$	13000
$\text{Cl}^-$	19000
$\text{F}^-$	300
$\text{Ca}^{2+}$	60000
$\text{Mg}^{2+}$	21000
$\text{Na}^+$	25000
$\text{K}^+$	7500
Fe (valence unspecified)	30
Alkalinity	175000
Total Organic Carbon	1000
Electrical Conductivity ( $\mu\text{S cm}^{-1}$ )	570
pH (log units)	7.75

Uncontaminated Hanford sediment was a silt loam (22% clay, 78% silt) obtained from Borehole 299-W15-46, SAF#F03-018, SAMP# B19NK8. The sample was collected on 4 January 2005 at 216-Z-9/C3426 from a depth of 421.5 ft to 423.5 ft using a split-spoon liner.

The mineralogy of the Hanford sediment was determined by x-ray diffraction of the whole sediment and of the clay (<2- $\mu\text{m}$  particle size) fraction according to the procedures of Amonette.<sup>1</sup> As discussed in Section 3.2.1, the results of this analysis were used to select four minerals for mono-mineralic heterogeneous hydrolysis experiments.

<sup>1</sup> Amonette JE. 1994a. Soil texture determinations and preparation of samples for mineralogical analysis by x-ray diffraction (XRD). PNL Procedure JEA-2, Revision 0, Pacific Northwest National Laboratory, Richland, Washington.

Amonette JE. 1994b. Mineralogical analysis of soil samples by x-ray diffraction (XRD). PNL Procedure JEA-3, Revision 0, Pacific Northwest National Laboratory, Richland, Washington.

## 2.3 Laboratory Procedures

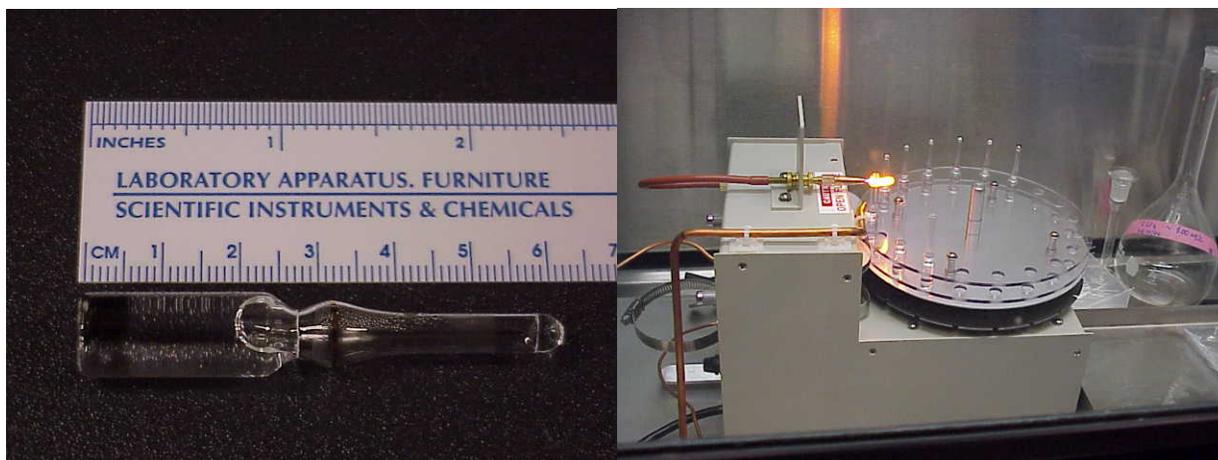
### 2.3.1 PNNL Methods

At PNNL, a stock solution saturated with CT is prepared by adding 8 ml of high-performance liquid chromatography- (HPLC-) grade CT (>99.9% pure, Sigma-Aldrich, 27 0652) to 1 L deionized H<sub>2</sub>O in a borosilicate glass bottle containing 10 glass beads. The mixture is shaken continuously on an orbital shaker at 150 rpm for several weeks before being used. The nominal concentration of CT in this stock solution is about 800 mg L<sup>-1</sup>.

For CF, 0.5 L of pesticide residue analysis- (PRA-) grade CF (>99.9% pure, Sigma-Aldrich, 324019) is purified to remove the amylene stabilizer by contact with 80 g of 13X molecular sieve followed by vacuum degassing. This purified reagent CF is then used to prepare a saturated stock solution by adding at least 100 ml to about 2 L of deionized H<sub>2</sub>O or Hanford groundwater in a volumetric flask that is capped and allowed to shake as for the CT solution for at least two weeks at room temperature. The nominal concentration of CF in the saturated stock solution is 8000 mg L<sup>-1</sup>.

Starting solutions for hydrolysis determinations are prepared in 1.2-L polytetrafluoroethylene (PTFE) gas sampling bags (Alltech 41004, Deerfield, Illinois). The appropriate masses of CT/CF stock solution and deionized water are filter-sterilized (Anotop 25, Whatman) and added to the sampling bag using a sterile glass syringe driven by a syringe pump. For CF experiments, pH control is provided by addition of H<sub>2</sub>SO<sub>4</sub> (pH 3) or a 0.1-M sodium phosphate buffer (pH 8 or 12). Also, 10 μL of neat perchloroethene (PCE), which has an hydrolysis half-life of 10<sup>9</sup> years (Jeffers et al. 1989), is added as an internal standard during gas chromatographic (GC) analyses. Some water is added and headspace in the bag eliminated before the CT/CF stock solution, pH reagent, and PCE are added. A typical final volume in the bag is 800 mL, and initial CT/CF concentrations are nominally 40 or 400 mg L<sup>-1</sup>. After addition, the contents of the bag are mixed by gently squeezing the bag. Then the outlet on the bag is attached to the inlet of a dispenser designed for organic liquids (Dispensette Organic, BrandTech Scientific, Essex, Connecticut), and the contents are dispensed through a large-bore stainless-steel needle into ampules for immediate sealing.

The hydrolysis experiments are conducted in 1-mL (nominal volume) glass ampules (Figure 2.1 left, Wheaton 176772, Millville, New Jersey). These ampules typically have an internal volume of 2.4 ml when sealed. We add 1.6 ml of aqueous sample to the ampule, leaving 0.8 ml as headspace. The ampules are sealed within 15 s of sample addition using an automatic ampule sealer (Figure 2.1, right; Ampulmatic Model 290 001, Bioscience, Inc., Bethlehem, Pennsylvania).



**Figure 2.1.** Ampule (left) and Automatic Ampule Sealer (right) Used for PNNL Hydrolysis Experiments

For each incubation temperature, 84 ampules are prepared. Seventy of these are incubated at the desired temperature and sampled in batches of seven after various periods to determine hydrolysis rate. The first batch is sampled immediately after ampule sealing and defines the starting conditions for the experiment (e.g., some hydrolysis can occur during the ampule-sealing process due to the high temperatures involved). The remaining 14 ampules are controls. Seven are incubated at 100°C until hydrolysis is complete and then analyzed to determine the *actual* starting concentration of CT/CF in the ampules. The other seven are stored at 4°C where hydrolysis rates are negligible (except for CF at pH 12, which hydrolyzes quite readily). These seven serve as reference points for the initial conditions in case any questions arise during the experiment.

During the ampule-preparation process, 8 of the 84 ampules are selected at regularly spaced intervals to provide data for the estimation of headspace volume (this is done by weighing the empty ampule and the same ampule after filling and sealing). After incubation, but before the ampules are opened during the sampling process, the ampules are reweighed to verify no leakage, and their headspace is determined by a differential density approach. A syringe large enough to contain the ampule is filled with water of known density and weighed. Some of the water is then displaced by the sealed ampule (the total volume within the syringe remains the same with no air bubbles), and the syringe with ampule is reweighed. From these data and the physical properties of the solutions and glass, the headspace within the ampule is calculated by

$$V_{\text{HS}} = (m_{\text{tot}}^{\text{A}} - m_{\text{tot}}^{\text{B}} + m_{\text{Amp+CT/CF}}) / \rho_{\text{H}_2\text{O}} - (m_{\text{Amp}} / \rho_{\text{Amp}}) - (m_{\text{CT/CFsoln}} / \rho_{\text{CT/CFsoln}}) \quad (2.1)$$

where  $m_{\text{tot}}^{\text{A}}$  = mass of syringe filled with H<sub>2</sub>O,  $m_{\text{tot}}^{\text{B}}$  = mass of syringe filled with sealed ampule and H<sub>2</sub>O,  $m_{\text{Amp+CT/CF}}$  = mass of filled ampule,  $\rho_{\text{H}_2\text{O}}$  = density of water,  $m_{\text{Amp}}$  = mass of empty ampule,  $\rho_{\text{Amp}}$  = density of glass in ampule,  $m_{\text{CT/CFsoln}}$  = mass of solution in ampule, and  $\rho_{\text{CT/CFsoln}}$  = density of solution in ampule.

The 70 ampules for hydrolysis measurement are arranged in labeled metal racks (Figure 2.2, left) and incubated at the desired temperature using an air-flow incubator (Figure 2.2, right; Incumax IC 150 or IC 150R, Amerex Instruments, Lafayette, California). Temperature inside each incubator is continuously measured by two thermocouples located near the top and bottom of the incubator volume and recorded on a datalogger (CR3000, Campbell Scientific, Logan, Utah). Thermocouples were calibrated initially using a NIST-certified platinum-resistance thermometer (Hart Scientific 1502A, American Forks, Utah).



**Figure 2.2.** Set of Ampules in Rack (top left) Ready for Insertion into Incubator (bottom left) and Incubator Array Used in PNNL Experiments (right)

After appropriate periods whose length depends on the expected hydrolysis rate and the sensitivity of our analytical determinations, seven samples are removed from the incubator, and the hydrolysis reaction is quenched. For CT and all CF samples except those at pH 12, quenching is achieved by storage in a 4°C refrigerator. When convenient for analysis (or immediately for pH-12 CF samples), five samples from each time period are opened and their contents transferred to precleaned glass ion chromatography (IC) vials. The precleaning procedure to remove traces of chloride from the IC vials involves soaking them in deionized H<sub>2</sub>O for several days, with two changes of H<sub>2</sub>O during the first day and one change on each subsequent day. The transferred samples remain at 4°C until IC analysis. For all CF samples, 0.5 mL of hexane is added to the vial to extract CF from the aqueous solution. This is necessary to prevent damage to the IC column. If the expected levels of the analyte (chloride ion) are greater than 100 mg L<sup>-1</sup>, then 5x dilutions with deionized H<sub>2</sub>O are made from these vials prior to analysis. Otherwise, the vials are analyzed without dilution. Chloride concentrations are determined by IC (Dionex DX-500, AS11-HC column, suppressed conductivity detection). The remaining two samples from each time period are reserved for GC analysis to verify that only hydrolysis reactions occurred (e.g., reduction of CT would yield some chloroform as a product, which is easily detected by GC methods).

### 2.3.2 SUNY–Cortland Methods

At SUNY–Cortland, the same general approach is used as at PNNL (i.e., hydrolysis in sealed glass container at temperatures in the 20°–70°C range). Differences are found, however, in the type of container, the headspace-to-liquid ratio, and in the type of incubator. These measurements utilized two

water baths constructed this year, controlled with mercury sensors and electronic relays; they were easily adjusted to desired temperatures and were stable within 0.1 degree for intervals as long as a month (the longest duration of the actual measurements). Temperatures were measured with mercury thermometers reading to 0.1 degree, and the calibration was checked with ice/deionized water.

Early experiments were conducted using sealed bulbs made from borosilicate glass tubing. The bulbs were drawn from 8-mm-outside diameter tubing and typically had a volume of about 1 mL with a void volume of 0.04–0.1 mL at 20°C. At high temperature, 70°C, the void volume was reduced to 0.02–0.08 mL (value determined by both calculation and measurement). A problem that became apparent early in the work was the appearance of measurable  $Cl^-$  in  $t = 0$  bulbs, due to inadvertent heating of the solution during the sealing process. Redesign of the bulbs reduced this problem but failed to eliminate it. A second problem observed in an early bulb experiment at 60°C was the clear evidence of microbial activity. This problem was solved by treating all glassware and other implements that would touch the solution by heating at 120°C overnight and wearing surgical gloves for bulb filling. A third problem was associated with determination of the appropriate correction to the observed rate constant to account for partitioning of CT between liquid and headspace. The variable headspace in these bulbs and the consequential need to measure headspace on each and every bulb made corrections for CT partitioning tedious at best and added considerable uncertainty to the data, particularly at the higher temperatures.



**Figure 2.3.** Zero-Headspace Reactor (top) and Apparatus for Determination of Liquid-Vapor Partition Coefficients (bottom) Fabricated and Used for Hydrolysis Experiments at SUNY–Cortland

To avoid the problems with premature hydrolysis and uncertain headspace, a zero-headspace reactor (ZHR) was designed, fabricated, and used with significant success in these studies. The body of the ZHR (Figure 2.3, top) is a 10-cm length of 20-mm Pyrex tubing with a 10-cm length of 2-mm inside-diameter Pyrex capillary at one end and a 25-cm length of 8-mm outside-diameter Pyrex tubing at the other end. The capillary is flared at the end to fit inside a 0.25-in. Swagelok fitting and affords a glass- to 10-mm-GC septum seal. The 8-mm tubing is bent in a U and terminates in a 2-mm Teflon stopcock with a 2-cm by 10-mm Pyrex reservoir at the top, which extends slightly beyond the capillary end. The reactor is filled using a 50-mL glass syringe with a long wide-bore needle until the solution just spills out past the loosened Swagelok nut, which is then secured. The ZHR is placed into a water thermostat bath with only

the ends above water, and the stopcock remains open until the solution is temperature-equilibrated. Samples are drawn into a 1-mL glass syringe fitted with a 15-cm 17-gauge needle that extends to the middle of the reactor body. The stopcock is opened for the sampling process, and fresh reaction mix is placed in the reservoir above the stopcock. Typically, 0.2–0.3 mL of solution are withdrawn for analysis. Thus, a run totaling 10 samplings drains far less solution than is contained in the 8-mm feed tube, while the very narrow-gauge sampling needle causes little mixing in the capillary sampling arm.

The ZHR and all associated glassware, syringes, and needles are heat-sterilized before use. The deionized water is boiled and sparged with a flow of He to remove dissolved air. This prevents the formation of air bubbles inside the reactor to which reactant could partition during a run and is an important precaution to take at all temperatures above 40°C.

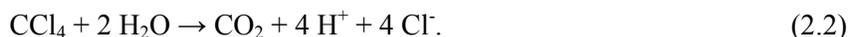
An essential quantity in calculating the rate constant is the initial concentration of reactant. For experiments in deionized water, this value can be measured by complete hydrolysis of the reactor solution at the end of a run, measuring the total chloride ion liberated. Initially, with CT, about 1 mL of solution was withdrawn from the reactor, injected into a 1.2-mL bulb drawn from 8-mm Pyrex tubing. The bulb was then quickly flame-sealed and placed in a 130°C oven for about 30 hr. CT has a half-life of about 2 hr at 130°C, so hydrolysis should have been complete. The bulb was opened, and the solution quantitatively diluted to a range appropriate for IC analysis. A recent significant improvement has been to do the dilution prior to hydrolysis by drawing 7-cm-long bulbs from 12-mm Pyrex tubing, adding a weighed amount of deionized water, then injecting about 0.3–0.4 mL solution with the sampling syringe, carefully keeping the needle tip near the bottom of the bulb, then quickly flame-sealing and re-weighing to determine the dilution factor. The revised process allows very little opportunity for reactant to diffuse out of solution before the bulb is sealed and results in very close agreement on concentration with duplicate samples.

The SUNY–Cortland experiments with CF utilized 0.01 M NaOH solutions. Concentrations of CF were about 50–150 mg L<sup>-1</sup>, or 0.00126–0.00378 M, low enough that the base concentration changed little during the experiment (<10% completion) and pseudo-first-order kinetics could be assumed. Advantages of the dilute base approach are that the OH<sup>-</sup> concentration can be measured directly and there is no temperature dependence on any acid/base equilibrium constant, as would be the case with any buffer solution. Another advantage is that kinetics properly uses concentration rather than activity, which is the quantity reported by a pH meter. The concentration can be measured directly and accurately by titration of a primary standard, potassium hydrogen phthalate in this case. Finally, at this base concentration, CF hydrolyzes to completion in 2 days at 70°C, so to determine final concentration the entire ZHR could be placed in an oven, stopcock open until the temperature had equilibrated, affording the entire reactor contents for final analysis.

## 2.4 Calculations

### 2.4.1 Carbon Tetrachloride

The hydrolysis of CT follows the overall reaction



The rate law for this reaction is

$$-d[\text{CCl}_4]/dt = (1/4)d[\text{Cl}^-]/dt = k[\text{CCl}_4] \quad (2.3)$$

which, upon integration, yields

$$[\text{Cl}^-]_t = 4[\text{CCl}_4]_0[1 - \exp(-kt)]. \quad (2.4)$$

Rearranging and taking the natural log of both sides yields

$$\ln\{1 - [\text{Cl}^-]_t/(4[\text{CCl}_4]_0)\} = -kt. \quad (2.5)$$

A plot of the left side of Equation 2.5 versus time yields a straight line with a slope of  $-k$ , the apparent rate constant.

In our work, we determine  $[\text{CCl}_4]_0$  by the difference between the final  $[\text{Cl}^-]$  with complete hydrolysis [i.e., data from long-term hydrolysis at 100°C (PNNL) or 130°C (SUNY–Cortland)] and the initial  $[\text{Cl}^-]$  [data from time = 0 samples]. We then calculate the value of the left side of Equation 2.5 for each time data point in the given experiment. Regression of these values against the corresponding incubation times yields the slope, from which the apparent rate constant ( $k_{\text{app}}$ ) is obtained by multiplying by  $-1$ . For reaction vessels with headspace, partition equilibrium is assumed and the apparent rate constant is corrected to obtain a rate constant normalized to zero headspace ( $k_{\text{zhs}}$ ) by

$$k_{\text{zhs}} = k_{\text{app}} [1 + (K_{\text{H}}')(V_{\text{v}}/V_{\text{l}})] \quad (2.6)$$

where  $K_{\text{H}}'$  is the dimensionless Henry's law vapor-partition coefficient, and  $V_{\text{l}}$  and  $V_{\text{v}}$  are the equilibrium liquid and vapor volumes.

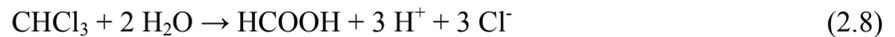
## 2.4.2 Chloroform

The hydrolysis of CF follows two parallel pathways. One of these is independent of pH, whereas the other is first order in  $\text{OH}^-$ . The rate of CF hydrolysis, therefore, is the sum of the rates of the two pathways:

$$-d[\text{CHCl}_3]/dt = (k_{\text{N}} + k_{\text{B}}[\text{OH}^-])[\text{CHCl}_3] \quad (2.7)$$

where  $k_{\text{N}}$  is the rate constant for the neutral (pH-independent) pathway, and  $k_{\text{B}}$  is the rate constant for the base-catalyzed pathway.

The neutral hydrolysis pathway is

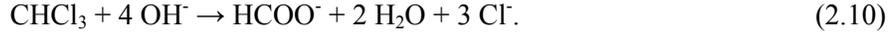


and the corresponding integrated and rearranged rate law is analogous to that for CT shown in Equations 2.3 through 2.5:

$$\ln\{1 - [\text{Cl}^-]_t/(3[\text{CHCl}_3]_0)\} = -k_{\text{N}}t. \quad (2.9)$$

Neutral hydrolysis is the dominant pathway at pH < 4, and Equation 2.9 can be used to estimate CF hydrolysis under those conditions.

At pH greater than 4, the base-catalyzed hydrolysis pathway becomes important (and is dominant at pH > 8) due to the strong neutrophilic character of the hydroxyl ion. The overall reaction can be written as



The rate law for the base-catalyzed hydrolysis reaction is second-order overall, being first-order in both CHCl<sub>3</sub> and OH<sup>-</sup>:

$$-d[\text{CHCl}_3]/dt = -(1/4)d[\text{OH}^-]/dt = (1/3)d[\text{Cl}^-]/dt = k_B[\text{CHCl}_3][\text{OH}^-] \quad (2.11)$$

When the concentrations of CHCl<sub>3</sub> and OH<sup>-</sup> differ by a factor of 10 or more, the reactant at higher concentration remains essentially constant during the first stages of the reaction and the reaction becomes pseudo-first-order (PFO). Thus, at pH 12 and higher, where OH<sup>-</sup> is in excess, the PFO rate law becomes

$$-d[\text{CHCl}_3]/dt = -(1/4)d[\text{OH}^-]/dt = (1/3)d[\text{Cl}^-]/dt = k_{\text{Bpfo1}}[\text{CHCl}_3] \quad (2.12)$$

where  $k_{\text{Bpfo1}}/[\text{OH}^-]_0 = k_B$ . By analogy to Equations 2.4 and 2.5, the rearranged integrated rate law then becomes

$$\ln \{1 - [\text{Cl}^-]_t / (3[\text{CHCl}_3]_0)\} = -k_B t \quad (2.13)$$

At pH 8, where CHCl<sub>3</sub> is in excess and the base-catalyzed rate is still much faster than the neutral rate, the PFO rate law becomes

$$-d[\text{CHCl}_3]/dt = -(1/4)d[\text{OH}^-]/dt = (1/3)d[\text{Cl}^-]/dt = k_{\text{Bpfo2}}[\text{OH}^-] \quad (2.14)$$

where  $k_{\text{Bpfo2}}/[\text{CHCl}_3]_0 = k_B$ , and by analogy to Equations 2.12 and 2.13,

$$\ln \{1 - [\text{Cl}^-]_t / (3[\text{OH}^-]_0)\} = -k_B t \quad (2.15)$$

At pH greater than 8, then Equation 2.13 or 2.15 can be used to estimate overall CF hydrolysis given the dominance of  $k_B$ . Between pH 4 and pH 8, neither hydrolysis mechanism (i.e., neutral or base-catalyzed) is dominant, and the overall hydrolysis rate for chloroform is best approximated using both rate constants as in Equation 2.7.

### 2.4.3 Half-Life

Half-lives can be calculated when first-order kinetics apply. They can be calculated also for second-order kinetic systems, if these are converted to PFO and with the caveat that the concentration of the “constant” reactant indeed remains constant for the duration of the reaction. Thus, for CT, and for CF at pH less than 4 or greater than 8, the half-life is estimated by

$$t_{1/2} = (3.168e-8)\ln(2)/k \quad (2.16)$$

where the first factor on the right side converts the rate constant from seconds to years, and  $k$  can be  $k_{zhs}$ ,  $k_N$ , or  $k_B$ . For CF between pH 4 and pH 8, the half life can be estimated by substituting  $k_N + k_B[\text{OH}^-]$  for  $k$  in Equation 2.16.

#### 2.4.4 Activation Energy

Activation energies are calculated from values of  $k$  at several temperatures using the logarithmic form of the Arrhenius expression

$$\ln(k) = \ln(A) - (E_a/R)(1/T) \quad (2.17)$$

where  $k$  can be  $k_{zhs}$ ,  $k_N$ , or  $k_B$  ( $\text{s}^{-1}$ ),  $A$  is the pre-exponential factor ( $\text{s}^{-1}$ ),  $E_a$  is the activation energy ( $\text{J mol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the reaction temperature (K). Regression of  $\ln(k)$  versus  $(1/T)$  yields a slope of  $E_a/R$ , from which  $E_a$  is readily calculated. As with half-lives, the use of PFO rate constants (such as  $k_B$ ) carries the assumption that the “constant” reactant remains constant and the values of  $A$  and  $E_z$  thus calculated are valid for only the specific concentration of “constant” reactant.

#### 2.4.5 Determination of Liquid-Vapor Partition Coefficients

An apparatus was designed and fabricated, and techniques were developed to measure liquid-vapor partition coefficients at the temperatures and conditions of our experiments, as the only available data (Gorgenyi et al. 2002) did not extend beyond  $60^\circ\text{C}$  and were not necessarily valid for the high concentrations we were using. The apparatus (Figure 2.3, bottom), which consists of a 50-mL round-bottom Pyrex bulb with the neck replaced by a 5-cm length of 1-mm-inner diameter capillary glass flared at the top and fitted with a 0.25-in. fitting (Swagelok) so that a rubber septum directly sealed to the glass, is similar to the ZHR but with no second fill-tube. The bulb can be rinsed, filled, and drained using a syringe. In practice, the bulb is weighed empty, filled using a 50-mL syringe and long wide-bore needle, weighed full, and sampled with a 1-mL syringe and 17-gauge needle, then drained about one-third using the 50-mL syringe, quickly sealed, reweighed, and immersed in the thermostat bath. The bulb is shaken several times over a 15–30-min interval, then sampled through the septum while still in the bath, to determine an equilibrium solution concentration. During the draining process, some solution is deposited in the capillary to serve as an indicator that no solution or vapor escapes through the septum. The initial and equilibrium samples are then hydrolyzed to completion as with the ZHR experiments. The dimensionless partition coefficient turns out to be simply calculated as

$$K_{lv} = [(C_0 - C_f)/C_f](V_l/V_v) \quad (2.18)$$

where  $C_0$  and  $C_f$  are the initial and equilibrium liquid concentrations of Cl<sup>-</sup> in ppm, and  $V_l$  and  $V_v$  are the equilibrium liquid and vapor volumes.

## 3.0 Hydrolysis Rate Experiments

### 3.1 Homogeneous Chloroform Experiments

The status of the homogeneous chloroform hydrolysis experiments at PNNL as of September 2008 is summarized in Table 3.1. As each experiment involves sampling at 10 separate time periods, the progress is given in terms of the number of sampling periods that have occurred (i.e., percentage of the initial ampules filled that have been terminated). As can be seen, a total of four homogeneous hydrolysis experiments with CF have been started, two at pH 3, one at pH 8, and one at pH 12. Hydrolysis is rapid at pH 12, and those experiments are complete (Table 3.1). In addition, the highest-temperature (50°C through 70°C) experiments at pH 8, and the 70°C experiments at pH 3 are complete (Table 3.1). The hydrolysis rates are considerably slower at pH 8 and temperatures below 50°C, and several years may be required to obtain useful data at 20°C. Several years will also be required to obtain hydrolysis rates at some of the lower temperatures for pH 3, where only neutral hydrolysis is important.

**Table 3.1.** Status of PNNL Homogeneous CF Hydrolysis Experiments

	pH 3, 33 ppm CF, 1 mM H <sub>2</sub> SO <sub>4</sub>	pH 3, 229 ppm CF, 1 mM H <sub>2</sub> SO <sub>4</sub>	pH 8, 182 ppm CF, 0.1 M phosphate	pH 12, 285 ppm CF, 0.1 M phosphate
Temperature, °C	----- Percentage of experiment sampled as of September 2008 -----			
70	100	100	100	--
60	60	60	100	--
50	50	50	100	100
40	40	40	40	100
30	--	30	20	100
20	--	30	20	100

At SUNY–Cortland, seven experiments at six temperatures between 22°C and 60°C and pH 12 have been completed. As noted in Table 3.1, only base-catalyzed experiments conducted at pH 8 and 12, and the 70°C experiments at pH 3, are at a stage where rate constants can be calculated. These data are summarized in Table 3.2 and Table 3.3 along with the initial reactant concentrations and the dimensionless Henry’s law constants derived from Gorgenyi et al. (2002). Note that all the PNNL data at pH 8 and 12 were collected in 0.1 m phosphate buffers. All rate constant values must be considered provisional pending further review of the data.

**Table 3.2.** Provisional Rate Constants for Neutral Homogeneous Hydrolysis of CHCl<sub>3</sub>

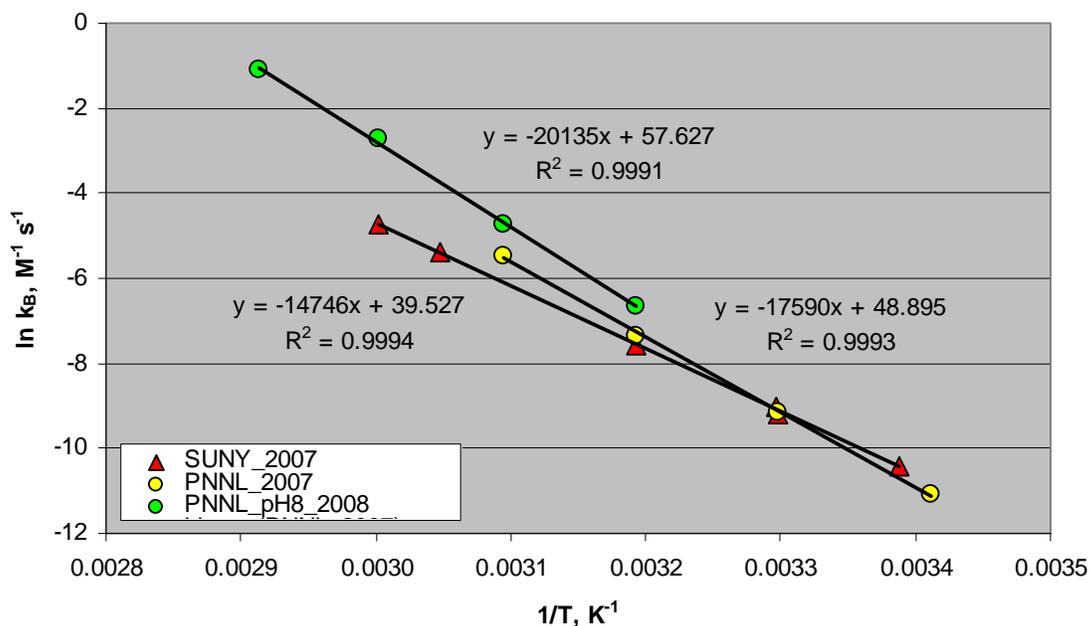
Temperature, °C	Initial CHCl <sub>3</sub> Concentration, mg kg <sup>-1</sup>	$k_N$ , PNNL (1 mM H <sub>2</sub> SO <sub>4</sub> ), s <sup>-1</sup>	$K_H'$ (Gorgenyi et al. 2002)
70	38	2.68e-9	0.752
70	334	2.89e-9	0.752
60	38	5.46e-10	0.541
60	334	6.55e-10	0.541

**Table 3.3.** Provisional Rate Constants for Base-Catalyzed Homogeneous Hydrolysis of CHCl<sub>3</sub>

Temperature, °C	Initial CHCl <sub>3</sub> Concentration, mg kg <sup>-1</sup>	Initial OH <sup>-</sup> Concentration, mol kg <sup>-1</sup>	$k_B$ , SUNY, kg mol <sup>-1</sup> s <sup>-1</sup>	$k_B$ , PNNL (0.1 m phosphate), kg mol <sup>-1</sup> s <sup>-1</sup>	$K_H'$ (Gorgenyi et al. 2002)
70	182	1.72e-6	--	3.33e-1	0.752
60	182	1.72e-6	--	6.67e-2	0.541
60	58	9.74e-3	8.70e-3	--	--
55	157	9.59e-3	4.55e-3	--	--
50	182	1.72e-6	--	8.84e-3	0.417
50	285	2.44e-2	--	4.19e-3	0.417
40	182	1.72e-6	--	1.27e-3	0.296
40	157	9.59e-3	5.18e-4	--	--
40	58	9.74e-3	5.18e-4	--	--
40	285	2.44e-2	--	6.46e-4	0.296
30.15	50	1.01e-2	1.22e-4	--	--
30	190	9.74e-3	1.00e-4	--	--
30	285	2.44e-2	--	1.05e-4	0.209
22	157	9.59e-3	2.98e-5	--	--
20	285	2.44e-2	--	1.57e-5	0.137

The neutral hydrolysis results (Table 3.2) show excellent agreement between the experiments conducted at the same temperature, even though the initial CF concentrations differ by a factor of ten. This result is consistent with expectations that solute concentration has negligible impact on liquid–vapor partition coefficients (Schwarzenbach et al. 1993, pp. 112–114) and hence on the amount of solute in contact with water, the hydrolyzing agent. The neutral hydrolysis rate constants are roughly eight orders of magnitude smaller than the base-catalyzed rate constants shown in Table 3.3.

An Arrhenius plot of the base-catalyzed homogeneous rate data is shown in Figure 3.1. From this plot and Table 3.3, it is clear that the PNNL and SUNY data collected at pH 12 are in good agreement, although the slopes (activation energies) differ by about 14%. The PNNL rate constants from pH 8 data, however, are quite a bit higher than one would expect from the pH 12 data.



**Figure 3.1.** Arrhenius Plot of Base-Catalyzed Homogeneous Hydrolysis Data for CF

The two primary differences between the PNNL and SUNY experimental approaches are the presence of headspace in the ampules and the use of phosphate buffer in the PNNL experiments. The headspace would influence the results only if the Henry's law constants were very large and in doubt. This does not seem to be the case for CF, and so we think it likely that the differences are due to the use of a phosphate buffer. Hydrogen phosphate ( $\text{HPO}_4^{2-}$ ) ions, like hydroxyl ions, are strong nucleophiles and can initiate hydrolysis-like reactions that would release  $\text{Cl}^-$  ions to solution (Swain and Scott 1953; Schwarzenbach et al. 1993, pp. 359–365). Differences in the speciation of phosphate with pH (predominantly  $\text{PO}_4^{3-}$  at pH 12 and a mixture of  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  at pH 8) could account for the difference in values of  $k_B$  between the data collected at these two pHs. Apparently the protonated phosphate ions are much stronger nucleophiles than the  $\text{PO}_4^{3-}$  ion. However, extrapolation of the pH 8 data to groundwater temperatures (ca. 20°C) yields rates that are indistinguishable from those obtained at pH 12. We conclude, therefore, that little impact on hydrolysis rates in typical groundwaters would be expected due to the presence of phosphate ions, or even bicarbonate ions ( $\text{HCO}_3^-$ ), which are ubiquitous in groundwaters and roughly equivalent to  $\text{HPO}_4^{2-}$  in terms of their nucleophilicity (Schwarzenbach et al. 1993, p. 359).

The activation energies for base-catalyzed CF hydrolysis are 123  $\text{kJ mol}^{-1}$  for the SUNY experiments at pH 12, 140  $\text{kJ mol}^{-1}$  for the PNNL experiments in 0.1 m phosphate at pH 12, and about 167  $\text{kJ mol}^{-1}$  for PNNL experiments in 0.1 m phosphate at pH 8. These compare with a value of 105  $\text{kJ mol}^{-1}$  reported from high-temperature experiments by Jeffers et al. (1989) using minimal headspace (ca. 2%) ampules without correction for Henry's law.

## 3.2 Heterogeneous Experiments

### 3.2.1 Sediment Characterization and Selection of Minerals

The results of the textural and mineralogical analysis of the Hanford sediment are summarized in Table 3.4. Based on the particle-size analysis, the sediment can be classified as a silt loam. Quartz was the most abundant mineral, followed by smectite and plagioclase feldspar (60% anorthite/40% albite). Other layer silicates, such as mica/illite and kaolin/serpentine were present in measurable quantities.

Based on this analysis and the ready availability of mineralogically pure samples, we selected montmorillonite (a type of smectite), kaolinite, albite, and muscovite (a type of mica) as the four minerals for testing of heterogeneous effects on hydrolysis (Table 3.5). Quartz, although the most abundant mineral, was not selected because of its ubiquity in soils and sediments. Any heterogeneous effect seen in our tests with bulk sediment that exceeded that for the minerals selected for testing could be attributed to

**Table 3.4.** Texture and Mineralogy of Hanford Sediment

Weight Percent	
Particle Size Class	
Sand (>53 $\mu\text{m}$ )	0
Silt (2-53 $\mu\text{m}$ )	78
Clay (<2 $\mu\text{m}$ )	22
Bulk Mineralogy	
Quartz	49
Plagioclase (60:40 An:Al)	10
Potassium feldspar	1
Smectite	30
Mica/illite	6
Kaolin/serpentine	5

**Table 3.5.** Minerals Used in Heterogeneous Experiments and Their Source Locales

Mineral	Source Locale
Montmorillonite	Newcastle Formation, Crook County, Wyoming (SWy-2, Source Clay of The Clay Minerals Society)
Kaolinite	Bath, South Carolina (Peerless #2)
Albite	Kona, South Carolina (SRM 99a, Soda Feldspar, National Institute of Standards and Technology)
Muscovite	Stoneham, Maine (ground to silt size)

quartz or to a highly reactive mineral that could not be detected by our method. One such class of reactive minerals would be the iron and manganese oxides. If much higher reactivity is seen with the bulk sediment than with our mineralogically pure samples, further work could involve these more reactive but less abundant minerals. We were careful to select minerals that had no Fe(II) in their structures and ensured this by oxidatively sterilizing them with 10% hydrogen peroxide to convert labile Fe(II) to Fe(III).

We used 28 mg montmorillonite in each ampule and 20 mg of the other three minerals. In the initial experiment, the montmorillonite was sterilized by adding the appropriate amount of clay to each ampule as 1 mL of aqueous slurry, incubating for one week to induce vegetative growth of microorganisms, and then adding 0.5 ml of 30% H<sub>2</sub>O<sub>2</sub>. The ampules were wrapped in autoclave paper and oven-dried at 40°C. Once dry, the clay was re-wetted with 0.75 ml H<sub>2</sub>O and dried again. The clay was re-wetted one more time, dried, and then stored in the autoclave paper until use. The other three minerals were sterilized in batch mode before they were weighed into the ampules using a similar sequence of wetting, oxidation with H<sub>2</sub>O<sub>2</sub>, and drying.

### 3.2.2 Heterogeneous Carbon Tetrachloride Experiments

The status of the experiments with CT is summarized in Table 3.6. Three heterogeneous hydrolysis experiments were started in FY 2007 and the remaining one in early in FY 2008. All the experiments involve suspensions of minerals in Hanford groundwater (a separate experiment with Hanford sediment in Hanford groundwater had already been started under the Hanford Groundwater Project). As each experiment involves sampling at 10 separate time periods, the progress is given in terms of the number of sampling periods that have occurred (i.e., percentage of the initial ampules filled that have been terminated). Provisional rate constants for heterogeneous hydrolysis of CT at 50°C and 40°C are given in Table 3.7. Insufficient data have been collected to calculate provisional rate constants for experiments conducted at temperatures below 40°C.

A small, complementary set of experiments using the zero-headspace reactor approach was conducted at SUNY–Cortland with samples of the same kaolinite and montmorillonite minerals obtained from PNNL. These experiments, which were conducted at a single temperature (20°C), yielded highly variable results, which we chose not to report. Failure of the primary ion chromatograph, coupled with other demands on Prof. Jeffers’ time, did not allow further exploration of the issue.

**Table 3.6.** Status of PNNL Heterogeneous CT Hydrolysis Experiments in Hanford Groundwater

	Montmorillonite	Kaolinite	Albite	Muscovite
Temperature, °C	----- Percentage of experiment sampled as of September 2008 -----			
50	100	100	100	100
40	80	80	80	70
30	70	70	70	60
20	50	50	50	50

**Table 3.7.** Provisional Rate Constants for Hydrolysis of CT in Suspensions of Minerals in Hanford Groundwater

Mineral Phase	Temperature, °C	Initial CCl <sub>4</sub> Concentration, mg L <sup>-1</sup>	k <sub>zhs</sub> PNNL, s <sup>-1</sup>	k <sub>app</sub> PNNL, s <sup>-1</sup>	K <sub>H</sub> ' (Gossett 1987)
Muscovite	50	218	1.50e-08	5.46e-09	3.562
Kaolinite	50	284	1.33e-08	4.85e-09	3.562
Albite	50	271	1.40e-08	5.12e-09	3.562
Montmorillonite	50	328	1.25e-08	4.58e-09	3.562
Muscovite	40	218	3.10e-09	1.44e-09	2.377
Kaolinite	40	284	2.58e-09	1.20e-09	2.377
Albite	40	271	2.96e-09	1.37e-09	2.377
Montmorillonite	40	328	2.75e-09	1.27e-09	2.377

The results show little if any difference in the rates of CT hydrolysis among the four minerals tested. When compared to rates measured in homogeneous solution (Hanford groundwater) and for Hanford sediment in Hanford groundwater obtained in the Hanford Groundwater Project study<sup>1</sup>, these mineral-specific rates tend to be similar or slightly slower. As that project has demonstrated, however, the primary influence of heterogeneous surfaces on CT hydrolysis rates manifests itself at temperatures below 40°C. Completion of the experiments at lower temperatures, therefore, is needed before any conclusions can be drawn about the possible influence of these specific mineral phases on CT hydrolysis rates.

### 3.2.3 Heterogeneous Chloroform Experiments

The status of the heterogeneous experiments with CF is summarized in Table 3.8. Four experiments were started in FY 2007 and the remaining one early in FY 2008. All the experiments involve suspensions of minerals or Hanford sediment in Hanford groundwater. As each experiment involves sampling at 10 separate time periods, the progress is given in terms of the number of sampling periods that have occurred (i.e., percentage of the initial ampules filled that have been terminated). Provisional rate constants for heterogeneous hydrolysis of CF at 50°C are given in Table 3.9. Insufficient data have been collected to calculate provisional rate constants for experiments conducted at temperatures below 50°C.

In stark contrast to the mineral-specific rates obtained for CT, the heterogeneous hydrolysis rates obtained for CF vary by a factor of 20. This result likely stems from different pH values maintained by these minerals in contact with Hanford groundwater and is the subject of planned work in FY 2009.

<sup>1</sup> Amonette JE, PM Jeffers, O Qafoku, CK Russell, TW Wietsma, and MJ Truex. *Abiotic Degradation Rates for Carbon Tetrachloride: Progress in FY2008*. 2008 Draft Report, Pacific Northwest National Laboratory, Richland, Washington.

**Table 3.8.** Status of PNNL Heterogeneous CF Hydrolysis Experiments in Hanford Groundwater

	Hanford Sediment	Montmorillonite	Kaolinite	Albite	Muscovite
Temperature, °C	----- Percentage of experiment sampled as of September 2008 -----				
50	90-completed	70	70	70	70
40	50	40	60	60	30
30	40	30	30	30	30
20	40	30	30	30	30

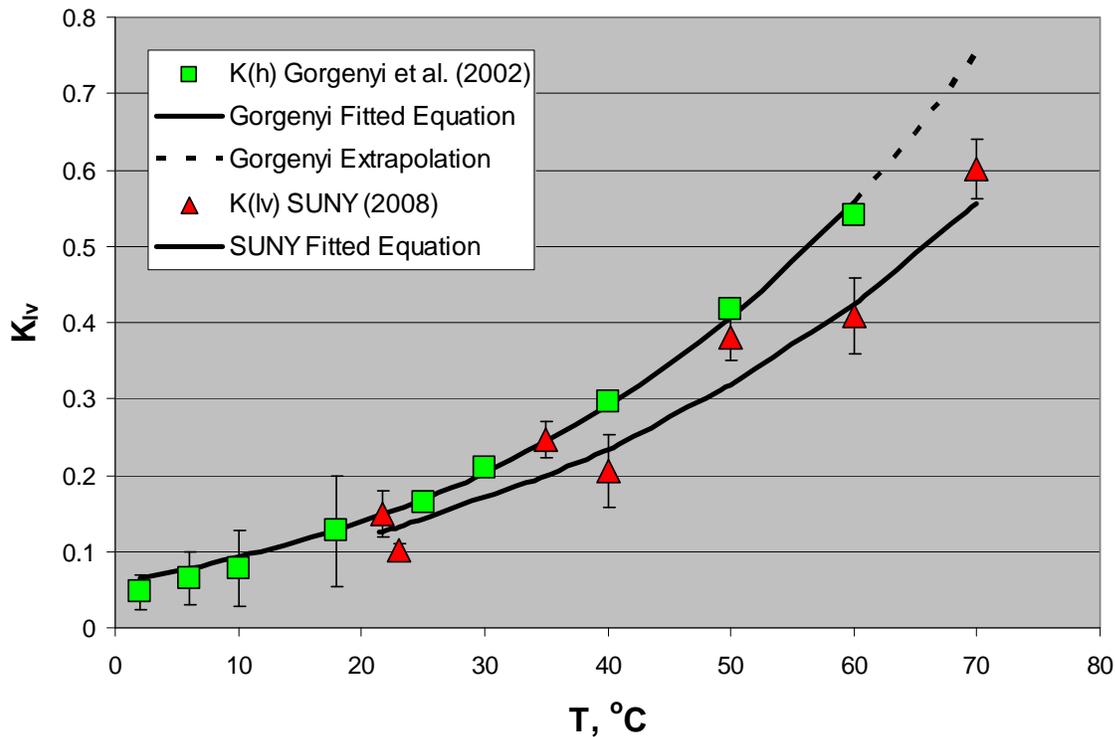
**Table 3.9.** Provisional Rate Constants for Hydrolysis of CF in Suspensions of Hanford Sediment or Specific Minerals in Hanford Groundwater

Solid Phase	Temperature, °C	Initial CHCl <sub>3</sub> Concentration, mg L <sup>-1</sup>	k <sub>zhs</sub> PNNL, s <sup>-1</sup>	k <sub>app</sub> PNNL, s <sup>-1</sup>	K <sub>H</sub> ' (Gorgenyi et al. 2002)
Hanford Sediment	50	276	9.42e-3	7.83e-3	0.417
Muscovite	50	276	8.15e-3	6.78e-3	0.417
Kaolinite	50	276	4.69e-3	3.90e-3	0.417
Albite	50	276	5.09e-3	4.23e-3	0.417
Montmorillonite	50	276	4.46e-4	3.71e-4	0.417

## 4.0 Liquid–Vapor Partition Coefficients

Recognizing that use of the Henry’s law constant ( $K_h$ ) is strictly valid only at infinite dilution, direct measurements of liquid–vapor partition coefficients ( $K_{lv}$ ) for CF at the concentrations used in our experiments were conducted at SUNY–Cortland in an attempt to provide experimental values valid under the conditions of our joint experiments.

A total of 32 separate measurements were made at SUNY that sampled essentially the entire range of temperatures and concentrations of our CF hydrolysis rate experiments. The mean values obtained for  $K_{lv}$  are shown Figure 4.1, together with values for  $K_h$  (measured and extrapolated) of Gorgenyi et al. (2002).



**Figure 4.1.** Mean Values of  $K_{lv}$  for CF Measured by SUNY–Cortland, Together with  $K_h$  Values for CF Reported by Gorgenyi et al. (2002)

Clearly, the  $K_{lv}$  results obtained by SUNY and the  $K_h$  values of Gorgenyi et al. (2002) differ, with good agreement obtained only at near-ambient temperatures. A more detailed analysis of the factors contributing to the differences is planned for FY 2009 in order to identify the best way to correct our experimental rate constants for effects of liquid-vapor partitioning. In this report, therefore, the  $K_h$  values of Gorgenyi et al. (2009) are used to calculate provisional rate constants.

## 5.0 Conclusions

Based on the work completed to date, 32 provisional rate constants have been determined. These were chiefly the high-pH and/or high-temperature treatments, for which hydrolysis rates are relatively fast. An additional 31 provisional rate constants remain to be determined as data from the lower-pH and lower-temperature experiments become available in the future.

Provisional activation energies were calculated for the homogeneous base-catalyzed experiments with CF. These were  $123 \text{ kJ mol}^{-1}$  for 0.01 M NaOH (pH 12),  $140 \text{ kJ mol}^{-1}$  for 0.1 M  $\text{Na}_3\text{PO}_4$  (pH 12), and  $167 \text{ kJ mol}^{-1}$  for 0.1 M phosphate buffer (pH 8). These results were substantially higher than the previously reported value of  $105 \text{ kJ mol}^{-1}$  obtained in NaOH. The higher value in NaOH is attributed to the corrections for liquid-vapor partitioning incorporated into the study. The even higher results obtained in phosphate buffers are attributed to parallel hydrolysis reactions caused by the nucleophilic character of the phosphate anions, particularly  $\text{HPO}_4^-$ . Although the activation energies in the phosphate buffers are higher than in NaOH, the rates observed are similar at groundwater temperatures. It is surmised that neither phosphate nor  $\text{HCO}_3^-$ , which is common in groundwaters and has a nucleophilic character comparable to  $\text{HPO}_4^-$ , significantly increases the rates of hydrolysis for CF over those observed in waters where they are absent.

A twenty-fold range in hydrolysis rate constants was obtained for CF in contact with various solid phases at  $50^\circ\text{C}$ . This high sensitivity to type of solid is likely due to the different pH values maintained by the solid surface in contact with the aqueous phase. Further work to clarify this is planned. In contrast, very little effect of mineral type on CT hydrolysis rates was noted. This is consistent with the pH hypothesis for CF because CT hydrolyzes only by a neutral, pH-independent mechanism.

At SUNY-Cortland, liquid-vapor partition coefficients ( $K_{lv}$ ) for CF were measured at the temperatures and CF concentrations used in our homogeneous hydrolysis experiments. These coefficients differed from the values for the Henry's law constant ( $K_h$ ) reported in the literature; in general, the  $K_{lv}$  values were lower, and the size of the difference from  $K_h$  increased with temperature.

Key achievements of this project have been the 1) initiation of 13 major low-temperature experiments at PNNL involving a total of nearly 4800 ampules; 2) completion of one major set of experiments at pH 12 for base-catalyzed hydrolysis of CF involving work at both PNNL and SUNY-Cortland; 3) collection of preliminary evidence suggesting that nucleophiles other than  $\text{H}_2\text{O}$  and  $\text{OH}^-$  (such as  $\text{HPO}_4^{2-}$  and  $\text{HCO}_3^-$ ) can accelerate the abiotic degradation of CF at high temperatures, but that their effects are negligible at temperatures and concentrations typical of groundwaters; and 4) measurement of  $K_{lv}$  values for CF demonstrating the departure from Henry's law under the conditions of our experiments. Our results confirm the large difference between the neutral and base-catalyzed homogeneous hydrolysis rates for CF in homogeneous solution. Consistent with the dominance of the base-catalyzed reaction, initial results for heterogeneous hydrolysis of CF suggest that the pH maintained at the solid surface will largely dictate the rate at which CF hydrolyzes.

Sampling and analysis of these experiments in the next several years to complete this unique dataset will result in an improved predictive capability that incorporates the effects of both temperature and solid phase. Such a capability is essential to a scientifically based approach to remediation of CT and CF contamination in groundwater systems.

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