Environ. Sci. Technol. 1988, 22, 658–663

(37) Kaiser, K. L. E. *Chemosphere* **1983**, *12*, 1159.
(38) Kenaga, E. *Environ. Sci. Technol.* **1980**, *14*, 553.
(39) Perkow, J.; Eschenroeder, A.; Goyer, M.; Stevens, J.; Wechsler, A. "An Exposure and Risk Assessment for 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin"; Office of Water Regulations and Standards, U.S. EPA: Washington, DC, 1980.
(40) Johnson, H. *Aquatic Fate Process Data for Organic Priority Pollutants*; Mabey, W. R., Ed.; EPA Final Report on Contract 68-01-3867; U.S. Government Printing Office: Washington, DC, 1982.
(41) Marple, L.; Berridge, B.; Throop, L. *Environ. Sci. Technol.* **1986**, *20*, 397.
(42) Schroy, J. M.; Hileman, F. D.; Chang, S. C. *Chemosphere* **1985**, *14*, 877.
(43) Schroy, J. M.; Hileman, F. D.; Chang, S. C. In *Aquatic Toxicology and Hazard Assessment*, 8th Symposium; Bahner, R. C., Hansen, D. J., Eds.; ASTM STP 891, American Society for Testing and Materials: Philadelphia, 1985; pp 409–421.
(44) Podoll, R. T.; Jaber, H. M.; Mill, T. *Environ. Sci. Technol.* **1986**, *20*, 490.
(45) Rordorf, B. F., Ciba Geigy Ltd., Switzerland, private communication, 1986.
(46) Rordorf, B. F. *Chemosphere* **1986**, *15*, 1325–1332.
(47) Chiou, C. T.; Manes, M. J. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 243.
(48) Burkhard, L. P.; Armstrong, D. E.; Andren, A. W. *Environ. Sci. Technol.* **1985**, *19*, 590.
(49) Gobas, F. A. C.; Shiu, W. Y.; Mackay, D.; Opperhuizen, A. *Chemosphere* **1986**, *15*, 1985.
(50) Opperhuizen, A.; Wahenaar, W. J.; Van der Wielen, F. W. M.; Van der Berg, M.; Olie, K.; Gobas, F. A. P. C. *Chemosphere* **1986**, *15*, 2049.
(51) Kuehl, D. W.; Cook, P. W.; Batterman, A. R. *Chemosphere* **1985**, *14*, 871.
(52) Muir, D. C. G.; Marshall, W. K.; Webster, G. R. B. *Chemosphere* **1985**, *14*, 829.
(53) Gobas, F. A. P. C.; Shiu, W. Y.; Mackay, D. In *QSAR in Environmental Toxicology—II*; Kaiser, K. L. E., Ed.; Reidel: Dordrecht, Holland, 1987; pp 107–123.

*Received for review February 2, 1987. Revised manuscript received November 24, 1987. Accepted December 18, 1987.*

# Effect of a Subsurface Sediment on Hydrolysis of Haloalkanes and Epoxides

**Werner R. Haag and Theodore Mill***

Chemistry Laboratory, SRI, Menlo Park, California 94025

■ Neutral and base-catalyzed hydrolyses of isopropyl bromide, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, and ethylene dibromide were studied in pure water and in barely saturated subsurface sediment at 25–60 °C. Half-lives in sediment at 25 °C were 2.1, 29, 450 (measured), and 1500 days (calculated), respectively. No significant differences in the kinetics or products were observed in the sediment pores compared to those in water at the same pH, indicating that the effects of ionic strength, surface catalysis, and adsorption are unimportant for the low-carbon sediment studied. Thus, kinetic and product data for haloalkanes obtained in pure water are applicable to such groundwater systems. On the other hand, epoxide hydrolysis can be affected by the presence of sediments; styrene oxide (acid catalyzed below pH 7) hydrolyzed 4 times faster in sediment than in buffered water and also formed benzaldehyde by oxidation.

## *Introduction*

Contamination of groundwater from landfills, hazardous waste dumps, septic systems, and underground storage tanks, etc. continues to be a major environmental problem. Although knowledge about the chemical and microbiological effects of (organic-rich) soils and surface sediments on the transport and transformation of chemicals is considerable (*1–3*), much less is known about such effects in low-carbon, subsurface sediments, which often represent the largest fraction of aquifer material. The purpose of this study was to evaluate whether or not these types of sediments substantially alter hydrolysis kinetics and pathways from those observed in surface waters. Such information will provide a basis for predicting hydrolysis rate constants and products in groundwater systems for a variety of hydrolyzable structures for use in fate and exposure models and will help develop generalizations about structure, reactivity, and the effect of varying sediment properties.

Hydrolysis rates and products can be affected by such factors as ionic strength, acid or base catalysis, surface catalysis, and partitioning into nonaqueous regimes (*3–5*). Recent work (*6, 7*) has shown that rates of acid-catalyzed hydrolysis of compounds in unsaturated clays can be orders of magnitude higher than rates in distilled water having the same bulk pH. This effect was attributed to an enhanced acidity at the clay surface. A potential for altered rates and products in such systems exists due to catalysis at the sediment surface and to ionic strength effects or general acid or base catalysis by the inorganic solutes present.

Other physical, chemical, and biological processes compete in the transport and transformation of compounds in surface water or groundwater. Microbial processes are often important, and oxidizing or reducing agents in sediments such as transition metals or sulfides may introduce alternate chemical pathways (*8*). However, hydrolysis of leached chemicals can be a significant transformation process in sediments even when hydrolysis rates are low, if competing processes are slow or absent. This can be true particularly for small halogenated compounds that are often not readily biotransformed (*9*). In this study, experiments were specifically designed to minimize intervention in hydrolysis by volatilization, biotransformation, or chemical reduction by using sealed, sterile sediments under aerated conditions; oxidation processes could occur, but with one exception, products indicated that losses were due entirely to hydrolysis.

We have chosen for study four halogenated organic compounds, isopropyl bromide (IPB), 1,1,1-trichloroethane (TrCE), 1,1,2,2-tetrachloroethane (TeCE), and 1,2-dibromoethane (ethylene dibromide, EDB) as examples of solvents or pesticides entering groundwaters. TrCE has come into widespread use as a solvent, particularly as a degreaser in the semiconductor industry, since trichloroethane was banned for this use in 1979 as a potential carcinogen (*10*). In general, such compounds exhibit no specific acid catalysis, but reaction may occur with OH$^-$ (*4*). Hydrolyses of haloalkanes typically are slow ($t_{1/2} \approx$ weeks to years) and can proceed either by elimination of hydrohalide to yield relatively stable haloolefins or by

0013-936X/88/0922-0658$01.50/0

HAR18701

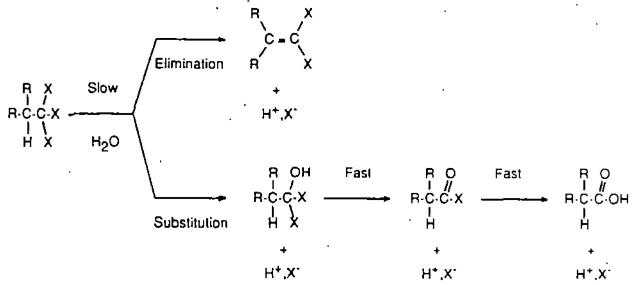

**Figure 1.** Generic hydrolysis scheme for haloalkanes.

substitution of OH for halogen (Figure 1). Haloolefins generally pose more of a threat to human health than substitution products because the former are potential mutagens and carcinogens (*11*).

In pure water IPB hydrolyzes rapidly ($t_{1/2}$ = 51.2 h at 25 °C) independent of pH from pH 3 to pH 11 to form 2-propanol as the only organic product (*5, 12*). TrCE hydrolyzes slowly ($t_{1/2} \approx$ 300 days at 25 °C) independent of pH from pH 3 to pH 11 (*13*). Pearson and McConnell (*14*) state qualitatively that 1,1-dichloroethene (DCE) is the major product at 10 °C while acetic acid (HOAc) forms predominantly at 70 °C. Vogel and McCarty (*15*) confirmed the formation of DCE (at 20 °C) but did not measure HOAc. TeCE is known to react by a base-promoted elimination to yield trichloroethene (TCE), but it has been studied only at high temperature or pH (*16–18*). Studies of EDB have reported half-lives of 1.5–4 years at 25 °C, and some uncertainty remains about the products (*19–21*). Vogel and Reinhard (*19*) and Jungclaus and Cohen (*20*) have detected the formation of vinyl bromide (VB), while Weintraub et al. (*21*) find ethylene glycol (EG) to be the major product and find no VB formation. In none of these cases was the effect of sediment on kinetics or pathways known.

In addition to these haloalkanes, we have studied two epoxides, styrene oxide (SO) and 2,3-epoxypropyl *p*-methoxyphenyl ether (EME) as examples of compounds that exhibit specific acid catalysis. Earlier work had shown that the hydrolysis rate of EME increases by up to a factor of 10 in unsaturated clays (*6*). The hydrolysis of SO in distilled water was studied extensively by Ross et al. (*22*).

## *Materials and Methods*

**Materials.** All compounds were obtained from commercial sources and used as received, except for TrCE, which was distilled. Solvents for use with GC/ECD (hexane and isooctane) were distilled to remove halogenated impurities. Aqueous solutions were prepared in Milli-Q water (Millipore Corp.) (abbreviated DW), typically by injecting 0.05–1.0 μL of neat compound into 60–250 mL of rapidly stirred water or buffer in a glass stopperable bottle with minimal headspace. Occasionally 0.1% acetonitrile was used as a cosolvent, but this had no noticeable effects on the results. Montmorillonite KSF (30–60 μm, Aldrich Chemical Co.) was converted to the sodium form by equilibration with NaCl, treated with $H_2O_2$ to destroy organics, washed 3 times with distilled water, and adjusted to pH ~7 with NaOH before drying at 110 °C. Amorphous ferric hydroxide was prepared by adjusting a solution of ferric perchlorate to pH 7 with NaOH and collecting the precipitate by filtration. It was used immediately without drying.

Sediments were provided by EPA Environmental Research Laboratory, Ada, OK, as Lula C1, a sandy material (composite of heaved and split spoon) collected at a depth of between 5.4 and 6.4 m near Lula, OK. The material had been air dried, sieved to give a ≤500-μm fraction, and riffle-split into several fractions. It was described as having a total organic carbon content of 0.02 ± 0.005%, a total surface area of 11 ± 1 $m^2$/g, and a cation-exchange capacity of 2.5 ± 0.2 mequiv $NH_4^+$/g (*23*). We further characterized Lula C1: porosity = 0.36, particle mass density = 2.43 g/mL, and bulk mass density = 1.59 g/mL.

Sediment-extracted pore water (SEW) was obtained by barely saturating sediment samples with Milli-Q water, allowing them to equilibrate overnight, and recovering the water at 1 bar using a 2-bar Tempe pressure cell (Soilmoisture Equipment Corp., Santa Barbara, CA). Ion chromatographic analyses of the pore water gave the following concentrations of constituents: 2 mM chloride, 0.60 mM sulfate, 0.27 mM nitrate, 0.02 mM nitrite, trace of phosphate, and <300 nM iron and copper ions. Carbonate, silicate, and cations were not determined. The pore water had a pH of about 7–7.5 and a buffering capacity of about 1 mM, as determined by titration.

**Sample Preparation.** Because most of the compounds studied are volatile, aqueous solutions were carefully added to vials or ampules by a syringe. Vials were fitted with Mini-nert caps, allowing essentially no headspace. Ampules had their necks drawn thin in order to minimize subsequent headspace upon heat sealing. The headspace remaining in the sealed ampules was estimated to contain only about 5% of the volume of the added aqueous solution.

Saturated sediment samples were prepared as follows. Sediments (6.8-g portions) were added to 1-dram vials, which were then tapped repeatedly to settle the sediments to the base of the neck. Aqueous samples (1.35 mL) were injected slowly into the bottom of the sediments to displace the air. This volume was precalibrated to just fill the sediment pores. Cylindrical glass inserts with notches on top were then placed into the necks of the vials to fill the headspace, and the vials were capped with Mini-nert caps. Ampules containing sediment were prepared similarly but without glass inserts. The headspace remaining in the sealed ampules with sediment was estimated to be about one-third the volume of the added aqueous solution.

Sediments, water, and glassware were sterilized when sediments were used or when kinetic runs were expected to last longer than a few days. Water and glassware were autoclaved at 125 °C and 1.4 bar before adding the organic compound. Sediments were sterilized either by heating overnight at 130 °C or by adding 0.1% w/w formaldehyde to the aqueous solutions before adding them to the sediments.

**Kinetic Runs.** Samples were incubated in a temperature-controlled bath (±0.1 °C) at the desired temperature. At appropriate time intervals, samples were quenched by cooling and stored at ~2 °C until analysis at the end of the run. Because activation energies of haloalkane and epoxide hydrolysis reactions are typically greater than about 80 kJ/mol (*4*), this storage temperature served to reduce the rates by at least a factor of 10. pH was measured before and after kinetic runs.

**Sample Analysis.** Halogenated compounds were analyzed by GC/ECD (HP 5880) after extraction with hexane or isooctane. EME, SO, and their hydrolysis products were analyzed by HPLC (HP 1090 with diode array UV detection) either directly or after mixing sediments with acetonitrile and centrifuging.

Extractions were performed as follows. Vials containing aqueous solutions were opened, 0.4- to 0.5-mL aliquots of solution were removed, equal volumes of organic solvent containing internal standard were added, and each vial was recapped and shaken for ≥5 min. Vials containing sedi-

Table I. Kinetic and Product Data for Hydrolysis of Haloalkanes[a]

| compd | $T$, °C | matrix or pH | $C_0$, $\mu$M | conversion, % | $10^8k$, $s^{-1}$ | product[b] | product yield, %[c] |
|---|---|---|---|---|---|---|---|
| IPB | 60 | DW[d] | 8–2000 | ≥80 | 35 400 ± 2700 | | |
| | | SEW[e] | 81 | 83 | 36 300 ± 5800 | | |
| | 50 | DW | 81 | 93 | 11 500 ± 300 | | |
| | 25 | 3–11[f] | 1000 | ≥72 | 379 ± 41 | iPrOH | 118 ± 31 |
| | | DW | 81 | 89 | 383 ± 33 | | |
| | | SEW | 81 | 87 | 372 ± 64 | | |
| | | sed[g] | 81 | 88 | 420 ± 80 | | |
| TrCE | 80 | 7.1[h] | 5 | 79 | 3 500 ± 300 | | |
| | 60.5 | DW | 1.8 | 90 | 408 ± 22 | | |
| | 60 | DW | 75 | 75 | 364 ± 30 | DCE | 22 ± 1 |
| | | | | | | HOAc | 78 ± 23 |
| | | sed | 75 | 77 | 294 ± 44 | DCE | 35 ± 10 |
| | | | | | | HOAc | 79 ± 22 |
| | 55 | 7.1[h] | 2.5–5 | ≥70 | 176 ± 20 | | |
| | 40 | DW | 75 | 58 | 22.6 ± 1.1 | DCE | 17 ± 1 |
| | | | | | | HOAc | 80 ± 40 |
| | | clay[i,j] | 75 | 87 | 18.4 ± 7.6 | DCE | ~13 |
| | 25 | 3–11[h] | 5 | ≤18 | 2.6 ± 1.3 | | |
| | | DW[j] | 75 | 39 | 1.93 ± 0.40 | DCE | 22 ± 1 |
| | | | | | | HOAc | 80 ± 50 |
| | | | | | | $Cl^-$ | 271 ± 57 |
| | | DW[k] | 75 | 40 | 2.04 ± 0.47 | DCE | 21 ± 2 |
| | | | | | | HOAc | 120 ± 30 |
| | | sed[j] | 75 | 25 | 1.8 ± 0.9[l] | DCE | 18 ± 9 |
| TeCE | 60 | 5.1 | 1.4 | 67 | 104 ± 18 | TCE | 66 ± 14 |
| | 40 | 6.3 | 1.4 | 90 | 22.6 ± 5.4 | TCE | >40 |
| | | Clay[i,j] | 1.4 | 40 | 2.6 ± 1.0 | TCE | nq[m] |
| | 25 | 6.05 | 0.7 | 34 | 1.4 ± 0.4 | TCE | 104 ± 48 |
| | | 7.01 | 1.4 | 74 | 22.0 ± 3.5 | TCE | 98 ± 14 |
| | | 9.0 | 0.7 | 81 | 1 500 ± 250 | | |
| | | 9.0 | 1.4 | 81 | 2 920 ± 640 | TCE | 95 ± 4 |
| | | 10.0[h] | | 91 | 12 100 ± 1400 | | |
| | | sed | 1.4 | 68 | 27.6 ± 4.0 | TCE | 61 ± 9 |
| EDB | 100 | DW | 87 | 52 | 3 130 ± 370 | VB | nq |
| | | | | | | EG | 76 ± 8 |
| | 60 | DW | 87 | 83 | 41.9 ± 2.5 | VB | 12 ± 3 |

[a] Error estimates are 95% confidence intervals. Each run results from 4 to 10 concentration time points including a zero time point. [b] iPrOH = isopropanol, HOAc = acetic acid, TCE = trichloroethane, VB = vinyl bromide. [c] Expressed as percent of lost parent compound. [d] Unbuffered, distilled water. [e] Sediment-extracted water, pH = 7.3. [f] From Mill et al. (*12*). [g] In sediment pores, pH ≈ 7.3. [h] From Mill et al. (*13*). [i] In Na montmorillonite, pH ≈ 4.4, 130% w/w saturated. [j] Contained 0.1% w/w $CH_2O$ as sterilant. [k] Autoclaved. [l] Includes 41% correction due to larger headspace in the ampules. [m] nq = product observed but not quantified.

ments were opened, the inserts were removed, 0.2–0.3-mL aliquots of water were added to improve fluidity, 0.4–0.5-mL aliquots of solvent (containing internal standard) were added, and each vial was recapped and shaken for ≥15 min. Ampules were fitted with $^3/_4$ in. male Swagelok connectors using Teflon ferrules. Aliquots of solvent containing internal standard were added, along with small amounts of water in the case of sediment samples, and then the ampule necks were broken, allowing solvent to enter the ampules without loss of compound. Finally, Swagelok caps were screwed on and the ampules shaken as described above.

Organic product yields were calibrated by preparing aqueous standards, filling them into vials with or without sediment, and extracting and analyzing them in the same fashion as the hydrolyzed samples. Ethylene glycol was determined spectrophotometrically after cleavage to formaldehyde and derivitization with chromotropic acid (*24*). 2-Bromoethanol did not interfere in the latter method. Anionic product yields were determined by ion chromatography (Dionex 2000i) on aqueous aliquots, obtained either directly or, in the case of sediment samples, after removal of organic solvent, mixing with additional water, and centrifuging. Products were identified by retention time and, in the case of HPLC, also by UV spectra.

**Sorption.** Sorption of TrCE and TeCE was shown by the following experiments to be minor, as expected for a low-carbon sediment (*23*). Nine grams of Lula sediment was mixed with 5.8 mL of aqueous TrCE (1.4 $\mu$M) or TeCE (0.7 $\mu$M) in capped tubes without headspace and set on a tumbler. Supernatant samples (0.5 mL) were then extracted as described above. Seven percent of the TrCE was lost after 4 h, with no further loss up to 20 h. TeCE was consumed at a slow rate close to that expected from the hydrolysis rate constant in distilled water at the same pH (pH 7.6).

**Statistics.** In general, only one run was performed under a given set of conditions, with duplicate or triplicate sample analyses of individual time points. It was generally considered unnecessary to repeat experiments because, with few exceptions, rate constants agreed very well with literature data or values extrapolated from literature data. Errors are reported as 95% confidence intervals on slopes (rate constants) or on averages of product yields.

## *Results and Discussion*

A summary of the kinetic and product data obtained is given in Tables I and II. The focus of this work was to study hydrolyses under conditions approximating groundwater environments as closely as possible; therefore, most experiments were performed at 25 °C. In some cases, elevated temperatures were used to speed the reactions, although it was recognized that product distributions could be affected.

**Sterilization.** A preliminary set of experiments was performed with IPB in order to establish effects of steri-

Table II. Kinetic and Product Data for Hydrolysis of Epoxides[a]

| compd | $T$, °C | matrix or pH | $C_0$, μM | conversion, % | $10^8k$, $s^{-1}$ | product[b] | product yield, %[c] |
|---|---|---|---|---|---|---|---|
| EME | 25 | 2.19 | 100 | 70 | 1620 ± 40 | diol | nq[d] |
| | | 6.75[e] | 62 | 90 | 74.9 ± 1.2 | diol | 92 ± 1 |
| | | sed[e,f] | 62 | 93 | 106 ± 10 | diol | 79 ± 9 |
| SO | 25 | 7.25[e] | 50 | 73 | 434 ± 12 | PED | 99 ± 3 |
| | | sed[e,f] | 50 | 86 | 1690 ± 620 | PED | 77 ± 8 |
| | | | | | | BA | 7 ± 4 |
| | | Fe[e,g] | 50 | 53 | 530 ± 280 | PED | nq |

[a] Error estimates are 95% confidence intervals. Each run results from 4 to 10 concentration time points including a zero time point. [b] diol = glycol from opening of epoxide ring, PED = 1-phenyl-1,2-ethanediol, and BA = benzaldehyde. [c] Expressed as percent of lost parent compound. [d] nq = product observed but not quantified. [e] Contained 0.1% w/w $CH_2O$ as sterilant. [f] In sediment pores, pH = 7.3. [g] In suspension of 2.8 mM ferric hydroxide, pH ≈ 7.0.

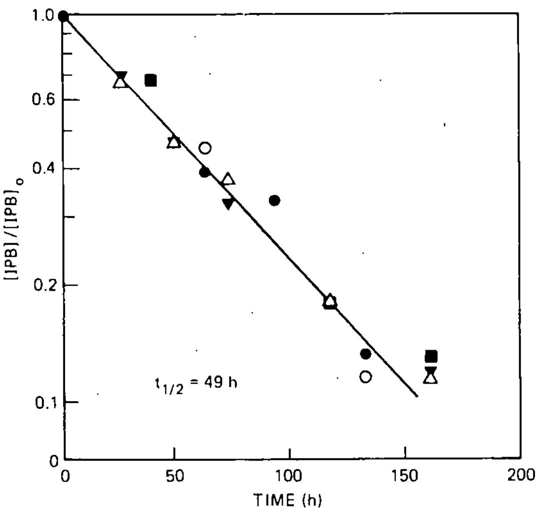

**Figure 2.** First-order plot of hydrolysis of IPB at 25 °C in various media: (○) distilled water; (●) sediment extracted water; (△) untreated Lula sediment; (▼) Lula sediment with 0.1% formaldehyde; (■) heat-treated Lula sediment.

lization methods, if any, on hydrolysis rates. Figure 2 shows a plot of IPB loss in DW, SEW, untreated sediment, heat-sterilized sediment, and in sediment pores containing 0.1% w/w formaldehyde. All the points lie essentially on the same line, indicating that none of the sterilization methods had a demonstrable effect on the kinetics and that biological processes were not responsible for the losses observed. This, in turn, suggests no effect of sterilization on product distributions as well. 1-Phenyl-1,2-ethanediol (PED) apparently was biotransformed in untreated sediment at 25 °C ($t_{1/2} \approx 4$ days), but this was completely inhibited by 0.1% formaldehyde, demonstrating the effectiveness of this sterilant.

**Isopropyl Bromide (IPB).** Additional kinetic results with IPB (Table I) showed no differences in rate constants in DW, SEW, and in sediment pores at 25 °C nor between DW and SEW at 60 °C. The rate constants measured agree with those in the literature (*4*). The half-life at 25 °C is about 50 h.

**1,1,1-Trichloroethane (TrCE).** Hydrolysis of TrCE in water led to the formation of both acetic acid by substitution and 1,1-dichloroethene by elimination (Table I). Neither the rate constants nor products of TrCE hydrolysis were significantly affected by the presence of Lula sediment at both 60 and 25 °C. This conclusion is based mostly on the kinetics of TrCE loss and the percentages of DCE formation; acetic acid analyses showed considerably greater variability, particularly in the sediments and clay, whose pore waters exhibited partially interfering peaks by ion chromatography. The lack of differences in rate constants at 25 °C among runs in autoclaved water, formaldehyde-treated water, and formaldehyde-treated sediment again indicates that biological processes were unimportant. The stoichiometric factor of 2.71 mol of $Cl^-$ formed per mol of TrCE lost, observed at 25 °C, is in agreement with the value of 2.56 calculated assuming 22% DCE formation. The observation that the yield of DCE is nearly independent of temperature is somewhat surprising in that it means that the activation energies of elimination and substitution are about the same. This contradicts the results of Pearson and McConnell (*14*), who reported that DCE becomes the major product at low temperatures. The data in montmorillonite clay at 40 °C, although semiquantitative, also indicate no differences from DW.

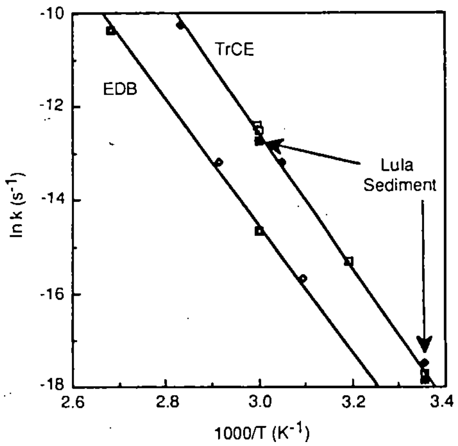

**Figure 3.** Arrhenius plots for hydrolysis of TrCE and EDB: (□) in unbuffered, distilled water; (■) in Lula sediment pores; (♦) from Mill et al. (*13*); (◊) from Vogel and Reinhard (*19*).

It should be noted that the rate constant in sediment at 25 °C contains a 41% correction assuming equilibrium distribution of the TrCE between the headspace and the aqueous phase and no reaction in the headspace. This run proceeded over 10 months and was performed in ampules to minimize losses during incubation; unlike aqueous solutions, ampules containing sediment had a significant headspace to aqueous phase ratio, estimated to be about 0.3, since most of the volume was taken up by the sediment. The Henry coefficient required for the correction was calculated from a water solubility of 720 mg/L and a vapor pressure of 123 Torr at 25 °C (*13*).

An Arrhenius plot of the data (Figure 3) yields an activation energy of 118 ± 5 kJ/mol and an $A$ factor of $1.1 \times 10^{13}$ $s^{-1}$. The half-life calculated from these parameters is 350 days at 25 °C.

**1,1,2,2-Tetrachloroethane (TeCE).** As expected, the hydrolysis of TeCE yielded trichloroethene as the major, if not sole, product. The few cases in which less than 100% yield was observed might be attributed to volatilization

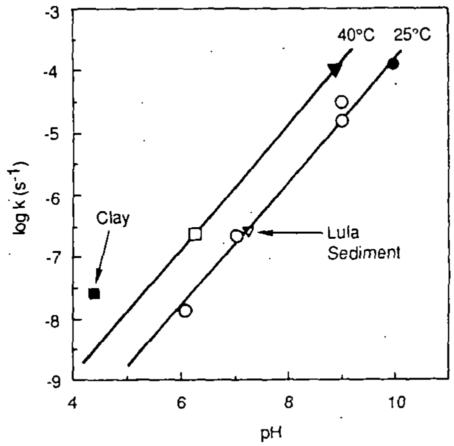

**Figure 4.** TeCE hydrolysis rate constant vs pH: (○, □) in 5 mM phosphate buffered, distilled water; (▽) in Lula sediment pores; (●) from Mill et al. (*18*); (■) in Na montmorillonite pores; (▼) from Cooper et al. (*17*).

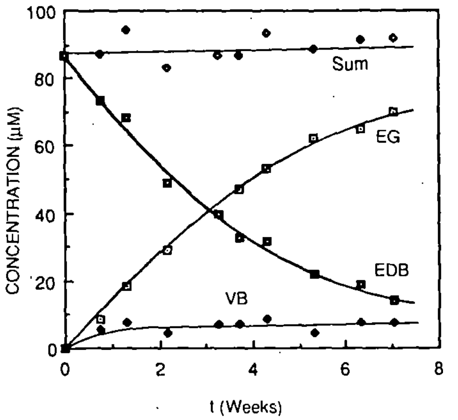

**Figure 5.** EDB hydrolysis in distilled water at 60 °C.

losses; however, we were not able to analyze for the potential substitution product, dichloroacetaldehyde. The moderately low recovery in sediment may be due to adsorption to the sediment and the short extraction time (*25*).

Figure 4 shows a plot of log $k$ vs pH. Interestingly, the base-catalyzed process appears to dominate even at pH values as low as pH 6, with no evidence for a neutral process. Again, both product and kinetic data indicate no major changes between results in DW and those obtained in the presence of solid aquifer material. The rate constant in clay at 40 °C was about 1 order of magnitude greater than expected from the data at higher pH extrapolated to the pH of the clay. This may reflect a catalysis by the clay material but also could be due to volatilization losses or to neutral hydrolysis. Unfortunately, a more direct comparison with results in DW could not be made because the pH of the clay mixture dropped during the run, probably during the initial heating to 40 °C. Nevertheless, the experiment in clay serves to show that the rate constant is not lower than predicted from the regression line at high pH, as might have been expected if "surface acidity" had been important.

These data yield a base-catalyzed rate constant $k_B$ of 1.8 ± 0.9 $M^{-1}$ $s^{-1}$ at 25 °C, which is a factor of 2 higher than those given by Cooper et al. (*17*) for 0.1 M phosphate buffer (ionic strength ≈ 0.3 M) and by Walraevens et al. (*16*). Our data were obtained using minimal buffer concentrations, at most 5 mM, and correspond to a half-life of 45 days at pH 7 and 25 °C.

**1,2-Dibromoethane (EDB).** Because of the lack of effect found for the other haloalkanes, EDB was not studied in sediment. Figure 5 illustrates the product mass balance obtained for hydrolysis in unbuffered DW at 60 °C in sealed ampules. Ethylene glycol (EG) accounts for 91% of the products, but vinyl bromide (VB) also is formed. Tests with authentic 2-bromoethanol showed that it does not interfere in the determination of EG. Therefore, the former compound must hydrolyze rapidly to form EG; otherwise a mass balance would not have been obtained. The data of Blandamer et al. (*26*) indicate that 2-bromoethanol hydrolyzes 2.6 times as fast as EDB at 60 °C. These results are in agreement with both those of Vogel and Reinhard (*19*), who observed VB formation by GC/MS, and those of Jungclaus and Cohen (*20*), who recovered about 2 mol of $Br^-$ per mol of EDB lost and detected small amounts of VB. Weintraub et al. (*21*) reported high yields of EG and $Br^-$ but detected no VB.

Figure 3 combines our data with those of Vogel and Reinhard (*19*) in an Arrhenius plot yielding an activat energy of 107 ± 22 kJ/mol and an $A$ factor of 3.3 × 1 $s^{-1}$. The calculated half-life at 25 °C is 4.1 years.

**Styrene Oxide (SO) and 2,3-Epoxypropyl *p*-Me oxyphenyl Ether (EME).** Because the haloalkanes hibited only neutral and base-catalyzed reactions, E and SO were chosen as compounds subject to acid-c lyzed as well as neutral hydrolysis. Neutral hydrolysi EME in sediment was only slightly faster than in DW about the same measured pH (pH ≈ 7, Table II). Howe an effective pH of about 3 would have been required acid catalysis to compete with the neutral process, beca the rate constant for acid catalysis, $k_A$, was found to be 2 orders of magnitude lower [$k_A$ = (2.42 ± 0.06) × $10^{-3}$ $M^{-1}$ $s^{-1}$] than expected from previous work in this laboratory (*6*).

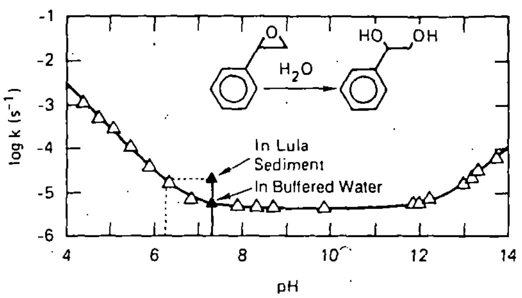

**Figure 6.** Rate constant for styrene oxide hydrolysis vs pH: (▲) this work; (△) data of Ross et al. (*22*).

SO exhibits acid catalysis at pH values higher than for EME (pH ≈ 7, see Figure 6) (*22*) and closer to those found in the environment. SO hydrolyzed about 4 times faster in Lula sediment than in DW at the same pH (pH 7.25), suggesting an effective pH in sediment nearly 1 unit below the measured, bulk pH of the sediment. However, this effect is not observed for all compounds, since TeCE base-promoted hydrolysis was not slowed in the sediment. The major product from SO, in both cases, was 1-phenyl-1,2-ethanediol (PED, see Table II). In addition, at least two minor products were formed from SO in sediment that were not found in DW, one of which was identified as benzaldehyde. The other product, which is more polar, is not acetophenone, phenylacetaldehyde, or benzyl alcohol. The formation of benzaldehyde was reproducible and is significant in that it requires a 2-electron oxidation. Benzaldehyde does not arise from oxidative cleavage of first formed PED because PED was quite stable in $CH_2O$-sterilized sediments over the time period of the SO hydrolysis. A possible explanation is that insoluble ferric or manganic oxides are present which both catalyze hydrolysis and oxidize SO (*27*). However, a model experiment with freshly prepared ferric hydroxide (Table II) showed no effect on rate constant and no benzaldehyde formation.

## Conclusions

These results suggest that hydrolyses of haloalkanes will be largely unaffected by the presence of sediment or clay minerals similar to those in Lula sediment, and thus the rates and products of hydrolyses in these groundwaters are expected to be the same as in surface waters or distilled water. Therefore, it should be possible to use the large body of available data obtained in distilled water (*4*) to predict hydrolysis rate constants of such compounds in these types of sediments. Hydrolysis rates represent minimum environmental transformation rates since hydrolysis will always occur, regardless of the rates of competing processes. Further research on a broader variety of sediments and compounds is needed to test the generality of these conclusions.

One important result of this study is that hydrolyses of haloalkanes often form some haloolefins, which are more persistent and generally pose a greater threat to human health than substitution products (*11*).

Styrene oxide hydrolysis is catalyzed by the Lula sediment surface and yields, in addition to glycol, benzaldehyde, a product requiring an oxidative step. More work is needed to identify the oxidant(s) and establish the generality of the oxidative process.

## Acknowledgments

We thank Alan Richardson for performing some of the experiments with TeCE and IPB.

**Registry No.** VB, 593-60-2; TCE, 79-01-6; IPB, 75-26-3; TrCE, 71-55-6; TeCE, 79-34-5; EDB, 106-93-4; DCE, 75-35-4; SO, 96-09-3; EME, 2211-94-1; EG, 107-21-1; iPrOH, 67-63-0; HOAc, 64-19-7.

## Literature Cited

(1) Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. *Handbook of Chemical Property Estimation Methods—Environmental Behavior of Organic Compounds*; McGraw-Hill: New York, 1982; Chapters 4 and 7.
(2) Senesi, N.; Testini, C. *Chemosphere* **1984**, *13*, 461–468.
(3) Macalady, D. L.; Wolfe, N. L. *J. Agric. Food Chem.* **1985**, *33*, 167–173.
(4) Mabey, W.; Mill, T. *J. Phys. Chem. Ref. Data* **1978**, *7*, 383–415.
(5) Macalady, D. L.; Wolfe, N. L. *ACS Symp. Ser.* **1984**, *No. 259*, 221.
(6) El-Amamy, M. M.; Mill, T. *Clays Clay Miner.* **1984**, *32*, 67–73.
(7) Saltzman, S.; Mingelgrin, U.; Yaron, B. *J. Agric. Food Chem.* **1976**, *24*, 739–743.
(8) Macalady, D. L.; Tratnyek, P. G.; Grundl, T. J. *J. Contam. Hydrol.* **1986**, *1*, 1–28.
(9) Wilson, J. T.; McNabb, J. F.; Wilson, B. H.; Noonan, M. J. *Dev. Ind. Microbiol.* **1983**, *24*, 225–233.
(10) Iwamura, T., Santa Clara Valley Water District, CA, personal communication, 1986.
(11) Bolt, H. M.; Laib, R. J.; Filser, J. G. *Biochem. Pharmacol.* **1982**, *31*, 1–4.
(12) Mill, T.; Bawol, R.; Partridge, I.; Mabey, W. R. "Evaluation and Optimization of Hydrolysis Screening Protocols"; SRI Final Report to Battelle Columbus Laboratories, Sept 1980; Contract T-6417(7197)-031, 86 p.
(13) Mill, T.; Mabey, W. R.; Winterle, J. S.; Davenport, J. E.; Barich, V. P.; Dulin, D. E.; Tse, D. S.; Lee, G. "Design and Validation of Screening and Detailed Methods for Environmental Processes"; EPA Report, July 1982; Contract 68-01-6325, 176 p.
(14) Pearson, C. R.; McConnell, G. *Proc. R. Soc. London, B* **1975**, *189*, 305–332.
(15) Vogel, T. M.; McCarty, P. L. *J. Contam. Hydrol.* **1987**, *2*, 299–308.
(16) Walraevens, R.; Trouillet, P.; Devos, A. *Int. J. Chem. Kinet.* **1974**, *6*, 777–786.
(17) Cooper, W. J.; Mehran, M.; Riusech, D. J.; Joens, J. A. *Environ. Sci. Technol.* **1987**, *21*, 1112–1114.
(18) Mill, T.; Mabey, W. R.; Podoll, R. T.; Dulin, D.; Drossman, H.; Liu, A.; Barich, V.; Jaber, H.; Irwin, K. "Data Generation for Process and Property Constants Used in Fate Assessment"; EPA Final Report, 1984; Contract 68-03-2981, pp 5–17.
(19) Vogel, T. M.; Reinhard, M. *Environ. Sci. Technol.* **1986**, *20*, 992–997.
(20) Jungclaus, G. A.; Cohen, S. Z. "Hydrolysis of Ethylene Dibromide," Abstr., *Am. Chem. Soc., Div. Environ. Chem.* **1986**, *26*(*1*), 12–16.
(21) Weintraub, R. A.; Jex, G. W.; Moye, H. A. In *Evaluation of Pesticides in Ground Water*; Garnet, W. Y., Honeycutt, R. C., Nigg, H. N., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1986; pp 294–310.
(22) Ross, A. M.; Pohl, T. M.; Piazza, K.; Thomas, M.; Fox, B.; Whalen, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1658–1665.
(23) Piwoni, M. D., U.S. Environmental Protection Agency, personal communication, 1986.
(24) Rajagopal, G.; Ramakrishnan, S. *Anal. Biochem.* **1975**, *65*, 132–136.
(25) Reinhard, M., Stanford University, personal communication, 1986.
(26) Blandamer, M. J.; Golinkin, H. S.; Robertson, R. E. *J. Am. Chem. Soc.* **1969**, *91*, 2678–2683.
(27) Stone, A. T.; Morgan, J. J. *Environ. Sci. Technol.* **1984**, *18*, 617–624.

*Received for review March 23, 1987. Accepted December 29, 1987. This work was supported by the Robert S. Kerr Environmental Research Laboratory under EPA Grant CR8141-01-0. Although the research described in this paper has been funded in part by the U.S. Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.*