Dechlorination of Lindane, Dieldrin, Tetrachloroethane, Trichloroethene, and PVC in Subcritical Water

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Pure water has been used to dechlorinate aliphatic organics without the need for catalysts or other additives. Dehydrohalogenation (loss of HCl with the formation of a double bond) occurred at temperatures as low as 105-200 °C for 1,1,2,2-tetrachloroethane, lindane (1,2,3,4,5,6hexachlorocyclohexane, γ -isomer), and dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo, exo-1,4:5,8-dimethanonaphthalene). Complete loss of the parent compounds was achieved in less than 1 h at 150, 200, and 300 °C for 1,1,2,2-tetrachloroethane, lindane, and dieldrin, respectively. The initial dechlorination of lindane had an activation energy of 84 kJ mol⁻¹ with an Arrhenius pre-exponential factor of $1.5 \times 10^6 \text{ s}^{-1}$. Dehydrohalogenation of lindane formed trichlorobenzenes, followed by subsequent hydrolysis and hydride/chloride exchange to form chlorophenols, lower chlorobenzenes, and phenol as the major final product. Reaction of poly(vinyl chloride) at 300 °C for 1 h formed aromatic hydrocarbons ranging from benzene to anthracene and a char residue with a ca. 1:1 carbon-to-hydrogen ratio (mol/mol). The residue contained <1 wt % of chlorine compared to 57 wt % chlorine in the original polymer. All compounds tested yielded chloride ion as the major product (at higher temperatures), indicating that complete dechlorination of some aliphatic organochlorines may be feasible.

Introduction

Organochlorine compounds represent one of the largest groups of anthropogenic compounds found in the environment. In addition to the concern for the environmental effects of the parent compound (e.g., toxic effects of chlorinated solvents and pesticides in groundwater), the presence of organochlorines can inhibit the treatment and recycling of waste streams. For example, poly(vinyl chloride) (PVC) is a major source of chlorine for chlorinated dioxin formation during the incineration of municipal wastes. A number of studies have investigated degradation of chlorinated pollutants via reductive dehalogenation to transform chlorinated organics into their non-chlorinated analogues (1-10). Recent degradation experiments involving chlorinated aliphatic (7)and aromatic compounds (8-10) have been performed in supercritical water (i.e., at temperatures and pressures higher than the critical point of 374 °C and 221 bar) and subcritical water (defined as hot water with sufficient pressure to

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maintain the liquid state). In most of those studies, water was employed only as an intermediate media, and the degradation was related to reagents such as zerovalent iron or other metals (1-6, 8, 9), a strong base (7), or oxidants (10) which were added to the water. The majority of investigations using pure water to degrade chlorinated organics have been performed using supercritical water (11, 12). For example, the decomposition of poly(vinyl chloride) at temperatures ranging from 400 to 600 °C was reported (13). However, the use of subcritical water may have advantages over supercritical water (in addition to requiring lower temperatures and pressures) in that dechlorination reactions may be enhanced. For example, the dechlorination of methylene chloride was much faster using subcritical water than when using supercritical water (14).

Recently, pure water at so-called subcritical conditions has been used to extract and degrade high explosives and pesticides from highly contaminated soils (*15*, *16*), and a preliminary study has demonstrated the dechlorination of polychlorinated dibenzodioxins on incinerator fly ash (*17*). These results are apparently based on the ability of subcritical water to enhance the solubility of nonpolar organics by as much as 5 orders-of-magnitude (*18*, *19*), as well as promoting some organic reactions (*20*).

The present study investigates the use of subcritical water to dehalogenate aliphatic organochlorine compounds, including 1,1,2,2-tetrachloroethane and its degradation product 1,1,2-trichloroethene, 1,9-dichlorononane, lindane (1,2,3,4,5,6hexachlorocyclohexane, γ -isomer), dieldrin (1,2,3,4,10,10hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-*endo, exo*-1,4:5,8-dimethanonaphthalene), and PVC.

Experimental Section

Degradation Experiments. Unless otherwise noted, all reactions were performed using a static (no flow) 4-mL cell constructed from an Inconel 600 (21) threaded (npt) pipe fitting with end caps (63.5 mm long, 6.3 mm i.d.; Parker Hannifin Corporation, Columbus, OH). Inconel cells were selected on the basis of their inertness in corrosion tests with subcritical and supercritical water (21). For each experiment, 3 mL of water (HPLC grade; Fisher Scientific, Pittsburgh, PA), which had been purged with nitrogen for ~ 2 h to remove dissolved oxygen, was placed in the cell leaving about 1 mL of headspace when the vessel was capped. With this procedure, the internal pressure was governed by the steam/water equilibrium (i.e., pressures ranged from 1.3 to 170 bar for reactions performed over the 105 to 350 °C temperature range used in this study (22)). Thus, all pressures were substantially below the 428 bar rating of the Inconel reaction cells. [Safety note: It is imperative to have sufficient headspace in the vessel to ensure that interior pressure is maintained by the steam/water equilibrium to avoid excessive pressures which can occur with a completely full cell (23). At temperatures above 275 °C, the density of water drops so that the cell is full of liquid water, which can cause pressures above the gas/liquid equilibrium (22). Therefore, the proportion of water added to the cell should be <75% at higher temperatures to ensure that adequate headspace remains).

Initial reactions were performed in water spiked with 10 μ L of an acetone solution of tetrachloroethane (final concentration in water of 1 mM) and lindane (final concentration of 0.57 mM). To aid in determining reaction products and chlorine mass balance, experiments were also performed with higher concentrations (i.e., near their saturation concentrations at ambient conditions). Neat compounds were spiked in the water to obtain final concentrations of 16 mM

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for tetrachloroethane, 8.9 mM for lindane, and 19 mM for trichloroethane. Degradation experiments were also performed on 1,9-dichlorononane and dieldrin, with both at concentrations of 9 mM. PVC studies used 100 mg of powder (number average molecular weight, M_n , ca. 35 000; weight average molecular weight, M_w , ca. 62 000; supplied by Aldrich, Milwaukee, WI) in 3 mL of water for each test.

Reaction cells were heated in a GC oven (Hewlett-Packard model 5890). Because the heating rate of the interior solution was not initially known, a cell was modified by replacing the cap with a $1/_2$ in. npt $\times 1/_8$ in. tubing fitting to allow a $1/_8$ diameter thermocouple to be placed directly into the water inside the cell during the heating step. This modified cell was used to determine the optimal heating procedure for the subsequent reaction cell studies.

When the GC oven was heated from room temperature after placing the cell in the oven, the heating rate of the water inside the cell was quite slow (e.g., 15 min was required for the water temperature to reach 240 °C with an oven setpoint of 250 °C). Because more rapid heating of the reaction water was desired, the procedure was modified so that the oven was first preheated to 50 °C above the desired temperature, and then the cell was quickly inserted into the oven through the oven door. The GC oven temperature was maintained at 50 °C above the desired temperature until the cell interior temperature reached ca. 10 °C below the desired temperature, and then the oven temperature was lowered to the desired reaction temperature. With this procedure, the interior cell temperature monitored by the thermocouple reached within 10 °C of the desired temperature in 3-6 min (for 150 and 300 °C reaction temperatures, respectively) and never exceeded the desired temperature by more than 2 °C. For example, when the GC oven was preheated to 250 °C (for a desired reaction temperature of 200 °C), the interior cell temperature reached 190 °C in 4 min. At this time, the oven temperature was lowered to 200 °C (and was designated time zero for the reaction studies). After the desired heating times, the hot cells were immediately removed from the oven and immersed in tap water to quench the reaction.

After cooling, each cell was carefully opened and its contents transferred to a 7-mL vial. Organics were then extracted with three 1-mL aliquots of methylene chloride. 1-Chloronaphthalene was added as an internal standard at a concentration similar to the starting material, and the extracts were analyzed by gas chromatography with mass spectrometric detection (GC/MS). Because the methylene chloride extracts of the product water from the lindane reactions showed phenolic compounds, the water from the lindane reactions was acidified with 0.5 M HCl (to pH \sim 2) before methylene chloride extraction. To determine the quantitative efficiency of this method, the identical procedure (i.e., every step from spiking the water with the test compound in the cell to the methylene chloride extraction and GC/MS analysis) was applied for each test compound except that the cell was not heated. On the basis of a minimum of triplicate cells, the recoveries of unreacted test compounds were typically $95 \pm 10\%$.

Degradation Experiments in Glass. To verify the inertness of Inconel cells, selected experiments were performed in 3-mL reaction glass V-vials with Teflon stoppers (Aldrich) at temperatures of up to 150 °C (the maximum possible without leaks).

GC/MS Analyses. Analyses were performed using a Hewlett-Packard model 5890 GC with a Hewlett-Packard model 5972 MS in the full-scan mode (50-400 m/z), with electron impact ionization. Chromatographic separations were accomplished using a 30 m DB-5 column with a 0.25 mm i.d. and 0.25 μ m film thickness (J&W Scientific, Rancho Cordova, CA), with injections in splitless mode. The oven temperature was held at 40 °C for 1 min followed by a 10 °C

 $\rm min^{-1}$ ramp to 320 °C. Quantitations were based on the relative response factors of individual standards to the internal standard. Similarly, the identification and quantification of degradation products were based on comparisons of mass spectra and retention data of pure standards with those of the sample species, unless otherwise noted.

Solid-phase microextraction (SPME) with 7 μ m poly-(dimethylsiloxane) (PDMS) fibers was used (24) in an attempt to identify organics which were too volatile to be determined in the methylene chloride extracts. The analytes were directly recovered with SPME from the product water and the headspace above the water followed by direct thermal desorption in the injection port of the GC/MS.

Chloride Ion Determination. The determination of chloride ion content in the product waters from the reactions using the higher concentrations of test compounds was performed with a chloride ion selective electrode (Cole-Parmer, Vernon Hills, IL). All determinations were performed in triplicate or quadruplicate.

Results and Discussion

Lindane. Lindane was selected as a test compound for two reasons. First, it is a widespread toxic pollutant (*25, 26*). Second, our results obtained in pure subcritical water could be compared with the data previously obtained in hot water under alkaline conditions (*7*).

As shown in Table 1, the rate of lindane removal rapidly increased with the increase in temperature from 125 to 200 °C. Using the data presented in Table 1, linear regressions were obtained for the logarithm of lindane concentration (mean values) versus reaction time (as shown in Figure 1, top). Linear regression correlation coefficients (R^2) were 0.6716, 0.7585, 0.8582, and 0.8384 for the 125, 150, 175, and 200 °C reactions, respectively. On the basis of the rate constants for the initial dechlorination of lindane shown in Table 1, the half-lives ($t_{1/2}$) of lindane at different temperatures decrease from ca. 1000 min at 125 °C to 12 min at 200 °C. At 250 °C, the removal of lindane was completed in 15 min; therefore, it was not possible to obtain its rate constant and half-life.

On the basis of the data from Table 1 and Figure 1 (top), activation energies were calculated assuming a pseudo-firstorder reaction (excess of water) and assuming a secondorder reaction where the concentration of hydroxide ion is based on the dissociation constant of water at the different temperatures (27). For the pseudo-first-order assumption, the activation energy for the initial dechlorination of lindane in pure water was $\widetilde{84} \pm 24$ kJ mol⁻¹ (95% confidence interval based on linear regression analysis), with an Arrhenius preexponential factor A of $1.50 \times 10^6 \text{ s}^{-1}$. The second-order assumption yielded an activation energy of 69 ± 24 kJ mol⁻¹ and a pre-exponential factor of $1.40 \times 10^{10} \,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}$. These values correspond to the second-order activation energies of 86 kJ mol⁻¹ reported by Cristol et al. and 85 kJ mol⁻¹ reported by Ngabe et al. for the alkaline dehydrohalogenation of lindane at 30 °C (28, 29).

The degradation mechanism of lindane is complicated because of the high number of reaction products and intermediates identified in the product water. Possible degradation pathways are presented in Figure 2, and quantitative data on the major reaction products are presented in Figure 3. The first degradation intermediate, pentachlorocyclohexene, was presumably formed by elimination (loss of HCl with the formation of a double bond, or "dehydrohalogenation") (*30*). Alternatively, the reaction may occur by displacement of Cl⁻ by OH⁻ followed by rapid dehydration (*31*). Hydrolysis of the pentachlorocyclohexene yielded two isomers of hydroxytetrachlorocyclohexene at 150 °C, but both compounds accounted for less than 5% of the

TABLE 1. Effect of Time and Water Temperature on the Dehalogenation of Lindane (0.57 mM)

	% degraded \pm SD ^a					
time (min)	125 °C	150 °C	175 °C	200 °C	250 °C	
15	11 ± 3	21 ± 7	30 ± 8	61 ± 7	nd ^b	
20	С		04 + 44	54 ± 1		
25			34 ± 11			
30	11 ± 1	37 ± 8		72 ± 3	nd	
35			45 ± 8			
40				90 ± 2		
45			45 ± 8			
60	10 ± 3	45 ± 20		99 ± 1	nd	
75			60 ± 2			
95			68 ± 14			
120	14 ± 5	55 ± 15				
360	50 ± 8	80 ± 10		nd	nd	
840	38 ± 1					
1080	61 ± 13	nd		nd	nd	
$k (s^{-1})^d$	$(1.4 \pm 0.6) \ 10^{-5}$	$(8.2 \pm 2.8) \ 10^{-5}$	$(2.1 \pm 0.4) \ 10^{-4}$	$(8.6 \pm 3.6) \ 10^{-4}$		
$t_{1/2}$ (min) ^e	1030	190	72	12		
- 1/2 (. =	•=		

^a Standard deviations were calculated from triplicate degradation experiments. ^b nd: not detected; the detection limit for lindane was 0.2% of the original mass. ^c Not determined. ^d Rate constants (k) at different temperatures. ^e Half-lives at different temperatures.



FIGURE 1. (Top) Effect of temperature on degradation of lindane (0.57 mM) in subcritical water, where C_0 is initial concentration of lindane and *C* is actual concentration of lindane. (Bottom) Arrhenius plot (pseudo-first-order) of the reaction rates for lindane degradation.

original lindane content. At higher temperatures, neither isomer was observed.

The major reaction pathway for pentachlorocyclohexene was further dehydrohalogenation to form trichlorobenzenes, especially the 1,2,4-substituted isomer. Additional reactions formed dichlorophenols, either via hydrolysis of trichlorobenzenes or dehydrohalogenation of hydroxytetrachlorocyclohexenes. Dechlorination continued with the formation of dichloro- and monochlorobenzenes, presumably by H^{-}/Cl^{-} exchange. Monochlorobenzenes or from dichlorobenzenes or firm dichlorobenzenes or firm dichlorobenzenes or firmed with the hydrolysis of dichlorobenzenes or from dichlorobenzenes or firmed.



FIGURE 2. Possible degradation pathways of lindane. The isomers in boldface are typically found in \sim 10-fold higher concentrations than other isomers shown. All isomers for which a specific structure is shown were verified by GC/MS retention times and mass spectra of pure standards.

detected was phenol, which accounted for 18 mol % of the total lindane after 18 h at 350 °C. However, even phenol continues to degrade, as demonstrated by ca. 50% loss after 1 h at 250 °C when phenol was used as the test compound.

On the basis of the isomer distribution of the products, trichlorobenzenes with two adjacent chlorine atoms are preferentially formed via dehydrohalogenation of lindane. Regardless of reaction temperature, 1,2,4-trichlorobenzene was the most abundant isomer, while 1,2,3-trichlorobenzene was found at order-of-magnitude lower concentrations, and 1,3,5-trichlorobenzene was not observed. The same prefer-



FIGURE 3. Degradation of 0.57 mM lindane and formation of dechlorination products in subcritical water at different temperatures. Standard deviations presented are based on triplicate experiments.

ence was also reported previously in alkaline subcritical water (7) and alkaline dehydrohalogenation at ambient temperature (32). Subsequent dechlorination preferentially forms 1,4dichlorobenzene and 2,5-dichlorophenol, as opposed to their other isomers (Figure 2).

Because the reaction cells have a small gas headspace, it is possible that the reactions occur in the vapor phase rather than in the liquid. To test this possibility, the lindane reactions from Table 3 were repeated using a reaction cell with a floating piston to isolate the liquid (containing the lindane) and gas phases (no lindane). Degradation results with only liquid water in contact with lindane were identical (within typical reproducibilities) to those in Table 3, thus demonstrating that the headspace present in the routine cell did not affect the lindane reactions.

Effect of Temperature on Water Basicity. Previous studies on dechlorinating aliphatic organochlorine species in water have relied on added base (*7, 28, 29, 32*). Because dehydrohalogenation and subsequent substitution reactions we observed for lindane are catalyzed by base and because the dissociation constant of water increases with temperature (*27*), it is initially tempting to ascribe the rapid dechlorination observed at higher temperatures to increased hydroxide ion concentrations. The dissociation constant of water increases from 1.0×10^{-14} at ambient to 5.0×10^{-12} at the highest temperature used in this study (300 °C) (*27*). Assuming pure water, the concentration of hydroxide ion increases from 1.0×10^{-7} M at room temperature to 1.1×10^{-6} M at 125 °C. However, further increases in temperature have little effect, with the hydroxide ion concentration raising to 2.2×10^{-6} M at 200 °C to a maximum of 2.5×10^{-6} M at 250 °C and then dropping to 2.2×10^{-6} M at 300 °C.

Because dehydrohalogenation generates HCl, the hydroxide ion concentration actually drops much below that of room temperature (pure) water during dechlorination. For example, with the 9 mM solution of lindane at 200 °C, only 1% dechlorination is required to form enough HCl to reduce the hydroxide concentration to ca. 1×10^{-8} M (based on the water dissociation constants given in ref. 27), which is even lower than the hydroxide concentration in pure water at room temperature. In addition, the pH of the water (after cooling) from the 1 h, 200 °C degradation of lindane was 2.6, as would be expected for the dehydrohalogenation mechanism. Clearly, increased hydroxide concentration in high-temperature water is not responsible for the dramatic increase in dehalogenation reactions.

Tetrachloroethane and Trichloroethene. Dehydrohalogenation of tetrachloroethane was rapid, even at temperatures as low as 105 °C (Figure 4). The half-lives obtained for 105 and 150 °C, were 32 and 11 min, respectively, and the nearly 100% of the tetrachloroethane was removed after 15 min at 200 °C. At each temperature tested, ca. 100% of the tetrachloroethane found was converted to trichloroethene, and a slow loss of trichloroethene was observed at long reaction times (Figure 4).

Higher temperatures are required to degrade trichloroethene, which might be expected because dehydrohalogenation would require the formation of a triple bond. Studies



FIGURE 4. Degradation of 1 mM tetrachloroethane and formation of trichloroethene in subcritical water at different temperatures. Standard deviations presented are based on triplicate experiments.

using trichloroethene as the reactant showed only slow losses at 200 and 250 °C, and 300 °C was required to obtain a halflife of 45 min based on percent degradations of 55 ± 5 (after 10 min), 64 ± 7 (30 min), 77 ± 6 (60 min), and 87 ± 11 (90 min). In comparison, Gillham et al. reported a half-life of 14 h with the zerovalent iron in water at room temperature (*2*), while electrochemical reduction of trichloroethene with palladized iron electrodes has been used to reduce half-lives to a few minutes (δ). It should be noted that these previous studies used low trichloroethene concentrations (11 and 300 μ M, respectively), while we used higher concentrations (19 mM) to aid in determining the reaction products, which may result in reduced reaction rates (discussed later in the text).

No degradation products from the trichloroethene could be identified in the methylene chloride extracts of the product water. Because any such organic products might be very volatile (and thus be lost in the solvent peak during GC analysis), attempts were made to identify such volatiles using a gastight syringe to collect a 1-mL headspace sample after the reaction and SPME sorption both of the headspace and the product water. Both techniques allow solventless injection into the GC/MS so that MS monitoring can begin immediately upon injection. Unfortunately, no product species were identified using either technique.

Reproducibility and Inertness of the Experimental System. As the number of experiments for a cell increased, sporadic faster degradation rates were obtained. Close observation showed slight corrosion of the cells. Therefore, a brass brush was used in the cell during the washing procedure, which eliminated this artifact and resulted in better reproducibility among the replicate experiments. Additional tests into the inertness of the Inconel cells were performed by comparing reaction rates when the experiments were conducted in glass. Reaction conditions were chosen

TABLE 2. Comparison of Degradation Efficiencies Using Inconel and Glass Cells (1 h)

cell material	temperature	% degraded \pm SD ^a
Inconel glass Inconel glass	105 °C 105 °C 150 °C 150 °C	$\begin{array}{c} 71 \pm 14 \\ 68 \pm 12 \\ 58 \pm 10 \\ 71 \pm 8 \end{array}$
	cell material Inconel glass Inconel glass	cell material temperature Inconel 105 °C glass 105 °C Inconel 150 °C glass 150 °C

^a Standard deviations were calculated from triplicate experiments.

TABLE 3. Percent of Total Chlorine Found as the Test Compound, as Organochlorine Products, and as Chloride Ion

	% chlorine \pm SD ^a			
	lindane (9 mM)		tetrachloro- ethane (16 mM)	
temperature time (h) test compound organochlorine products ^c chloride ion total chlorine recovered	200 °C 1 25 \pm 4 3.6 \pm 0.3 37 \pm 7 66 \pm 7	200 °C 18 nd ^b 2.0 \pm 0.2 70 \pm 6 72 \pm 5	$150 \ ^{\circ}\text{C}$ 1 73 ± 9 22 ± 10 6.1 ± 0.5 101 ± 2	$300 \ ^{\circ}C$ 1 nd 19 ± 4 62 ± 10 80 ± 10

^a Standard deviations were calculated from triplicate experiments. ^b nd: not detected. The detection limits for lindane and tetrachloroethane were 0.2 and 0.05%, respectively. ^cOrganochlorine products were determined by GC/MS, as shown in Figure 3.

to give ca. 60-70% degradation of tetrachloroethane and lindane so that the relative rates obtained in glass and Inconel could be observed. Table 2 shows that data obtained in glass were within the range of error of the Inconel cell results. Unfortunately, the glass vials could not be used over 150 °C, so some enhancement of reaction rates by the Inconel cell may still be possible at higher temperatures. To guard against this possibility, all experiments done at temperatures above 150 °C were performed using replicate cells, some which had been heavily used and some which were nearly new. The results from new and old cells were within the quantitative reproducibilities typically seen for these experiments, indicating that Inconel cell age did not affect the reaction rates. However, as a matter of caution, we typically limit the working life of the Inconel cells at higher temperatures to ca. 100 h with lower concentrations of reactant (e.g., 1 mM) and ca. 40 h with higher concentrations of reactant (e.g., 20 mM).

Chlorine/Chloride Mass Balance. Previous investigations have generally not attempted to determine mass balance for the products of dechlorination, particularly for the organic components (2, θ), although Bunte et al. (7) did recover ca. 90% of the chloride ion from the complete degradation of lindane at 350 and 400 °C from reactions with water and added NaOH. In the present study, we attempted to account for all chlorine atoms (whether organochlorines or chloride ion) at conditions where the reaction was in its intermediate stages and conditions where nearly complete dechlorination occurred.

To aid in reproducibly detecting chloride ions, all experiments were performed with higher concentrations (9–20 mM) of test compounds. Also, to ensure that the Inconel cells did not remove chloride ions from the water, a recovery test on chloride was performed by placing 3 mL of a NaCl solution (2.85 mM in chloride) into triplicate Inconel cells and heating them for 1 h at 300 °C. Recoveries of chloride were $100 \pm 3\%$, demonstrating that Inconel does not adsorb chloride ion.

The results of attempts to achieve chlorine mass balance for lindane and tetrachloroethane are presented in Table 3. For lindane, the total mass balance for chlorine atoms was ca. 70%, whether the removal of lindane was complete (200



FIGURE 5. GC/MS chromatogram of degradation products from 100 mg PVC after 1 h at 300 °C in subcritical water.

IABLE 4. Degradat	tion of 1,9-D	ichlorononane	and	Dieldrin	after
1 h					

	temp (°C)	% of test compound degraded \pm SD ^a	% of chlorine as chloride \pm SD
1,9-dichlorononane dieldrin	200 200 300	$100 \\ 35 \pm 5 \\ 100$	$98 \pm 10 \\ 5 \pm 1 \\ 74 \pm 3$
^a Standard deviations	were calc	ulated from tri	plicate experiments

°C for 18 h) or only partial (200 °C for 1 h). Note that the mass balance attempted to account for the millimoles of chlorine both as chloride ions and by quantitating all of the intermediate organics formed from lindane, which are shown in Figure 2. Similarly, the total mass balance of chlorine from tetrachloroethane was 100 and 80% for partial removal (150 °C for 1 h) or complete removal (300 °C for 1 h) of the tetrachloroethane.

It should be noted that somewhat slower reactions occurred when using these higher concentrations of lindane and tetrachloroethane. For example, the removal of lindane at 200 °C after 1 h dropped from >99% (at 0.6 mM) to ca. 75% (with 9 mM). Similarly, the removal of tetrachloroethane at 150 °C (1 h) dropped from 97% (with 1 mM) to 25% (with 16 mM).

Dieldrin and 1,9-Dichlorononane. Limited tests were performed with 1,9-dichlorononane to determine whether aliphatic chlorines which are isolated yield rapid dehydrohalogenation (in contrast to the tetrachloroethane where all four chlorines are found on two adjacent carbon atoms). While reaction for 1 h at 150 °C resulted in ca. 50% loss, 1 h at 200 °C resulted in 100% removal of the 1,9-dichlorononane (Table 4). Also, the ca. 100% recovery of chloride ions demonstrated that complete dechlorination was achieved. Only one organic product was found by GC/MS, which had a mass spectrum consistent with the expected product, 1,8-nonadiene (however, standards were not available to allow the identity to be confirmed).

Dieldrin was investigated as a second example of a highly chlorinated pesticide which, like lindane, has six chlorine atoms bound to aliphatic ring carbons. As shown in Table 4, removal of dieldrin at 200 °C (1 h) was similar to that achieved for lindane. However, no significant intermediate organic products could be found in the water extract from the dieldrin degradation, in contrast to the large number of reaction products found for lindane (Figure 2). Because only 5% of the chlorine could be found as chloride ion (Table 4), we expect that the intermediate products from dieldrin were too polar to be extracted by methylene chloride and determined by GC/MS and speculate that hydrolysis of dieldrin's epoxide group leads to the formation of carboxylic acids, which are too polar to be determined by our methods.

PVC Degradation. The final investigations were performed on poly(vinyl chloride). Because the weight average molecular weight was 62 000 amu, the use of PVC allowed us to study the dehalogenation of compounds which should have no significant solubility in water, even at elevated temperatures. To allow for gravimetric measurements of the mass loss of the PVC, 100 mg of PVC was used per 3 mL of water for each test. After the reaction was completed, the PVC residue was air-dried and weighed to determine the mass lost. All reactions were performed for 1 h.

No detectable loss in PVC mass occurred at 200 °C, although a slight yellowing of the polymer was observed. However, when the reaction temperature was raised to 250 °C, 50% of the mass was lost (Table 5). At both 300 and 370 °C, ca. 44 wt % of the initial PVC mass remained as residue. Because PVC is 56.6% chlorine by weight, the ca. 56% weight loss found for the 300 and 370 °C reactions corresponds almost perfectly with the weight loss expected if all chlorine was removed from the polymer.

Attempts to identify organic products by GC/MS showed no organochlorine molecules but did show a range of aromatic hydrocarbons from benzene to anthracene (Figure 5). However, the total quantity of these products accounted for only ca. 1% of the total PVC mass. Carbon and hydrogen content of the residue and chloride ion concentrations in the product waters were also performed in an effort to achieve mass balance. Elemental analysis of the PVC residues showed a 1:1 carbon/hydrogen molar ratio, as would be expected if

TABLE 5. Mass Balance for PVC after 1 h Degradation in Subcritical Water

	product mass from 100 mg PVC (mg \pm SD) a				
	residue				
temp (°C)	total	as C ^b	as H ^b	chloride in water	
250 300 370	$\begin{array}{c} 49.5 \pm 0.3 \\ 43 \pm 1 \\ 44 \pm 1 \end{array}$	$\begin{array}{c} 41 \pm 2 \\ 40 \pm 5 \\ 39 \pm 1 \end{array}$	$\begin{array}{c} 3.6 \pm 0.2 \\ 3.3 \pm 0.5 \\ 3.5 \pm 0.1 \end{array}$	$\begin{array}{c} 44\pm3\\ 46\pm5\\ 47\pm8\end{array}$	

^a Standard deviations were calculated from triplicate experiments. ^b Content of each element in the residues was determined with a C,H,N analyzer.

the polymer residue was formed of high molecular weight conjugated alkenes $(-CH=CH-CH=CH-)_n$, as would be formed from dehydrohalogenation. In addition, mass balance for the residue (the sum of carbon and hydrogen as compared to residue mass) was ca. 98%, which demonstrates that no significant chlorine remains in the PVC residue after water treatment. Finally, ca. 80% of the total chorine was found as chloride ion in the product water (Table 5).

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