# Effects of FeS on the Transformation Kinetics of $\gamma$ -Hexachlorocyclohexane

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Distinctly different rates and pathways were observed for abiotic transformation of  $\gamma$ -hexachlorocyclohexane ( $\gamma$ -HCH) between homogeneous systems and systems containing FeS solid. The observed half-lives of  $\gamma$ -HCH decrease from about 1136 and 126 d in homogeneous systems to about 55 and 50 d in heterogeneous systems at pH  $\sim$ 6.9 and pH ~8.3, respectively. While no appreciable difference in the measured rate was found between the two tested heterogeneous systems of pH 6.9 and pH 8.3, the observed hydrolysis rate constant for the homogeneous systems is highly pH dependent, being constant at  $\sim 0.0005 \text{ d}^{-1}$  in pH 2.26-6.73, and increased by an order of magnitude per pH unit from pH 6.73 to pH 12.02. A dehydrohalogenation pathway from  $\gamma$ -HCH to pentachlorocyclohexene followed by parallel reactions to three trichlorobenzenes is proposed for the hydrolysis reaction in the homogeneous systems. For the heterogeneous systems, the reactions likely follow both the hydrolysis pathway and pathways from  $\gamma$ -HCH to tetrachlorocyclohexene (TeCCH) and to dichlorocyclohexadiene (DCCD) via dichloroelimination followed by dehydrohalogenation from TeCCH to dichlorobenzenes or from DCCD to chlorobenzene. This study suggests that environmental modeling using hydrolysis rate data measured in homogeneous systems may bear significant inaccuracy for the predicted fate and transport of HCH isomers in highly heterogeneous ecosystems at the regional or mega scales.

# Introduction

 $\gamma$ -Hexachlorocyclohexanes ( $\gamma$ -HCH) or lindane is the effective component and 12–14 wt % of the technical HCH, a mixture of all eight HCH isomers (1). The worldwide annual production of the technical HCH was about 6 000 000 t in 1970s (2). Because of its relatively long half-lives in ecosystems and its proven adverse effects on kidney, liver, and nerve, immune, and endocrine systems, the technical HCH was phased out in 1970s in developed countries (3), but it is still in use in some developing countries; pure  $\gamma$ -HCH is allowed for restricted use in developed countries including the United States (4). The heavy utilization of  $\gamma$ -HCH has caused its wide spreading and accumulation even in such cold and

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pristine areas as the North Pole through long-range atmospheric transport and ocean currents following a possible global distillation process (3, 5, 6). Recently reported  $\gamma$ -HCH concentrations ranging from <1 to 20 ng/L in surface waters and as high as 10 ng/g in river sediments and fish (7–11) suggested potential risks the chemical possesses to ecosystems and human beings. Research focusing on fate and transport of  $\gamma$ -HCH is necessary for better monitoring and assessing its environmental risks at various spatial and time scales (3, 12).

This study examines the hydrolysis reactions of  $\gamma$ -HCH under anoxic conditions in both homogeneous and heterogeneous systems.  $\gamma$ -HCH was shown in previous studies to undergo biotic and abiotic transformations, and the rates of its degradations depend largely upon the environmental conditions. Several studies demonstrated that  $\gamma$ -HCH can be degraded under both aerobic and anaerobic conditions by mixed cultures; that 1,3,4,5,6-pentachlorocyclohexene (PCCH) and 2,3,4,5-tetrachlorcyclohexene (TeCCH) were believed to be the major intermediates; and that chlorobenzene, benzene, and carbon dioxide were found as the final products (1, 13, 14). HCH is relatively stable under sunlight due to its lack of UV absorbance above 300 nm, but it is reactive in the presence of hydroxyl radical (15). Because of its polychlorinated structure and relatively high redox potential, reductive transformations under anoxic conditions are potentially significant, especially in the presence of reducing mineral species such as iron sulfide and vermiculite. Such reactions have not been investigated even under restricted laboratory conditions, however (16). Hydrolysis has been cited as the most important abiotic transformation for HCH, and its rates may be slow but significant according to previous studies (17). Prior hydrolysis studies reported half-lives for  $\gamma$ -HCH of 115.5, 281.7, and 35.4 d at room temperature and pH 3, 7, and 9, respectively (4), but detailed hydrolytic pathways and pH dependence of the rates have not been delineated.

This study was set out to systematically investigate the kinetics of  $\gamma$ -HCH hydrolysis in the presence and absence of FeS. A series of batch reactors with or without FeS were set up for quantifying the time-dependent concentrations of  $\gamma$ -HCH and the intermediate and final products. We identified intermediate and final products of the hydrolysis reaction, measured the rates of  $\gamma$ -HCH disappearance, and measured the rates of intermediate and final product formation. Reaction pathways were proposed on the basis of the identified intermediate and final products and their stereochemistry, and possible mechanisms of  $\gamma$ -HCH hydrolysis in both homogeneous and heterogeneous systems were characterized. Since hydrolysis is highly pH dependent, the reactions in the absence of FeS were examined over a wide range of pH conditions, and the reaction order with respect to hydroxyl ion was determined from quantitative relationships between the apparent hydrolysis rates and the solution pH. The effects of FeS on the hydrolytic reaction were delineated by comparing the differences of the reaction rates and pathways between the two systems.

# **Experimental Section**

**Chemicals, Solutions, and Experimental Setups.**  $\gamma$ -HCH; 1,2,4-, 1,2,3-, 1,3,5-TCBs; 1,3-, 1,4-, 1,2-dichlorobenzene (DCBs); chlorobenzene (CB); and the chemicals used for preparing pH buffer and background electrolyte solutions were purchased in their highest grades available from Sigma Chemical Co. and used as received. FeS, commonly called mackinawite, was chosen as a representative reducing

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TABLE 1. Solution Chemistry, pH Buffers, and Observed Hydrolysis Rate Constants of the Eight Homogeneous Systems

| рН    | buffer solutions<br>(0.05 N)                                     | $(d^{-1})$              | (d)   | $k_{ m b}{}^a$ (5 $	imes$ 10 $^3$ M $^{-1}$ d $^{-1}$ ) |
|-------|--|-------------------------|-------|---|
| 2.26  | glycine + NaCI-HCI   | $0.00051 \pm 0.00004$   | 1360  |   |
| 4.67  | ĂĂc–NaAc   | $0.00052 \pm 0.00004$   | 1333  |   |
| 6.73  | K <sub>2</sub> HPO <sub>4</sub> -KH <sub>2</sub> PO <sub>4</sub> | $0.00061 \pm 0.00007$   | 1136  |   |
| 8.32  | Tris-HCI   | $0.0057 \pm 0.0004^{b}$ | 121.6 | $2.73 \pm 0.092^{\circ}$                                |
| 9.24  | glycine + NaCl-NaOH  | $0.045 \pm 0.0013^{b}$  | 15.4  | $2.58 \pm 0.091^{\circ}$                                |
| 9.97  | Na <sub>2</sub> CO <sub>3</sub> -NaHCO <sub>3</sub>              | $0.425 \pm 0.065^{b}$   | 1.63  | $4.55 \pm 0.089^{\circ}$                                |
| 11.03 | glycine + NaCl-NaOH  | $3.86 \pm 0.39^{b}$     | 0.18  | $3.60 \pm 0.089^{\circ}$                                |
| 12.02 | glycine + NaCl-NaOH  | $46.6 \pm 13.1^{b}$     | 0.02  | $4.45 \pm 0.094^{\circ}$                                |

mineral species because it is a metastable mineral formed under sulfate-reducing environments (18-20) and is very effective for reductive dechlorination of polychlorinated organic compounds such as carbon tetrachloride (CT) (21), trichloroethylene (TCE) (22), chloroform (CF) (23), and hexachloroethane (HCA) (24). The FeS solid used in this study was synthesized in our laboratory following a procedure developed by Butler and Hayes (24) with minor adjustments. In brief, aqueous FeCl<sub>2</sub> and Na<sub>2</sub>S solutions in equal molarities were mixed and reacted in a container placed in a glovebox filled with a N2 gas. After the reaction was completed, the slurry was centrifuged, washed six times with deoxygenated Milli-Q water, and freeze-dried. The FeS solid was then stored in sealed glass ampules with headspace filled by N<sub>2</sub> gas until use in characterization and kinetics experiments. The solid has a BET specific surface area of  $10 \text{ m}^2/\text{g}$  and has poor degree of crystallinity according to its powder X-ray diffraction pattern.

Table 1 lists the eight different aqueous solutions and the chemicals used as pH buffers. The solutions were prepared in an anaerobic chamber using N2 gas-purged Milli-Q water, and their ionic strengths were adjusted to 0.1 M with NaCl. All eight solutions were used in homogeneous systems; two solutions at pH 6.9 and 8.3, respectively, were used in heterogeneous systems. The rate of  $\gamma$ -HCH transformation in each system was examined by setting up a group of 20 precleaned and sterilized glass ampules (5 mL), each filled with 4.95 mL of a given buffer solution or FeS solid suspension of a fixed pH using a calibrated automatic pipet. The ampules containing the solutions or suspensions were then spiked with a  $\gamma$ -HCH methanol stock solution. The resulting solution contained ~1% methanol by volume and an initial  $\gamma$ -HCH concentration of ~18  $\mu$ M, which was below its aqueous solubility of 25.7  $\mu$ M (25). After the solution spiked, the ampules were covered with aluminum foil, immediately removed out of the glovebox, sealed in a methane-oxygen flame, placed in the dark, and mixed horizontally at 180 rmp on a shaker preset at 25 °C. The reaction times were recorded since the start of mixing. Each ampule has a headspace of about 3 mL that contains approximately 0.78% of  $\gamma$ -HCH on the basis of a Henry's law constant of 0.0032 L atm mol<sup>-1</sup> at the tested temperature condition (25). The amounts of the reactant and products partitioning to the headspace were thus not considered in mass balance calculations.

For the heterogeneous systems, FeS was added in the glovebox to each reactor to obtain a final FeS suspension concentration of ~10 g/L, and the reactor was immediately spiked with  $\gamma$ -HCH, sealed in the flame, and mixed. An 8–10% of reduction in  $\gamma$ -HCH at t = 0 was observed because of solute adsorption on FeS surfaces via hydrophobic interactions. This reduction was accounted in mass balance calculation by assuming that the reactant adsorbed on the solid is chemically reactive, an assumption that was tested in a prior study (*24*). As shown later in this paper, adsorption of the reactant on FeS solid surfaces may be an essential step for FeS-facilitated transformation of  $\gamma$ -HCH.

Duplicate reactors were taken from the shaker at predetermined times, centrifuged in the case of FeS-containing reactors, and broken open. An aliquot (50  $\mu$ L) was withdrawn immediately from each reactor and extracted with HPLCgrade hexane (1 mL) in a 2-mL GC vial. Pentachloronitrobenzene (PCNB) in hexane solution was added to each extraction bottle as an internal standard at a level of 0.5  $\mu$ M for evaluating extraction efficiency, mass loss of the target organic solutes during extraction and analysis procedures, and relative peak positions of all the detected solutes on gas chromatographs. After being mixed for 3 min on a mixer, the samples were immediately analyzed for the reactant, intermediate, and final products using GC and GC–MS following the procedure described below.

Detection and Quantification of the Reactant and Products. The gas chromatography used was an Agilent 6890 GC equipped with a micron electron capture detector ( $\mu$ -ECD), an on-column injector, and a Chrompack CP-sil 5CB column (50 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m). Detector temperature was set at 315 °C. Oven temperature was initially isothermal at 35 °C for 1 min, ramped from 35 to 150 °C at a rate of 15 °C/min and isothermal at 150 °C for 4 min, then ramped at 6 °C/min to 225 °C and isothermal for 2 min, and again ramped at 15 °C/min to 250 °C and isothermal for 4 min. N<sub>2</sub> gas at 99.99% purity was used as both the carrier at a flow rate of 1 mL/min and the makeup gas at 60 mL/min. The concentrations of  $\gamma$ -HCH and the final products were calculated from their respective GC peak areas against sixpoint standard curves established using external hexane solution standards. The concentrations of the intermediate product were quantified using a mass balance approach detailed in the next section. The peak area and the concentration of the internal standard (PCNB) were also referred for solute quantification as well as for evaluating the stability of both instruments.

Hexane extracts of selected aqueous samples were analyzed on a GC–MS (Finnigan model GC8000<sup>TOP</sup> voyager) equipped with an HP-5 column (50 m × 0.32 mm × 0.25  $\mu$ m, J&W Scientific, Folsom, CA) for identifying the intermediate and final products of the reactions. The conditions set for GC–MS were similar to those mentioned above for GC–ECD. The retention times of final products were determined by co-injection of their hexane solution standards. The GC–MS spectra of the target solutes were compared with their respective spectra from the standard library and those of the co-injected standards. The measurements were repeated six times to confirm the detected solutes and to determine the standard deviations for the reported concentrations.

#### **Results and Discussion**

**Identified Intermediate and Final Products.** In the FeSfree systems, three final products (1,2,4-, 1,2,3-, and 1,3,5-TCBs) were identified and confirmed with three external standards using GC–MS (Figure S1 and S2 in Supporting Information). An intermediate product (PCCH) was identified



FIGURE 1. Concentration profiles of  $\gamma$ -HCH, intermediate, and final products for the homogeneous systems at pH conditions of 2.26, 4.67, 6.73, 8.32, 9.24, 9.97, 11.03, and 12.02, respectively. Symbols represent experimental data, and lines represent the model fits of the data.

with detailed analysis of GC–MS spectra but was not confirmed with external standard because the chemical is not commercially available. In the FeS-containing systems, seven final products (CB; 1,2-, 1,3-, and 1,4-DCBs; and the three TCBs identified in the homogeneous systems) were detected and confirmed using their respective external standards. In addition to PCCH, TeCCH and dichlorocyclohexadiene (DCCD) were detected as two other intermediate products at relatively lower concentration levels in pH 8.3 systems. These two intermediates were further confirmed for a reactor system run independently at pH 8.3, t = 42 d (Figure S3 in Supporting Information), initial  $\gamma$ -HCH concentration of 200  $\mu$ M, and FeS = 100 g/L; here, higher concentrations of both  $\gamma$ -HCH and FeS were chosen for achieving higher concentrations of the intermediate products for better GC–MS detection.

The concentrations of PCCH in all reactors of FeS-free and FeS-containing systems were estimated on the basis of



FIGURE 2. Concentration profiles of the final products for the heterogeneous systems at pH 6.90 and pH 8.30. Symbols represent experimental data, and lines represent the smooth lines of the data.

a responsive ratio of 0.6 relative to the mole to peak area of PCNB; i.e.

$$C_{\rm PCCH} = 0.6 \frac{V_{\rm aqueous}}{V_{\rm hexane}} \frac{C_{\rm PCNB} A_{\rm PCCH}}{A_{\rm PCNB}}$$
(1)

where A<sub>PCCH</sub> and A<sub>PCNB</sub> are GC peak areas of PCCH and PCNB, respectively;  $C_{PCCH}$  (in aqueous phase) and  $C_{PCNB}$  (in hexane phase) are their respective concentrations; and  $V_{\text{aqueous}}$  and  $V_{\text{hexane}}$  are the volume of aqueous phase extracted and hexane added, respectively. The responsive ratio of 0.6 was an average value of 10 points obtained using a mass balance approach for the homogeneous systems of pH 9.24 and reaction time for 16 d, by which the sum of molar concentrations of  $\gamma$ -HCH, TCBs, and PCCH is assumed equal to the initial  $\gamma$ -HCH concentration. The underlying assumptions, which are valid according to high mass recovery indicated below, are that PCCH and the three TCBs are the only intermediate and final products formed during the reaction and that there is no measurable system loss for each of these chemicals. The reactors specified were chosen because they contained relatively high concentrations of PCCH and because the aqueous phase PCCH concentrations in duplicate reactors were not sensitive to the errors in reaction time due to sufficiently slow rate of reaction. Concentrations of TeCCH and DCCD in the FeS-containing systems were too low to be estimated using this technique.

Figure 1 presents the concentration profiles of the reactant, intermediate, and final products of the homogeneous systems at the eight pH conditions. It shows that 1,2,4-TCB is the major product (>50% of total products) under all tested base conditions and that 1,2,3-TCB was the second important product (>30% of total products) whereas 1,3,5-TCB is the minor one. The distribution pattern of the three products is also dependent upon the solution pH. At pH  $\leq$  8.32, no 1,3,5-TCB was detected, whereas at pH 9.24 and pH 12.02, 1,3,5-TCB consists of ~2% and 20% of the total products, respectively. The mass balance of the remaining  $\gamma$ -HCH, intermediate, and final products was performed for each reactor, and the results showed total 92–104% mass recovery in all reactors tested.

Figure 2 presents the concentration profiles of the reactant, intermediate, and final products of the FeS-containing systems at pH 6.9 and pH 8.3. At pH 6.9, 1,4-DCB (>36%), 1,2-DCB (> 15%), and 1,2,4-TCB (>15%) are the major products whereas 1,2,3-TCB is a minor product. At pH 8.3, 1,4-DCB (50%) and 1,2-DCB (25%) are dominant products, whereas 1,2,4-TCB and 1,2,3-TCB have relatively lower concentrations. 1,3,5-TCB and 1,3-DCB are not detected in both cases.

A comparison of the concentration profiles of the two systems at the approximately same pH conditions shows



FIGURE 3. Concentration profiles of  $\gamma$ -HCH at pH 6.73 or pH 6.9 showing dramatic enhancement of  $\gamma$ -HCH degradation in the presence of iron sulfide (10 g/L).

that the rate of  $\gamma$ -HCH degradation in the FeS-containing systems is much greater than in the FeS-free systems. Figure 3 shows that, after 104 d of reaction,  $\gamma$ -HCH concentration was decreased from 17.2 to 5.1  $\mu$ M in the FeS-containing system (pH 6.9) as compared to a decrease of the reactant from 17.8 to 16.7  $\mu$ M in the FeS-free system (pH 6.7). The estimated half-life of  $\gamma$ -HCH is about 55 d as compared to 1135 d for the homogeneous systems at the approximately same pH condition. More importantly, two TCBs and two DCBs were detected at appreciable concentrations in the heterogeneous systems, whereas no final product was detected in the FeS-free system at pH 6.7.

**Proposed Hydrolysis Pathway for the Homogeneous Systems.** Figure 4 schematically shows a possible pathway of  $\gamma$ -HCH hydrolysis reaction proposed for the FeS-free systems based on the identified intermediate and final products. The first step of hydrolysis is likely the formation of PCCH via anti-periplanar dehydrohalogenation (eq 2), a commonly believed base hydrolysis mechanism, through a bimolecular elimination (E2) reaction in which abstraction of the hydrogen on the carbon occurs simultaneously with cleavage of the C–X bond, forming a carbon–carbon bond.



PCCH may be further dehydrochlorinated via two possible mechanisms. The first mechanism may be direct formation of TCBs via simultaneous eliminations of two chlorine and two hydrogen atoms from PCCHs (27), and the second mechanism may involve two steps from PCCHs to TCBs via



FIGURE 4. Possible pathway of  $\gamma$ -HCH dehydrohalogenation in both the homogeneous and heterogeneous systems.



FIGURE 5. Possible pathways of reductive dichloroelimination + dehydrohalogenation of  $\gamma$ -HCH in the presence of iron sulfide.

a second intermediate tetrachlorocyclohexadiene (TeCCD). However, TeCCD was not detected, suggesting that the second mechanism may be unlikely or that the reactions from TeCCD to TCBs may be rapid.

In addition to the dehydrochlorination pathways delineated in Figure 4, formation of substitution intermediates during the reaction was considered for the homogeneous systems. In general, hydrolysis is defined as a chemical transformation in which an organic molecule (RX) reacts with water, resulting in the formation of a new covalent bond with OH<sup>-</sup> and simultaneous cleavage of the covalent bond with X, the leaving group, on the original molecule (*26*). The fact that the substitution intermediates were not detected in the tested systems is probably because polyhalogened carbon atoms are not reactive with water via the nucleophilic substitution by OH<sup>-</sup> (*26*). As a result, this substitution mechanism was not included as an alternative in our hypothesized pathways.

**Proposed Reaction Pathways in the FeS-Containing** Systems. Two separate pathways are proposed for the reactions of  $\gamma$ -HCH in the presence of FeS. The first pathway is exactly the same as shown schematically in Figure 4. The second pathway shown in Figure 5 involves two intermediate products of TeCCH and DCCD and final products of DCBs and CB. It is assumed that  $\gamma$ -HCH undergoes dichloroelimination to form TeCCH as shown in Figure 5. TeCCH can be further degraded either to DCBs via double dehydrohalogenation or to DCCD via dichloroelimination. DCCD may react to form either CB, which is detected, via dehydrohalogenation or benzene, which is not detected, via dichloroelimination. A third possibility may be formation of trichlorocyclohexadiene (TCCD) via dichloroelimination of PCCH or dehydrohalogenation from TeCCH. This possibility, however, is not considered here as a major pathway because TCCD was not detected.

The pathways proposed above are based on the following two major hypotheses: (i) the dissolved reducing species (Fe(II) and S(II)) have no effect on the chemical reactions and (ii) TCBs and DCBs are stable products in the presence of FeS. To test the two hypotheses, we set up two sets of batch experiments following the same procedures described above. The first set of experiments consisted of reactors containing aqueous solutions of  $\gamma$ -HCH + FeS + FeCl<sub>2</sub> (6 mM) or  $\gamma$ -HCH + FeS + Na<sub>2</sub>S (6 mM). The results showed no effect of aqueous FeCl2 or Na2S on the reaction rates under the same pH conditions, suggesting that the surfaces of FeS, instead of the reducing species dissolved in solution phase, are likely responsible for degradation of  $\gamma$ -HCH and the intermediate products. The finding is consistent with Butler and Hayes (24) and further implies that  $\gamma$ -HCH has to be adsorbed at the surface before it is degraded. The second set of experiments was initiated with TCBs and DCBs as the reactants in the FeS-containing systems. After 65 d of mixing at temperature of 35 °C, neither change of the reactant concentrations nor formation of new species was observed, indicating that TCBs and DCBs are stable in the presence of FeS over the observed time period and that DCBs and CB are possibly formed from the intermediate polychlorinated cyclohexenes.

A major difference in the reaction mechanisms between the homogeneous and the heterogeneous systems is that the reactions occurring at the surfaces of FeS could follow either dichloroelimination or dehydrohalogenation. In the presence of FeS surfaces, electrons provided by the solid may attack  $\gamma$ -HCH and the polychlorinated cyclohexenes, forming a double bond by eliminating two Cl<sup>-</sup> from each of these molecules. It is expected that whether a reaction follows dehydrohalogenation or dichloroelimination depends largely on the reactivity of the reactant and the relative positions of chlorines on the cyclic structures. Cyclohexenes having four or more chlorines have greater chances to possess chlorines on two neighboring carbon positions and, hence, can be degraded via dichloroelimination. According to the distribution of the final products (Figure 2), formation of DCBs is



FIGURE 6. pH dependence of the apparent rate constants for (A) the disappearance of  $\gamma$ -HCH ( $k_{1,obs}$ ) and (B) formation of the three TCBs ( $k_{21'}$ ,  $k_{22'}$ ,  $k_{22'}$ ,  $k_{23'}$ ) in homogeneous systems.

favored over TCBs whereas CB is the least favored product, suggesting that the reaction pathway from PCCH to TeCCH to DCBs is favored at the test conditions.

**Rates of**  $\gamma$ -**HCH Hydrolysis in FeS-Free Systems.** Hydrolysis can be catalyzed by acids or bases, but  $\gamma$ -HCH hydrolysis rate under acidic conditions is much slower than in basic conditions according to the concentration profiles shown in Figure 1. Under neutral and basic conditions, the hydrolysis reaction can be approximated using the following:

$$\frac{\partial a_{\rm HCH}}{\partial t} = -k_1 a_{\rm HCH} a_{\rm OH} \tag{3}$$

where  $a_{\text{HCH}}$  is the activity of  $\gamma$ -HCH and *t* is the reaction time (in d). At constant pH and under dilute solution condition, eq 3 can be further approximated to

$$\frac{\partial a_{\rm HCH}}{\partial t} = -k_{1,\rm obs}C_{\rm HCH} \tag{4}$$

or

$$C_{\rm HCH} = C_{\rm HCH,0} e^{-k_{\rm 1,obs}t}$$
(5)

where  $C_{\rm HCH}$  and  $C_{\rm HCH,0}$  are the time-dependent and the initial aqueous-phase concentrations of  $\gamma$ -HCH, respectively, and  $k_{\rm 1,obs}$  is the pseudo-first-order rate constant of the reaction.

Formation of intermediate and final products can be modeled using the pathway shown in Figure 4 (i.e., a reaction from  $\gamma$ -HCH to PCCH followed by parallel reactions to the three final products). The Supporting Information shows the detailed mathematic derivation of the kinetics model, and the reduced time-dependent concentrations of PCCH and the three TCBs are given here:

$$C_{\rm PCCH} = \frac{C_{\rm HCH,0} k_{\rm 1,obs}}{k'_2 - k_{\rm 1,obs}} (e^{-k_{\rm 1,obs}t} - e^{-k'_2})$$
(6)

$$C_{1,2,3-\text{TCB}} = C_{\text{HCH},0} \left[ \frac{k'_{21}}{k'_{2}} - \frac{k'_{21}}{k'_{2} - k_{1,\text{obs}}} e^{-k_{1,\text{obs}}t} + \frac{k_{1,\text{obs}}(k'_{21}/k'_{2})}{k'_{2} - k_{1,\text{obs}}} e^{-k'_{2}t} \right]$$
(7)

$$C_{1,3,5-\text{TCB}} = C_{\text{HCH,0}} \left[ \frac{k'_{22}}{k'_2} - \frac{k'_{22}}{k'_2 - k_{1,\text{obs}}} e^{-k_{1,\text{obs}}t} + \frac{k_{1,\text{obs}}(k'_{22}/k'_2)}{k'_2 - k_{1,\text{obs}}} e^{-k_2't} \right]$$
(8)

$$C_{1,2,4-\text{TCB}} = C_{\text{HCH},0} \left[ \frac{k'_{23}}{k'_2} - \frac{k'_{23}}{k'_2 - k_{1,\text{obs}}} e^{-k_{1,\text{obs}}t} + \frac{k_{1,\text{obs}}(k'_{23}/k'_2)}{k'_2 - k_{1,\text{obs}}} e^{-k_2't} \right]$$
(9)

where  $C_{PCCH}$ ,  $C_{1,2,3-TCB}$ ,  $C_{1,3,5-TCB}$ , and  $C_{1,2,4-TCB}$  are the timedependent aqueous phase concentrations of PCCH and TCBs,

TABLE 2. Distribution and Pseudo-First-Order Rate Constants for the Three Hydrolytic Products in Homogeneous Systems

| рН                  |                          | <i>k</i> (d <sup>-1</sup> ) | product distribution (%) |
|---------------------|--------------------------|-----------------------------|--------------------------|
| 12.02               | <i>k</i> <sub>21</sub> ′ | $10.3\pm1.29$               | 26.7 (1,2,3-TCB)         |
|                     | k <sub>22</sub> '        | $5.51\pm0.71$               | 18.2 (1,3,5-TCB)         |
|                     | k <sub>23</sub> '        | $21.3 \pm 2.44$             | 55.1 (1,2,4-TCB)         |
| 11.03               | $k_{21}'$                | $0.820 \pm 0.043$           | 29.4 (1,2,3-TCB)         |
|                     | $k_{22}'$                | $0.157 \pm 0.016$           | 5.0 (1,3,5-TCB)          |
|                     | k23'                     | $1.71 \pm 0.17$             | 62.8 (1,2,4-TCB)         |
| 9.97                | $k_{21}'$                | $0.076 \pm 0.0084$          | 29.9 (1,2,3-TCB)         |
|                     | k22'                     | а                           | 1.2 (1,3,5-TCB)          |
|                     | $k_{23}'$                | $0.176 \pm 0.015$           | 68.6 (1,2,4-TCB)         |
| 9.24                | $k_{21}'$                | $0.0203 \pm 0.0007$         | 31.2 (1,2,3-TCB)         |
|                     | $k_{22}'$                | $0.0012 \pm 0.0003$         | 0.9 (1,3,5-TCB)          |
|                     | k23'                     | $0.0369 \pm 0.0014$         | 56.9 (1,2,4-TCB)         |
| 8.32 <sup>d</sup>   | $k_{21}'$                | $0.0018 \pm 0.0001$         | 11.4 (1,2,3-TCB)         |
|                     | K22'                     | а                           | - (1,3,5-TCB)            |
|                     | k <sub>23</sub> '        | $0.00406 \pm 0.0002$        | 26.5 (1,2,4-TCB)         |
| <sup>a</sup> Not de | termined                 | because of insufficien      | t data.                  |

and  $k_{21}'$ ,  $k_{22}'$ , and  $k_{23}'$  are the pseudo-first-order rate constants for the formation of the three TCBs.  $k_2'$  is the sum of  $k_{21}'$ ,  $k_{22}'$ , and  $k_{23}'$ .

For each set of rate data obtained at a given pH condition, eq 4 was used to fit the experimental data of  $C_{\rm HCH} > 1 \,\mu M$ using a nonlinear quasi-Newton procedure (Systat 10.0) for obtaining the apparent rate constant  $(k_{1,obs})$  of the hydrolysis reaction. Data points of  $C_{\rm HCH}$  < 1  $\mu$ M, which are beyond approximately 4 half-lives of the reaction, are not included in order to avoid possible artifacts caused by near-equilibrium conditions. Equations 6-9 were used to fit the concentration profiles measured for PCCH and three TCBs using the same statistical procedure to obtain  $k_{2'}$ ,  $k_{21'}$ ,  $k_{22'}$ , and  $k_{23'}$ , respectively. Specifically,  $k_{2}'$  was first obtained using eq 5 and  $k_{1,obs}$ values listed in Table 1, and the resulting  $k_2'$  value, along with  $k_{1,obs}$ , was then used for fitting the three rate constants using eqs 7–9. The resulting  $k_{1,obs}$ ,  $k_{21}'$ ,  $k_{22}'$ , and  $k_{23}'$  values, along with their respective 95% confidence intervals, are listed in Table 2. The fitted concentration profiles are also shown in Figure 1 for the reactant, intermediate, and final products, which indicate adequate model fits to the data under all pH conditions.

pH Dependence of Reaction Rate Constants and Hydrolysis Mechanisms. The fitted  $k_{1,obs}$  and  $k_{21}'$ ,  $k_{22}'$ , and  $k_{23}'$ are plotted in Figure 6 against the solution pH. This figure shows that the change of the logarithmic value of  $k_{1, obs}$  as a function of pH can be divided into two regions. From pH 2.26 to pH 6.73, the  $k_{1,obs}$  value is relatively constant (0.0005– 0.0006 d<sup>-1</sup>) at pH  $\leq$  6.73, but it increases rapidly from 0.0006 to 30.7 d<sup>-1</sup> as pH increases from 6.73 to 12.02. The slopes of the two regions shown in Figure 6 are 0.017 and 1.01, respectively, and the pH value of the intersection of the two regions is 7.37. The unit slope indicates that the base catalyzed hydrolysis is likely a first-order reaction with respect to hydroxyl ion at pH  $>\sim$ 7.4, consistent with eq 4. The much smaller slope at pH <7.4 suggests that the acid-catalyzed and neutral hydrolysis is likely a zeroth-order reaction with respect to hydroxyl ion.

The base-catalyzed second-order hydrolysis rate constant  $k_b$  can be calculated using the following:

$$k_{1,\text{obs}} = k_{\text{b}} a_{\text{OH}} \tag{10}$$

The calculated values of  $k_b$  at 25 °C are 2.726, 2.581, 4.554, 3.603, and 4.445 × 10<sup>3</sup> M<sup>-1</sup> d<sup>-1</sup> at pH 8.32, 9.24, 9.97, 11.03, and 12.02, respectively (Table 1). These values compare favorably to the value calculated (2.801 × 10<sup>3</sup> M<sup>-1</sup> d<sup>-1</sup>) from the reported activation energy (84.6±7.8kJ/mol) for the reaction (*17*). The slopes of the plots of log  $k_{21}'$ , log  $k_{22}'$ , and log  $k_{23}'$  versus pH in Figure 6 are 0.994, 1.301, and 0.991, respectively, suggesting that formation of TCBs is likely first-order reaction with respect to hydroxyl ion.

**Rates of**  $\gamma$ **-HCH Transformation in the FeS-Containing Systems.** The rate of  $\gamma$ -HCH transformation can be estimated using a pseudo-first-order rate model in the following form:

$$C_{\rm HCH} = C_{\rm HCH,0} e^{-k_3' t} \tag{11}$$

where  $k_{3'}$  is the overall rate constant for disappearance of  $\gamma$ -HCH due to hydrolysis (Figure 1) and dichloroelimination/ dechlorination (Figure 5). The best-fit  $k_{3'}$  values are 0.013 and 0.011 d<sup>-1</sup> for the heterogeneous systems at pH 6.9 and pH 8.3, respectively, which are far greater than the  $k_{1,obs}$  values for the homogeneous systems at their respective pH conditions (Table 1).

This study provides insight information on the fate of HCH isomers in the aquatic ecosystems. It is expected that transformation of other HCH isomers such as  $\alpha$ - and  $\beta$ -HCH may be enhanced similarly in FeS-containing systems. Such enhanced transformation rates should be incorporated to the models for predicting fate and transport of HCH in aquatic systems. Modeling exercises using the hydrolysis rate parameters measured for homogeneous systems may significantly overestimate the persistency of HCH in large-scale environmental systems. As less chlorinated aromatic products such as DCBs are relatively more volatile and can undergo aerobic degradation and photolysis at much faster rates than their parental HCHs (*28*), monitoring the environmental fate of these finial products of HCH transformation along with the HCH isomers should be considered.

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# Supporting Information Available

Three figures (representative GC chromatograms and GC– MS spectra indicating the presence of intermediate and final products) and details of mathematical derivation of kinetics model equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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