

# Kinetics of Base-Catalyzed Dehydrochlorination of Hexachlorocyclohexanes: I. Homogeneous Systems

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## ABSTRACT

Base-catalyzed dehydrochlorination of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hexachlorocyclohexane (HCH) was examined at different pH and temperature conditions. No reaction was observed for  $\beta$ -HCH under all tested conditions likely due to the fact that all chlorines are at the equatorial positions. Highly pH- and temperature-dependent reaction rates were observed for  $\alpha$ - and  $\gamma$ -HCH, and pentachlorocyclohexenes (PCCHs) and 1,2,4- and 1,2,3-trichlorobenzene (TCB) were detected as the intermediates and final products of the transformation of both  $\alpha$ - and  $\gamma$ -HCH. The pseudo-first-order rate constants of each step of the reactions were calculated at different  $T$  and pH conditions. For the first step, the rate constants were at approximately  $0.0005 \text{ d}^{-1}$  in solutions below pH 7.0, and increased by about an order of magnitude per pH unit from pH 7.01 to pH 12.02. The second-order reaction rate constants ( $k_b$ ) of this step were  $3.57 \pm 0.03$  and  $3.19 \pm 0.19 \text{ M}^{-1} \text{ d}^{-1}$ , respectively, and the associated activation energies ( $E_a$ ) at pH 9.26 were  $60.4 \pm 7.8$  and  $67.7 \pm 8.7 \text{ kJ mol}^{-1}$ , respectively, for  $\alpha$ - and  $\gamma$ -HCH. The rate constants for the formation of 1,2,3-TCB ( $k_{21}$ ) and 1,2,4-TCB ( $k_{22}$ ) were  $0.0032 \pm 0.0001 \text{ d}^{-1}$  and  $0.051 \pm 0.003 \text{ d}^{-1}$  from  $\alpha$ -HCH, and  $0.0017 \pm 0.0001 \text{ d}^{-1}$  and  $0.0041 \pm 0.0002 \text{ d}^{-1}$  from  $\gamma$ -HCH at pH 8.28 and  $25^\circ\text{C}$ . Both  $k_{21}$  and  $k_{22}$  also showed an increase by about one order of magnitude per pH unit from pH 8.28 to pH 12.02. The  $E_a$  values were  $64.4 \pm 6.8$  and  $88.8 \pm 5.2 \text{ kJ mol}^{-1}$ , respectively, for the formation of 1,2,4-TCB and 1,2,3-TCB from  $\alpha$ -HCH, and  $70.6 \pm 8.7$  and  $92.0 \pm 4.9 \text{ kJ mol}^{-1}$ , respectively, for the formation of 1,2,4- and 1,2,3-TCB from  $\gamma$ -HCH at pH 9.26. Data provided by this study may be used for calculation of the percentages of the TCBs formed at different environmental conditions.

TECHNICAL HEXACHLOROCYCLOHEXANE (HCH) is an organochlorine pesticide widely used 30 years ago for pest control in the agricultural production of fruits, vegetables, and forest crops. It is a mixture of five HCH isomers commonly comprised by 60 to 70% of  $\alpha$ -HCH, 5 to 12% of  $\beta$ -HCH, 10 to 12% of  $\gamma$ -HCH, 6 to 10% of  $\delta$ -HCH, and 3 to 4% of  $\epsilon$ -HCH (Willett et al., 1998). These isomers differ only in their relative orientations of the six chlorine atoms bound to the six carbons as shown in Fig. 1 (Cristol et al., 1951; Willett et al., 1998). Among the five isomers,  $\gamma$ -HCH, also known as lindane, is the active constituent. Because of their relatively long persistence in ecosystems (e.g., the persistence of lindane in soil and sediment was estimated as 2900 and 1200 h) and

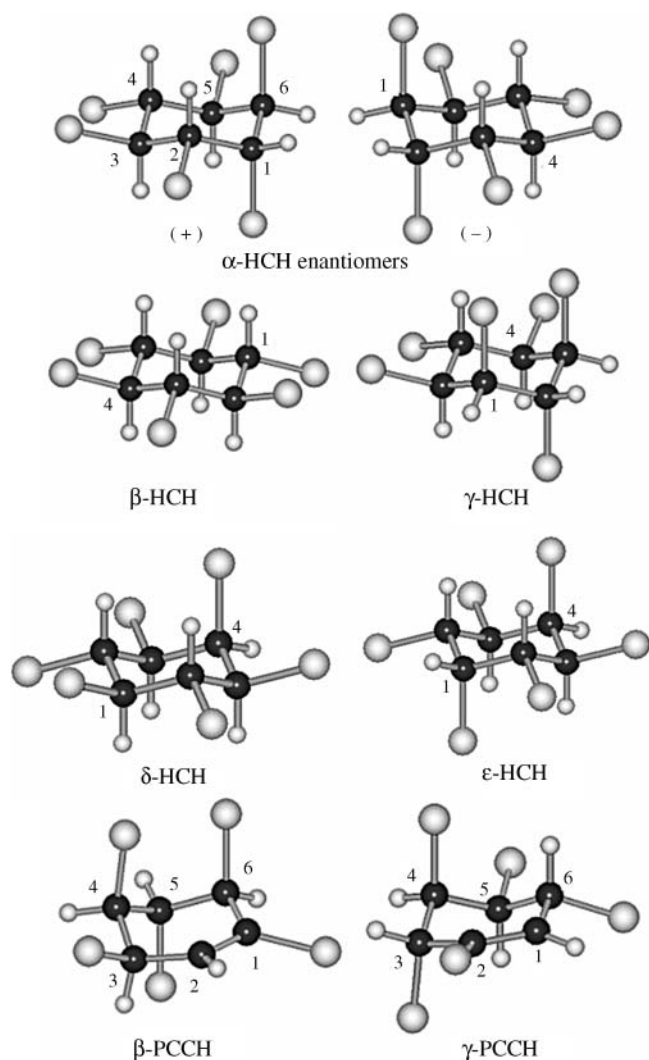
their proven adverse effects on kidney, liver, nerve, immune, and endocrine systems of human and animals (Willett et al., 1998), the technical HCH mixture was banned in the 1970s in developed countries and in the 1980s in some developing countries. However, the mixture is still in use in some developing countries, and lindane in its pure form is allowed for restricted use in developed countries including the United States (Li, 1999). It was reported that the total technical HCH used between 1948 and 1995 in China, Japan, India, and the United States was up to 6 million metric tons (Li et al., 1998; Walker et al., 1999). Heavy utilization and the relative high volatility of these compounds resulted in rapid water partitioning and water-gas phase exchange of HCHs, and hence their rapid and wide dispersion in lakes, oceans, and other surface aquatic systems (Cotham and Bidleman, 1991; Hinckley et al., 1991; McConnell et al., 1993; Hillery et al., 1998; Lakaschus et al., 2002). Long-range atmospheric transport and ocean currents, coupled with a possible distillation process, have led to significant accumulation of HCHs in cold areas such as the Arctic, which, in return, becomes a new source of these contaminants even after technical HCH had been phased out in many countries (Li et al., 1996; Willett et al., 1998; Walker et al., 1999; Lakaschus et al., 2002). Research focusing on the fate and transformation of HCHs is necessary for better monitoring and assessing their environmental risks at various spatial and time scales (Breivik and Wania, 2002).

Hexachlorocyclohexanes are relatively persistent in aquatic systems (Willett et al., 1998) and can be transformed at slow rates to less chlorinated compounds via biological or abiotic chemical reactions. Several studies have demonstrated that HCHs can be biodegraded to final products including chlorobenzene and benzene under anaerobic conditions (Beland et al., 1976; Buser and Muller, 1995; Middeldorp et al., 1996). Aerobic degradation of HCHs by bacteria (Sahu et al., 1995) or fungi (Singh and Kuhad, 2000) follows a pathway with tetrachlorocyclohexene (TeCCH) as one proposed intermediate, even though it was not really detected, and the reported half-lives of HCHs range from several hours to days, depending on microorganisms and environmental conditions. Hexachlorocyclohexanes also undergo abiotic transformations via different pathways. Reductive dehydrochlorination of HCH to form TeCCH as an intermediate, and dichlorobenzenes (DCBs), chlorobenzene (CB), and benzene as final products was observed for  $\gamma$ -HCH in the presence of reducing agents (e.g., FeS)

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**Abbreviations:** CB, chlorobenzene; DCB, dichlorobenzene; HCH, hexachlorocyclohexane; PCCH, pentachlorocyclohexene; PCNB, pentachloronitrobenzene; TCB, trichlorobenzene; TeCCH, tetrachlorocyclohexene.



**Fig. 1.** Three-dimensional structures of  $\alpha$ -,  $\beta$ -,  $\delta$ -,  $\epsilon$ -, and  $\gamma$ -hexachlorocyclohexane (HCH), and  $\beta$ - and  $\gamma$ -pentachlorocyclohexene (PCCH). Carbon, hydrogen, and chlorine atoms are in black, white (small), and white (large), respectively. The C=C bond is located on the left side of the number 1 carbon position for PCCH.

with or without addition of environmental catalysts (e.g., hydroxocobalamin) (Liu et al., 2003; Zinoviyev et al., 2004; Rodríguez-Garrido et al., 2004). Rapid and complete oxidative mineralization was also observed for  $\gamma$ -HCH in the presence of a photocatalyst (e.g.,  $\text{TiO}_2$ -pillared fluorine mica) and under UV light (Guo et al., 2000; Murayama et al., 2002).

Hydrolysis has been cited as the most ubiquitous abiotic transformation mechanism for HCH decomposition (Larson and Weber, 1994). A pathway of base-catalyzed dehydrochlorination to form pentachlorocyclohexene (PCCH) as an intermediate and trichlorobenzenes (TCBs) as the final products was proposed for  $\gamma$ -HCH in alkaline solutions (Liu et al., 2003). The dehydrochlorination rate constants for both  $\alpha$ - and  $\gamma$ -HCHs were reported at pH 7 to 9 (Ngabe et al., 1993), and the reaction rates over a wide pH range were detailed by Liu et al. (2003) for  $\gamma$ -HCH in both homogeneous systems and systems containing FeS as a reducing agent.

This study is an extension of the work by Liu et al. (2003) in an effort to elucidate the mechanisms of base-catalyzed dehydrochlorination reactions for major HCH isomers in aquatic systems. As summarized above, several prior studies (e.g., Cristol et al., 1951; Ngabe et al., 1993) focused on the rates of HCH transformation (i.e., the first step of the reaction), but did not provide the details of the kinetics of the final product formation. The recent study by Liu et al. (2003) elucidated the pathways and quantified the rate constants for each step, but it only examined  $\gamma$ -HCH. The goal of this study was to examine the rates of each step involved in this complex reaction for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HCHs, the three isomers with the highest contents in technical HCH, over a wide pH range with and without FeS as a catalyst. The reaction pathways and the pH dependence of the rates of each step of the reaction in the homogeneous systems are presented in this paper.

## MATERIALS AND METHODS

### Chemicals and Solutions

The  $\alpha$ -,  $\beta$ -,  $\gamma$ -HCH isomers, 1,2,3-TCB, 1,2,4-TCB, 1,2-, 1,3-, 1,4-DCB isomers, CB, benzene, and internal standard pentachloronitrobenzene (PCNB), all with purity of >99%, were purchased from Chem Service (West Chester, PA). High performance liquid chromatography grade hexane and methanol and the chemicals used for preparing pH buffer were purchased from Merck (Whitehouse Station, NJ). All chemicals mentioned above were used as received. Water used in this study was a product of the Milli-Q Plus water system (Millipore, Billerica, MA).

Eight different pH buffer solutions were prepared following the procedure described in Liu et al. (2003). Buffer solutions at pH 2.26 to 12.02 were prepared from Milli-Q water using the following electrolyte mixtures: glycine + NaCl-HCl for pH 2.26; HAc + NaAc for pH 4.67;  $\text{K}_2\text{HPO}_4$  +  $\text{KH}_2\text{PO}_4$  for pH 7.01; Tris-HCl + Tris for pH 8.28; glycine + NaCl-NaOH for pH 9.26, 11.03, and 12.02; and  $\text{Na}_2\text{CO}_3$  +  $\text{NaHCO}_3$  for pH 10.02. The ionic strength of all solutions was adjusted to 0.1 M with NaCl.

### Experimental Procedures

Procedures for maintenance of anaerobic conditions and sterilization of aqueous solutions and glassware were described elsewhere (Liu et al., 2003). In this study, 15-mL flame-sealed glass ampoules were used as the batch reactors for preventing loss of volatile reactants and products. Initial aqueous concentrations were set at about 5.0, 1.0, and 25.0  $\mu\text{M}$ , which were below their respective aqueous solubilities of 5.6, 2.4, and 25.7  $\mu\text{M}$  for  $\alpha$ -HCH,  $\beta$ -HCH (Kanazawa et al., 1971), and  $\gamma$ -HCH (Masterton and Lee, 1972), respectively. Each ampoule contained an initial aqueous solution (15 mL) and a headspace (approximately 4 mL) filled with  $\text{N}_2$ . According to Henry's law and utilizing the volumes of the two phases and the dimensionless Henry's constants for reactants and final products, the mass of the organic chemicals partitioning to the headspace was calculated to be less than 0.5% for the reactants. The loss of the chemicals to the headspace was hence ignored. After flame sealing, the ampoules were placed in the dark, and mixed horizontally at 180 rpm on a shaker with temperature preset at 15, 25, 35, and 45°C. At designated times, duplicate ampoules were taken out of the shaker and broken open, and an aliquot (100  $\mu\text{L}$ ) was withdrawn

immediately from each ampoule. The aliquot was extracted with 1 mL of hexane in a 2-mL gas chromatography (GC) vial. Pentachloronitrobenzene was added to the hexane at 0.2  $\mu\text{M}$  prior extraction as an internal standard for concentration analysis. The first sample was taken immediately after the reagents were added and before flame sealing. The chemical analysis of this first sample was used as the initial concentration of the reactant. The time scale of the experiments ranged from 0.5 d at pH 12.02 to 300 d at pH 2.26.

### Chemical Analysis and Product Identification

Chemical analysis of hexane extractions and quantification was performed on a GC (HP 6890 II; Agilent, Palo Alto, CA) with a Chrompack CP-Sil 5 CB column (50-m  $\times$  0.32-mm i.d.  $\times$  0.25- $\mu\text{m}$  film thickness), an on-column injector, and an electron capture detector ( $\gamma$ -ECD). Detector temperature was set at 315°C. Oven temperature was initially isothermal at 40°C for 2 min, ramped from 40°C to 150°C at a rate of 10°C  $\text{min}^{-1}$  and isothermal at 150°C for 2 min, then ramped at 6°C  $\text{min}^{-1}$  to 225°C and isothermal for 2 min, and again, ramped at 15°C  $\text{min}^{-1}$  to 280°C and isothermal for 4 min. Nitrogen gas at 99.99% purity was used as both the carrier at a flow rate of 1 mL  $\text{min}^{-1}$  and the make-up gas at 60 mL  $\text{min}^{-1}$ . During analysis, the peak area and the concentration of the internal standard (PCNB) were referred for solute quantification as well as for evaluating the stability of the instrument. External standards of HCHs and TCBS in hexane matrix were used for establishing standard curves. Because no PCCH is available commercially, the concentrations of  $\beta$ -PCCH and  $\gamma$ -PCCH were estimated according to the method described by Liu et al. (2003) with respect to mole-to-peak area ratios of 0.67 and 0.60 relative to that of the internal standard PCNB.

To identify and to confirm the intermediate and final products of the reactions, hexane extracts of selected aqueous samples were analyzed on a GC-mass spectrometer (MS) (Model GC8000<sup>TOP</sup> Voyager; Finnigan, Manchester, UK) equipped with an HP-5 column (50-m  $\times$  0.32-mm  $\times$  0.25- $\mu\text{m}$ ; Agilent). Oven temperature conditions for the separation were as follows: 35°C for 5 min, 10°C  $\text{min}^{-1}$  to 225°C, 25°C  $\text{min}^{-1}$  to 280°C, and then isothermal for 4 min. The time of solvent delay was set as 6 min. The final products (TCBs) of the reaction were confirmed with their characteristic retention times and the GC-MS spectra, which matched exactly with individual standards.

## RESULTS AND DISCUSSION

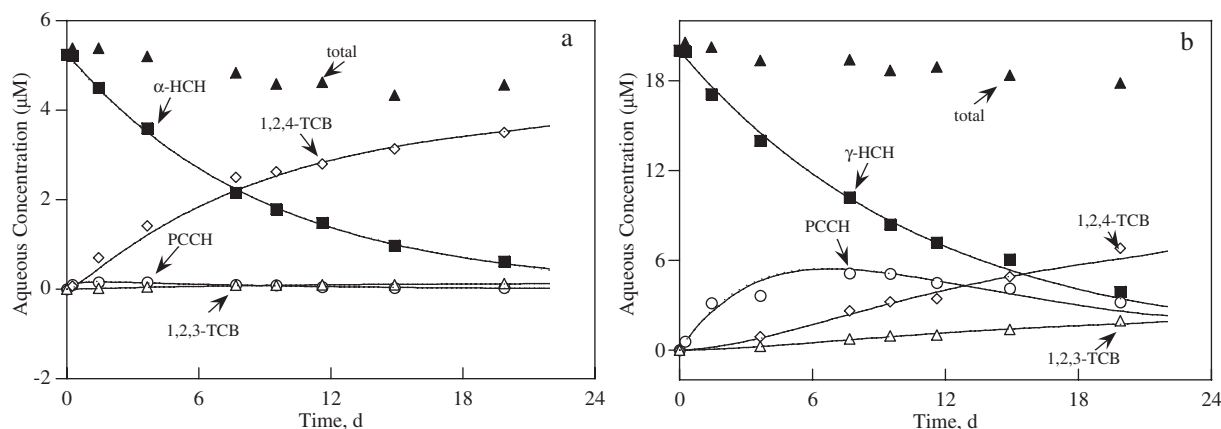
### Time-Dependent Concentrations of Hexachlorocyclohexanes, Intermediates, and Final Products

Among the three HCH isomers examined in this study,  $\beta$ -HCH exhibited no change of concentration in a time period of 202 d and at all pH conditions tested. This suggested that  $\beta$ -HCH isomer was stable even at high pH conditions mainly due to its special structural configuration. As shown in Fig. 1, each of the six chlorine atoms is at equatorial positions. This structural feature substantially decreases or prevents dehydrochlorination of the HCH isomer in base solutions (Cristol et al., 1951).

The results of the reaction systems involving the  $\alpha$ - and  $\gamma$ -HCH isomers showed that: (i) they both were transformed with the rates depending on pH and temperature, (ii) 1,2,4- and 1,2,3-TCBs were the final products, and (iii) two isomers of PCCHs were the intermediates of  $\alpha$ -HCH degradation whereas  $\gamma$ -PCCH was the only intermediate of  $\gamma$ -HCH degradation. In our study, DCBs, CB, and benzene were not detected. No hydroxyl compound was detected either using derivatization agent BSTFA, which suggested that  $\text{OH}^-$  did not act as a nucleophile attacking a carbon center.

The reaction systems were run over time periods ranging from about one half-life for very slow reactions to three half-lives for rapid reactions. Examples of concentration profiles against time were plotted in Fig. 2 for the reactants, intermediates, and products at pH 9.26 and 25°C. The figure also showed the mass balance (the sum of HCH, PCCH, and TCBS) of the reaction system, which was fairly constant and close to the initial concentration of the HCHs, suggesting that the major intermediate and final products were identified in the reaction systems.

The pseudo-first-order rate constants for the first steps of  $\alpha$ - and  $\gamma$ -HCH dehydrochlorination are listed in Table 1 and the rate constants for the second steps of formation of final products 1,2,4- and 1,2,3-TCBs are listed in Table 2. A reaction pathway, shown in Fig. 3,



**Fig. 2.** Change of aqueous concentration of reactants, intermediates, and final products with time (day) for the reaction systems at pH 9.24 and 25°C. HCH, hexachlorocyclohexane; PCCH, pentachlorocyclohexene; TCB, trichlorobenzene; total, sum concentration of HCHs, PCCHs, and TCBS. Symbols and lines represent the experimental data and the model fits of the data, respectively.



**Table 1. Reaction conditions and rate constants for hexachlorocyclohexane (HCH).**

T	pH	$k_{1,obs}^*$		$k_b^\dagger$	
		$\alpha$ -HCH	$\gamma$ -HCH	$\alpha$ -HCH	$\gamma$ -HCH
$^\circ\text{C}$		$\text{d}^{-1}$		$10^3 \text{ M}^{-1} \text{ d}^{-1}$	
25	2.26	0.00052 $\pm$ 0.00002	0.00051 $\pm$ 0.00004		
25	4.67	0.00053 $\pm$ 0.00002	0.00052 $\pm$ 0.00004		
25	7.01	0.00061 $\pm$ 0.00005	0.00061 $\pm$ 0.00007		
25	8.28	0.0095 $\pm$ 0.002‡	0.0077 $\pm$ 0.0004‡	4.93 $\pm$ 1.01	3.99 $\pm$ 0.22
15	9.26	0.0087 $\pm$ 0.0012‡	0.0058 $\pm$ 0.0002‡	1.06 $\pm$ 0.14	0.70 $\pm$ 0.03
25	9.26	0.069 $\pm$ 0.002‡	0.054 $\pm$ 0.002‡	3.75 $\pm$ 0.21	2.93 $\pm$ 0.12
35	9.26	0.253 $\pm$ 0.003‡	0.204 $\pm$ 0.003‡	6.63 $\pm$ 0.12	5.34 $\pm$ 0.09
45	9.26	0.899 $\pm$ 0.004‡	0.807 $\pm$ 0.001‡	12.21 $\pm$ 0.30	10.96 $\pm$ 0.04
25	10.02	0.572 $\pm$ 0.0197‡	0.425 $\pm$ 0.065‡	5.39 $\pm$ 0.17	4.01 $\pm$ 0.62
25	11.03	3.96 $\pm$ 0.050‡	3.86 $\pm$ 0.39‡	3.65 $\pm$ 0.04	3.37 $\pm$ 0.37
25	12.02	38.74 $\pm$ 0.37‡	35.61 $\pm$ 3.1‡	3.57 $\pm$ 0.03	3.19 $\pm$ 0.29

\* Significant at the 0.05 probability level.

† Calculated based on  $k_b = k_{1,obs}/a_{\text{OH}^-}$ .

‡ Based on experimental data collected over three half-lives.

was proposed to elucidate the mechanisms of the dehydrochlorination of  $\alpha$ - and  $\gamma$ -HCH.

As shown in Fig. 3, the reaction began with simultaneous elimination of a chlorine and a hydrogen atom from each isomer. For  $\alpha$ -HCH isomer, there may be two ways to eliminate HCl (each of the two axial Cl atoms) from each enantiomer, forming  $\beta$ -PCCH enantiomers (Buser and Muller, 1995). In our experimental system, only one PCCH isomer was detected in hexane extracts with a water-to-hexane ratio of 1:10 (v/v). When a larger water-to-hexane ratio (e.g., 10:1) was used, a second isomer of PCCH could be detected with low concentrations, suggesting that isomerization reactions or *cis*-eliminations (HCl) might have been involved. Structural details of the two PCCH isomers, termed PCCH1 and PCCH2 in this article, were not further confirmed because PCCHs were not available commercially. Gas chromatograms showed that the PCCH2 peak predominated over the PCCH1 peak, suggesting that PCCH2 was the likely  $\beta$ -isomer as indicated by Buser and Muller (1995) and Huhnerfuss et al. (1992). Only PCCH2 or  $\beta$ -PCCH was quantified in this study. For  $\gamma$ -HCH isomer, there may be two ways for eliminating HCl to form  $\gamma$ -PCCH (Buser and Muller, 1995). The second step may involve direct formation of TCBS via simultaneous elimination of two chlorine atoms and two hydrogen atoms from PCCH, or dehydrochlorination of PCCH by consecutive elimination of the axial Cl and the axial H to form TCBS. In both mechanisms, there should be a transition state in which intra-molecular shifts of chlorine constituents were required to form 1,2,3-TCB as one of the final products (Liu, 2002).

### Reaction Kinetics Modeling

Dehydrochlorination of HCHs can be catalyzed by  $\text{OH}^-$  and the reaction rates ( $k_1, \text{d}^{-1}$ ) of the first step can be approximated using the following equation:

$$\frac{da_{\text{HCH}}}{dt} = -k_1 a_{\text{HCH}} a_{\text{OH}^-} \quad [1]$$

where  $a_{\text{HCH}}$  and  $a_{\text{OH}^-}$  are the activities of HCH and  $\text{OH}^-$ , respectively, and  $t$  is the reaction time (d). At constant pH and under dilute solution condition, Eq. [1] can be further simplified to:

$$C_{\text{HCH}} = C_{\text{HCH},0} e^{-k_1,obs t} \quad [2]$$

where  $C_{\text{HCH},0}$  is the initial aqueous-phase concentration ( $\mu\text{M}$ ) of HCH.

Formation of intermediates and final products can be modeled using the simplified pathway shown in Fig. 3 for both  $\alpha$ - and  $\gamma$ -HCH. The details of derivation of the kinetics model were described elsewhere (Liu, 2002), and the reduced time-dependent concentrations of the intermediate PCCH and the two TCBS are given here:

$$C_{\text{PCCH}} = \frac{C_{\text{HCH},0} k_{1,obs}}{k_2 - k_{1,obs}} (e^{-k_1,obs t} - e^{-k_2 t}) \quad [3]$$

$$C_{1,2,3\text{-TCB}} = C_{\text{HCH},0} \left[ \frac{k_{21}}{k_2} - \frac{k_{21}}{k_2 - k_{1,obs}} e^{-k_1,obs t} + \frac{k_{1,obs} (k_{21}/k_2)}{k_2 - k_{1,obs}} e^{-k_2 t} \right] \quad [4]$$

**Table 2. Pseudo-first-order rate constants  $k_{21}$  and  $k_{22}$ , respectively, for the two hydrolytic products 1,2,3- and 1,2,4-trichlorobenzene (TCB) in homogeneous systems for hexachlorocyclohexane (HCH).**

T	pH	$k_{21}$		$k_{22}$	
		$\alpha$ -HCH	$\gamma$ -HCH	$\alpha$ -HCH	$\gamma$ -HCH
$^\circ\text{C}$		$\text{d}^{-1}$			
25	8.28	0.0032 $\pm$ 0.0001	0.0017 $\pm$ 0.0001	0.051 $\pm$ 0.003	0.0041 $\pm$ 0.0002
15	9.26	0.061 $\pm$ 0.004	0.0073 $\pm$ 0.0004	1.32 $\pm$ 0.08	0.028 $\pm$ 0.001
25	9.26	0.234 $\pm$ 0.003	0.021 $\pm$ 0.001	2.20 $\pm$ 0.06	0.075 $\pm$ 0.002
35	9.26	0.858 $\pm$ 0.003	0.074 $\pm$ 0.003	7.72 $\pm$ 0.08	0.133 $\pm$ 0.006
45	9.26	1.92 $\pm$ 0.07	0.272 $\pm$ 0.018	14.63 $\pm$ 1.05	0.515 $\pm$ 0.034
25	10.02	1.68 $\pm$ 0.51	0.076 $\pm$ 0.008	13.08 $\pm$ 4.05	0.176 $\pm$ 0.015
25	11.03	9.32 $\pm$ 0.65	0.860 $\pm$ 0.043	85.3 $\pm$ 2.4	1.71 $\pm$ 0.17
25	12.02	28.68 $\pm$ 2.65	10.3 $\pm$ 1.2	195.2 $\pm$ 27.4	21.3 $\pm$ 2.4

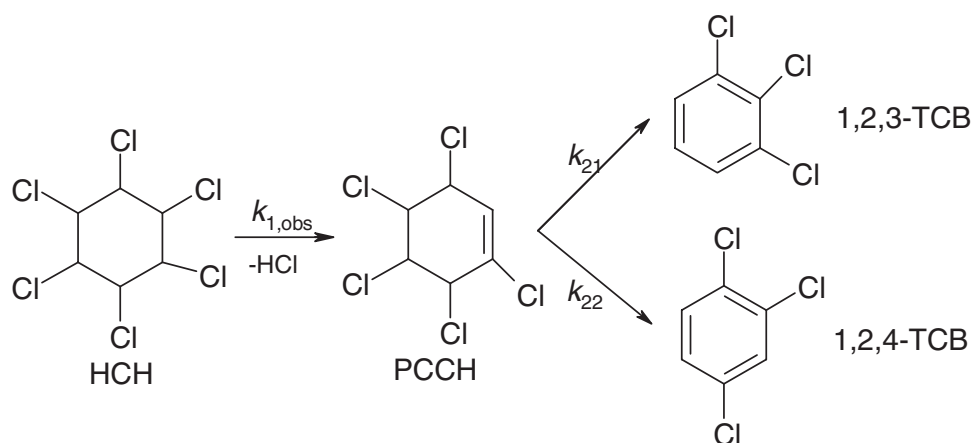


Fig. 3. Possible pathways of  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane (HCH) dehydrochlorination in alkaline solutions.

$$C_{1,2,4\text{-TCB}} = C_{\text{HCH},0} \left[ \frac{k_{22}}{k_2} - \frac{k_{22}}{k_2 - k_{1,\text{obs}}} e^{-k_{1,\text{obs}}t} + \frac{k_{1,\text{obs}}(k_{22}/k_2)}{k_2 - k_{1,\text{obs}}} e^{-k_2t} \right] \quad [5]$$

where  $C_{\text{PCCH}}$ ,  $C_{1,2,3\text{-TCB}}$ , and  $C_{1,2,4\text{-TCB}}$  are the time-dependent aqueous concentrations ( $\mu\text{M}$ ) of PCCH and the two TCBs;  $k_{21}$  and  $k_{22}$  are the pseudo-first-order rate constants ( $\text{d}^{-1}$ ) for 1,2,3- and 1,2,4-TCB, respectively; and  $k_2$  ( $\text{d}^{-1}$ ) is the sum of  $k_{21}$  and  $k_{22}$ .

In this study, the  $k_{1,\text{obs}}$  value of each reaction system was determined by fitting the time-dependent HCH concentrations ( $C_{\text{HCH}}$ ) into Eq. [2] using a nonlinear least squares regression approach and Systat computer software (Systat Software, 2004). Since the ratio of  $k_{22}$  to  $k_{21}$  in a specific reaction system is equal to the concentration ratio of the final products (Butler and Hayes, 1999), the calculated average concentration ratio of 1,2,4-TCB to 1,2,3-TCB,  $R_p$ , is 29.62 for  $\alpha$ -HCH and 3.50 for  $\gamma$ -HCH ( $N = 9$ ), indicating that 1,2,4-TCB was the dominant product. Since  $k_2 = k_{21} + k_{22}$ ,  $k_2$  was obtained through nonlinear regression of the measured PCCH concentrations ( $C_{\text{PCCH}}$ ) versus time using Eq. [3],  $C_{\text{HCH},0}$ , and  $k_{1,\text{obs}}$  values (listed in Table 1). The rate constants  $k_{21}$  and  $k_{22}$  were then calculated from  $R_p$  and  $k_2$ . The resulting data are summarized in Table 2. The model fits to the concentration profiles of the reactants, intermediates, and products were shown in Fig. 2.

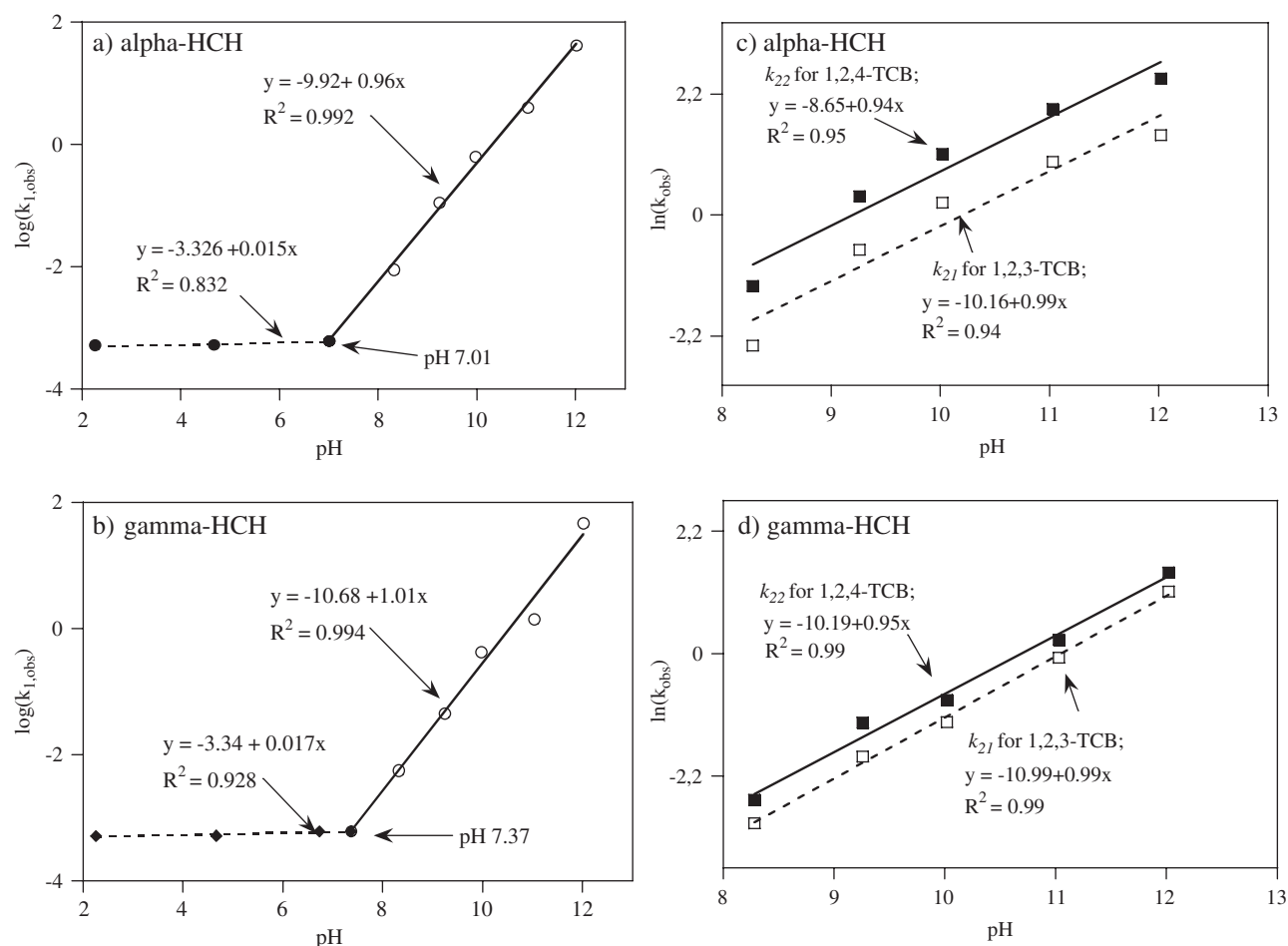
The reduced rate data shown in Table 1 indicates that, under the same experimental conditions, the rate of  $\alpha$ -HCH disappearance was slightly faster than that of  $\gamma$ -HCH. For example, at 25°C and pH 9.26, the calculated  $k_{1,\text{obs}}$  ( $\text{d}^{-1}$ ) values were 0.069 and 0.054 for  $\alpha$ - and  $\gamma$ -HCH, respectively. Moreover, the maximum concentration of the proposed intermediate,  $\gamma$ -PCCH, in the  $\gamma$ -HCH systems was about 27% of the initial  $C_{\text{HCH},0}$  whereas that the maximum concentration of the proposed intermediate,  $\beta$ -PCCH, in the  $\alpha$ -HCH system was about 2.9% of the initial  $C_{\text{HCH},0}$  under the same reaction conditions. A possible explanation was that transformation of  $\beta$ -PCCH to TCBS was likely much faster than that of  $\gamma$ -PCCH. As shown in Fig. 1, for  $\beta$ -PCCH derived from  $\alpha$ -HCH, the axial H atom at C-3 to be eliminated in

the next step is at the  $\alpha$ -position to the C=C, which has high reactivity because of the relative low bond dissociation energy of an allylic carbon-hydrogen bond compared with the bond dissociation energies of other carbon-hydrogen bonds (Xu, 1993; Solomons and Fryhle, 2004), and the coplanar axial Cl atom (at C-4) to be eliminated is at the  $\beta$ -position. On the other hand,  $\gamma$ -PCCH formed from  $\gamma$ -HCH has a molecular configuration favorable for elimination of the axial Cl at C-4 at the  $\beta$ -position to the C=C and its vicinal axial H at C-5 at the other  $\beta$ -position. It is easy to see that the influence of the double C-C bond on  $\beta$ -PCCH is greater than that on  $\gamma$ -PCCH. Therefore, the reactivity of  $\beta$ -PCCH is higher than that of  $\gamma$ -PCCH. As shown in Table 2, the pseudo-first-order dehydrochlorination rate constant ( $k_2$ ) was 2.43  $\text{d}^{-1}$  for the  $\beta$ -PCCH at pH 9.26 and 25°C, which was much greater than the  $k_2$  value (0.096  $\text{d}^{-1}$ ) for  $\gamma$ -PCCH alone at same pH and temperature conditions.

As indicated in Table 2, the rate of 1,2,4-TCB ( $k_{22}$ ) formed was always faster than that of 1,2,3-TCB ( $k_{21}$ ). For example,  $k_{21}$  and  $k_{22}$  for  $\alpha$ -HCH at pH 9.26 and 25°C were 0.234  $\text{d}^{-1}$  and 2.20  $\text{d}^{-1}$ , respectively. Previous studies also reported preferential formation of 1,2,4-TCB during alkaline treatment of HCH isomers (Cristol et al., 1951; Liu et al., 2003; Zinovyev et al., 2004). Zinovyev et al. (2004) suggested that an intermediate species, pentachlorocyclohexene, consisted of two conformations in equilibrium and that the energetically lower conformer underwent further dehydrochlorination to form 1,2,4-TCB.

### Influence of Solution pH and Temperature

Dehydrochlorination rates of  $\alpha$ - and  $\gamma$ -HCH depended strongly on solution pH and temperature conditions. The pH dependence of the rates was largely due to the attack of  $\text{OH}^-$  for simultaneous elimination of both H and Cl atoms from the HCH molecules (Liu et al., 2003). Figure 4 shows that the reaction rate was a function of solution pH in basic conditions, but it remained independent of pH in acidic solutions. For both  $\alpha$ - and  $\gamma$ -HCH, the  $k_{1,\text{obs}}$  values fell into a very small range of 0.0005 to 0.0006  $\text{d}^{-1}$  between pH 2.26 to neutral. As solution pH increased from neutral to 12.02, the



**Fig. 4.** The pH dependence of the apparent rate constants for the disappearance of  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane (HCH), and for the formation of trichlorobenzenes (TCBs) in homogeneous systems at 25°C.

$k_{1,obs}$  values increased rapidly from 0.0006 d<sup>-1</sup> to 41.7 d<sup>-1</sup> for  $\alpha$ -HCH and from 0.0006 d<sup>-1</sup> to 35.6 d<sup>-1</sup> for  $\gamma$ -HCH. The pH value of the intersection of the two regions was 7.01 for  $\alpha$ -HCH and 7.37 for  $\gamma$ -HCH (Fig. 4). The slope of the best-fit linear relation between  $\log k_{1,obs}$  and pH was 0.96 for  $\alpha$ -HCH and 1.01 for  $\gamma$ -HCH (Fig. 4). This suggested that the base catalyzed dehydrochlorination of both HCHs was a first-order reaction with respect to hydroxide ion at pH > 7 and that the same reaction was likely zeroth-order with respect to hydrogen ion. The fitted  $k_{21}$  and  $k_{22}$  values were also plotted in Fig. 4c and 4d against the solution pH. The slopes were between 0.94 and 0.99, suggesting that formation of TCBs was also a first-order reaction with respect to hydroxide ion.

The apparent base-catalyzed second-order rate constant  $k_b$  (M<sup>-1</sup> d<sup>-1</sup>) can be expressed by:

$$k_b = k_{1,obs}/a_{OH} \quad [6]$$

The activity of OH<sup>-</sup>,  $a_{OH}$ , can be approximated from pH measurements and the equation for the ion product of water as a function of temperature,  $T$  (K) (Harned and Owen, 1958):

$$\log K_w = \log \alpha_H \alpha_{OH} = 6.0875 - 4471/T - 0.01716T \quad [7]$$

The calculated values of  $k_b$  for  $\alpha$ - and  $\gamma$ -HCH at different pH and temperatures are listed in Table 1.

The dependence of the reaction rates on temperature can be delineated with the following Arrhenius equation:

$$\ln k = -E_a/RT + \ln A \quad [8]$$

where  $E_a$  is the activation energy (kJ mol<sup>-1</sup>) and  $R$  is the universal gas constant (8.31 kJ mol<sup>-1</sup> K<sup>-1</sup>). The  $k_b$  values obtained at pH 9.26 were plotted against  $10^3/RT$  in Fig. 5a and 5b for  $\alpha$ - and  $\gamma$ -HCH, respectively. The resulting  $E_a$  values were  $60.4 \pm 7.8$  and  $67.7 \pm 8.7$  kJ mol<sup>-1</sup> for  $\alpha$ - and  $\gamma$ -HCH, respectively. Note that these  $E_a$  values were slightly lower than  $78.3 \pm 7.6$  and  $84.6 \pm 7.8$  kJ mol<sup>-1</sup> reported by Ngabe et al. (1993) for the base dehydrochlorination of  $\alpha$ - and  $\gamma$ -HCH, respectively, but the  $E_a$  value obtained for  $\gamma$ -HCH was statistically consistent with the values of  $73.2 \pm 3.2$  and  $69 \pm 24$  kJ mol<sup>-1</sup> reported by Ellington et al. (1987) and Kubátová et al. (2002), respectively.

The temperature dependence of  $k_{21}$  and  $k_{22}$  at pH 9.26 is shown in Fig. 5c and 5d for  $\alpha$ -HCH and  $\gamma$ -HCH, respectively. The resulting  $E_a$  values were  $88.8 \pm 5.2$  and  $64.4 \pm 6.8$  kJ mol<sup>-1</sup> for the formation of 1,2,3-TCB and 1,2,4-TCB from  $\alpha$ -HCH, respectively, and  $92.0 \pm 4.9$  and  $70.6 \pm 8.7$  kJ mol<sup>-1</sup> for the formation of 1,2,3- and 1,2,4-TCB from  $\gamma$ -HCH, respectively. To our knowledge,

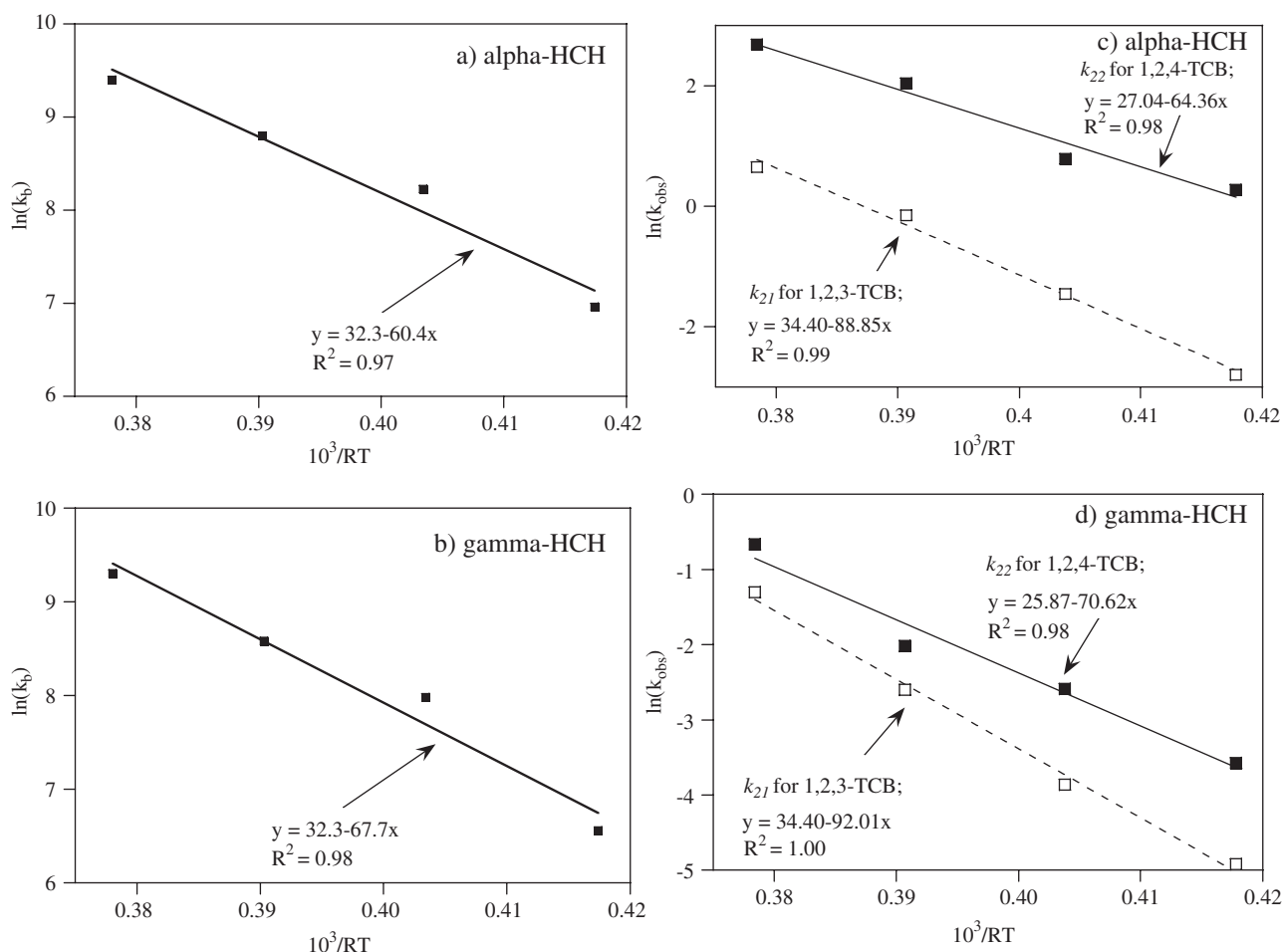


Fig. 5. The Arrhenius plots of the rate constants of the base-catalyzed dehydrochlorination ( $k_b$ ,  $M^{-1} d^{-1}$ ) of  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane (HCH) and formation of trichlorobenzenes (TCBs) ( $k_{21}$  and  $k_{22}$ ,  $d^{-1}$ ).  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ .

this is the first report in the literature for this complex reaction.

It is expected from the calculated activation energies that the half-lives of  $\alpha$ - and  $\gamma$ -HCH are about 73 and 90 d at pH 8.3 and 25°C and that the estimated half-lives are increased to about 20 and 29 yr, respectively, at pH 8.3 and 5°C. The latter data are slightly different from the half-lives of 26 and 42 yr for  $\alpha$ - and  $\gamma$ -HCH at pH 8 and 5°C reported by Ngabe et al. (1993), possibly because of different experimental conditions employed in the two different studies. In our study, the reactors were mixed horizontally at 180 rpm during the reaction whereas the reactors set up by Ngabe et al. (1993) were kept static. The base-catalyzed dehydrochlorination rates of both HCH isomers appear to be comparable to their biodegradation rates at room temperatures and pH > 8. Siddique et al. (2002) reported half-lives of  $\alpha$ - and  $\gamma$ -HCH of 17.5 and 21.2 d for microcosms in the presence of a *Pandora* species and under aerobic and room temperature conditions at pH 8. Satpathy et al. (1997) found that the half-lives  $\alpha$ - and  $\gamma$ -HCH in flooded rice fields were 15 and 7.5 d, respectively. In anaerobic sewage treatment systems the reported half-lives were 35 and 20 d for  $\alpha$ - and  $\gamma$ -HCH (Buser and Muller, 1995). These data suggest that both HCH isomers can be rap-

idly transformed abiotically and biologically in tropical regions. However, at lower temperature conditions, biodegradation rates of  $\alpha$ - and  $\gamma$ -HCH may be much slower. Manonmani et al. (2000) reported that transformation of  $\alpha$ -HCH at 4°C was about five times slower than at 30°C. Our results of the extremely long half-lives of  $\alpha$ - and  $\gamma$ -HCH at 5°C suggest that both HCH isomers could be highly recalcitrant in cold regions such as the Arctic region, where these chemicals have been accumulated over the last five decades due to the global distillation mechanism. Photolysis of HCHs in the Arctic region might be important as UV flux is high at certain time periods of each year. Its overall contribution may be limited because photolysis is limited to the surface of water and land, which are often covered by snow and ice in the Arctic region.

The data reported in this study can be used for calculation of the rate of TCB formation via base-catalyzed dehydrochlorination of HCHs under different environmental conditions. For example, at pH 8.3 and 25°C, about 3.1% and 50% of  $\alpha$ -HCH are likely transformed, respectively, to 1,2,3-TCB and 1,2,4-TCB after 100 d. With the same reaction time period and same pH condition but at 5°C, only 0.03% and 0.85% of  $\alpha$ -HCH are transformed to 1,2,3- and 1,2,4-TCB, respectively.



A major environmental implication of this study is that the identified final product TCBS are very toxic to aquatic lives and are more persistent in nature systems than their parental HCHs (Bosma et al., 1988; Lee et al., 1988). Future studies on fate and transport of HCHs in aquatic systems should pay more attention to the co-existing TCBS. Quantification of the concentrations of TCBS in water and sediments and the relative concentrations of 1,2,3- and 1,2,4-TCB may help assess potential environmental risk related to HCHs. Such quantification may also lead to distinguishing abiotic vs. biotic transformation of HCHs in aquatic systems since the final products of the two types of reactions are very different. As shown in this study, the abiotic dehydrochlorination reactions of HCHs form TCBS as the final products whereas anaerobic biodegradation of HCHs produces monochlorobenzene and benzene as final products.

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