

Base Hydrolysis of α - and γ -Hexachlorocyclohexanes

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Hexachlorocyclohexanes (HCHs) are the most abundant organochlorine pesticides in the world's oceans and large lakes, and knowing their chemical reactivity is important for determining environmental fate. Hydrolysis of α - and γ -HCHs was carried out in buffered distilled water poisoned with sodium azide in dark, tightly sealed bottles to avoid biodegradation, photolysis, and volatilization losses. Experiments were run at (a) constant temperature (45 °C) and pH 7-9 and (b) constant pH (9) and 5-45 °C over times of 4-248 d, depending on reaction conditions. At constant pH, breakdown of the HCHs followed pseudo-first-order kinetics. Second-order base rate constants (k_b , M⁻¹ min⁻¹) were calculated from pseudo-first-order rate constants (k' , min⁻¹), the measured pH, and the ion product of water as a function of temperature. At 20 °C, values of k_b were 1.57 (α -HCH) and 1.10 (γ -HCH). From the variation in k_b with temperature, activation energies of 78.3 and 84.6 kJ/mol were determined for α -HCH and γ -HCH. At pH 7, reaction with H₂O contributed to the breakdown of the HCHs; estimates of the neutral rate constant (k_n , min⁻¹) were 1.1×10^{-6} (α -HCH) and 2.0×10^{-6} (γ -HCH). At pH 8 and 5 °C, hydrolytic half-lives of α -HCH and γ -HCH were 26 and 42 yr. The relative contribution of hydrolysis to removing HCHs from cold, deep water in oceans and lakes requires that rates of other processes such as sedimentation and microbial attack be better established.

Introduction

Hexachlorocyclohexanes (HCHs) are heavily used throughout the world as insecticides, with a world production estimated at 200 000 t yr⁻¹ (1). A technical mixture of 65-70% α -HCH, 7-10% β -HCH, 14-15% γ -HCH, 6-10% δ -HCH, and other minor components is applied mainly in Asia, Eastern Europe, Mexico, and Brazil (1-3). India alone used 19 000-32 000 t yr⁻¹ in 1985-1987 (2). Manufacture of technical HCH in the United States began shortly after World War II and reached 20 000-50 000 t yr⁻¹ in the 1950s, but production declined sharply in the 1960s (4). The technical mixture was banned in Canada (1971) and the United States (1978), where annual usage of lindane (pure γ -HCH) today amounts to a few hundred ton (5). Lindane is also used in western Europe, Africa, and countries in the Southern Hemisphere (1, 2, 3, 6).

The high volatility of these compounds relative to other organochlorine pesticides has led to global dispersal through the atmosphere (3-15). HCHs partition readily into water and gas exchange accounts for a major share of their deposition into large lakes and oceans (7-11). In the Northern Hemisphere, α -HCH is the most abundant isomer in both air and water, presumably because of the larger tonnages of technical HCH used relative to lindane

(3). Increases in the proportion of γ -HCH in air have been ascribed to local usage during certain times of the year (7, 14, 15). The ratio of γ -HCH/ α -HCH is also higher in the southern troposphere and oceans (1, 3, 10). Concentrations of Σ HCHs in the Great Lakes (7) and ocean surface waters of the Northern Hemisphere (1, 9-13) are typically 1-5 ng/L, about 2 orders of magnitude above those of less soluble pesticides such as DDT, chlordane, and dieldrin (12). Henry's law constants of HCHs decrease as the temperature is lowered (16), resulting in enhanced gas exchange and higher concentrations in arctic surface waters (9-11).

Transfer of HCHs to deep water occurs by convection and sedimentation. HCHs are mainly dissolved with only a small fraction sorbed to particles (12, 17), rendering the latter process slow. Sedimentation residence times in the 100-m ocean mixed layer have been estimated to range from 2 to 10 yr in eutrophic and oligotrophic zones (17). Nevertheless, in their near half-century of use, HCHs have penetrated to the depths of the oceans. Water masses of the North Atlantic that originate in the Northern or Southern Hemisphere can be distinguished by their different ratios of α -HCH/ γ -HCH (1). In the Great Lakes, HCHs are found below the thermocline at concentrations similar to those in surface waters (7). These observations imply long lifetimes of these compounds in deep water, where photolysis and volatilization losses cannot occur. Here chemical breakdown competes with microbial attack and slow sedimentation in removing HCHs. Since mixing in large lakes and oceans occurs on time scales of decades, knowing these loss rates is important in formulating mass balance models (5).

Few studies have been done on reactions of the different HCHs in water. Cristol (18) dehydrochlorinated four isomers in 76% ethanol-water containing 0.005 M NaOH and found rates in the following order: δ -HCH \gg α -HCH $>$ γ -HCH. The β -isomer was unreactive even after 72 h at 20 °C, because of its inability to undergo trans-elimination. Other investigators (19-22) have worked in buffered distilled water or natural waters, but only with γ -HCH. Kucklick et al. (16) followed losses of α -HCH and γ -HCH in artificial seawater at 45 °C. Since chemical reactivities depend greatly on pH and temperature, this work was carried out to determine degradation rates of α -HCH and γ -HCH as functions of these properties in the range of natural systems.

Hydrolysis of Organic Compounds

A general rate law for hydrolysis which assumes second-order kinetics is (23):

$$-dC/dt = (k_b a_{OH} + k_a a_H + k_n a_w)C \quad (1)$$

where k_b , k_a , and k_n are second-order rate constants for the base, acid, and neutral reactions; and a_{OH} , a_H , and a_w are activities of hydroxide and hydronium ions and H₂O. In dilute solutions where $a_w = 1$ and at constant pH:

$$-dC/dt = k'C \quad (2)$$

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Table I. Reaction Conditions and Rate Constants

T (°C)	pH	total time (d)	k' (min ⁻¹)		k _b from eq 5 (M ⁻¹ min ⁻¹)	
			α-HCH	γ-HCH	α-HCH	γ-HCH
45	9.01	4	6.45 × 10 ⁻⁴	5.52 × 10 ⁻⁴	15.6 ± 1.0	13.3 ± 0.8
45	7.87	26	4.86 × 10 ⁻⁵	4.58 × 10 ⁻⁵	16.2 ± 0.9	15.3 ± 0.8
45	7.01	26	7.52 × 10 ⁻⁶	7.48 × 10 ⁻⁶	18.2 ± 0.9	18.1 ± 0.9
30	9.01	13	9.74 × 10 ⁻⁵	7.53 × 10 ⁻⁵	6.47 ± 0.38	5.01 ± 0.36
15	9.01	35	4.19 × 10 ⁻⁶	2.79 × 10 ⁻⁶	0.904 ± 0.068	0.602 ± 0.052
5	9.04	248	5.01 × 10 ⁻⁷	3.08 × 10 ⁻⁷	0.246 ± 0.027	0.151 ± 0.034

$$\log C/C_0 = -k't/2.303 \quad (3)$$

$$k' = k_b a_{OH} + k_a a_H + k_n \quad (4)$$

In basic solution, HCHs dehydrochlorinate to yield first pentachlorocyclohexene and then trichlorobenzenes (18–20). HCHs are acid-stable; in fact, sulfuric acid treatment of sample extracts in hexane is often used as an analytical cleanup step. Thus, the acid term is very small and is not considered here. If the reaction with water is also slow:

$$k' = k_b a_{OH} \quad (5)$$

The activity of OH⁻ is determined from pH measurements and the equation of Harned and Owen (24) for the ion product of water as a function of temperature:

$$\log K_w = a_H a_{OH} = 6.0875 - 4471/T - 0.01706T \quad (6)$$

The base rate constant is related to the energy of activation (E_a) and absolute temperature (T) by the Arrhenius equation:

$$\log k_b = A - E_a/2.303RT \quad (7)$$

Experimental Section

Buffer solutions at nominal pH values of 7, 8, and 9 were prepared from quartz-distilled deionized water and the following reagents: pH 7, 0.067 M Na₂HPO₄·12H₂O + 0.067 M KH₂PO₄; pH 8, 0.021 M Na₂HPO₄·12H₂O + 0.004 M KH₂PO₄; pH 9, 0.025 M Na₂B₄O₇·10H₂O adjusted to proper pH with acetic acid. Portions of these buffer solutions in 500-mL brown glass bottles (to avoid photolysis) were separately spiked with 17–24 μg/L α-HCH and 21–22 μg/L γ-HCH by adding standards in 1 mL of acetone. Sodium azide (0.05%) was added as a preservative, although microbial activity was not monitored during the experiment. The bottles were tightly sealed with polytetrafluoroethylene-lined caps to prevent volatilization and placed in a water bath at a fixed temperature ±0.05 °C (Table I).

To determine concentrations of unreacted HCHs, 1-mL water samples were extracted with 2 mL of isoctane containing 10 pg/μL hexachlorobenzene (HCB) as an internal standard. HCHs were quantified against injection standards containing 10 pg/μL of each HCH isomer and HCB. Analysis was done by capillary gas chromatography with electron capture detection on a Carlo Erba 4160 or Varian 3700 instrument under the following conditions: splitless injection (1–2.5 μL, open split after 30 s), DB-1 or DB-5 fused silica capillary column (0.25 mm i.d. × 25–30 m long, 0.25 μm film thickness, J&W Scientific Co.), carrier gas H₂ at 40 cm/s, injector 240 °C, detector 320 °C, and oven program: 90 °C, hold 1 min, 90–260 °C at 5–6 °C/min. Peak areas were determined by electronic integration.

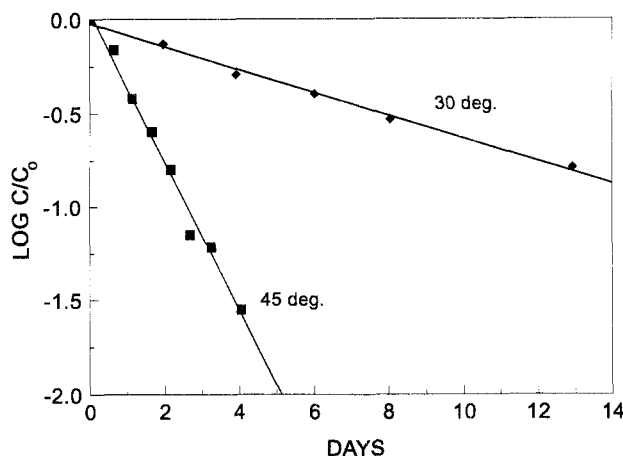


Figure 1. First-order plots for α-HCH at pH 9.0 and two temperatures.

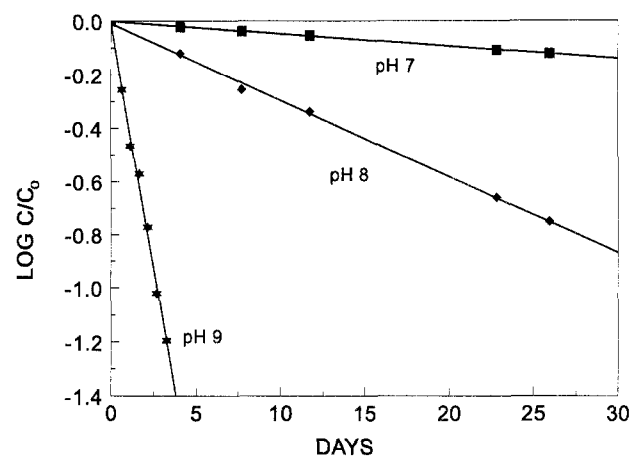


Figure 2. First-order plots for γ-HCH at 45 °C and three pH values.

Measurements of pH ±0.02 unit (Table I) were made with a combination glass-calomel electrode. Buffers in the pH 7–10 range were used for meter calibration (Baxter Scientific Co.).

Experiments were carried out under two sets of conditions: (a) constant temperature = 45 °C and nominal pH values of 7, 8, and 9 and (b) constant pH = 9 and temperatures of 5, 15, 30, and 45 °C. Concentrations of the HCHs were followed over time by analyzing replicate aliquots (2–4) of the 500-mL spiked solutions, as above. The analytical precision from pooled relative standard deviations was 2.2%.

Results and Discussion

Results were plotted according to eq 3, and the slopes (k'/2.303) were evaluated by linear regression. Examples of these plots at different temperatures and pH values are shown in Figures 1 and 2. The time scale of the experiments ranged from 4 d at pH 9 and 45 °C to 248 d

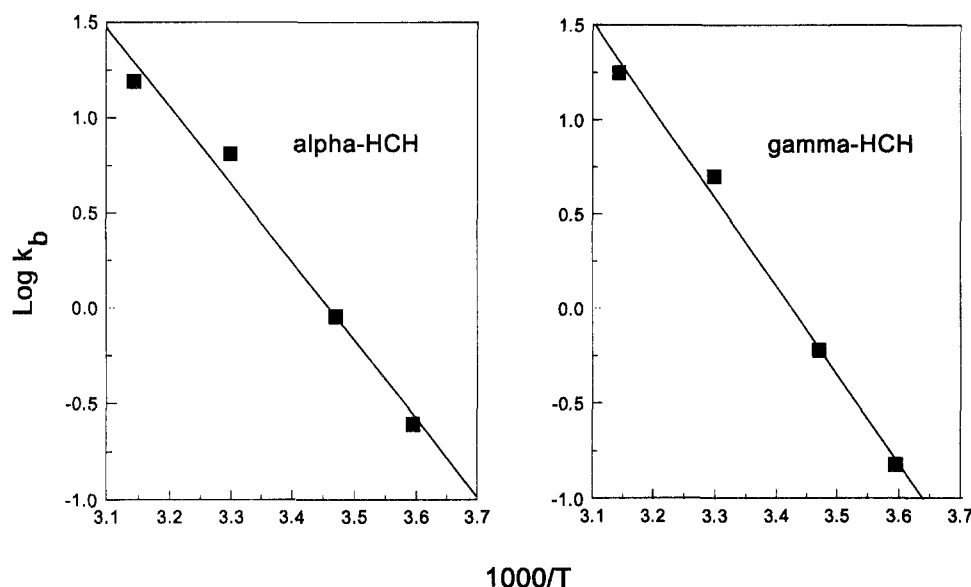


Figure 3. Log k_b ($M^{-1} \text{ min}^{-1}$) vs reciprocal temperature for α -HCH and γ -HCH.

at pH 9 and 5 °C. Apparent base rate constants (k_b , $M^{-1} \text{ min}^{-1}$) were calculated from the pseudo-first-order rate constants (k' , min^{-1}) by eq 5, using a_{OH^-} values obtained from pH measurements (Table I) and eq 6.

A summary of experimental conditions and rate constants is given in Table I. The precision (standard error) of k' values ranged from 10–20% at pH 9 and 5 °C to 4–7% at other pH values and temperatures. Precisions of k_b values (Table I) were derived by propagation of the uncertainties in k' and a_{OH^-} (4.5%, corresponding to ± 0.02 precision in pH).

The dependence of k' on pH at 45 °C indicates that breakdown of the HCHs occurs mainly by reaction with OH^- . Were this strictly true, however, k_b calculated from eq 5 would be invariant with pH. In fact, the apparent value of k_b increases between pH 9 and 7, suggesting that reaction with H_2O plays some part in HCH breakdown at the lower pHs. The actual k_b is best known from measurements at pH 9, where neutral hydrolysis is negligible. In principle, the neutral rate constant k_n can be evaluated from eq 4 (neglecting the $k_a a_{\text{H}^+}$ term) by plotting k' vs a_{OH^-} . The slope of this plot is k_b and the intercept is k_n . However in these experiments a_{OH^-} changes by 2 orders of magnitude, and the regression parameters of such a plot are dominated by the highest a_{OH^-} (the pH 9 experiments). Instead, k_n was calculated at 45 °C by the following process. Values of k_b ($M^{-1} \text{ min}^{-1}$) from the pH 9 experiments (Table I) were substituted into eq 4 (neglecting the acid term) along with k' (min^{-1}) at pH 7.01 (Table I) and $a_{\text{OH}^-} = 4.14 \times 10^{-7}$. The latter value was calculated from $K_w = 4.046 \times 10^{-14}$ at 45 °C (eq 6) and a_{H^+} corresponding to pH 7.01. The k_n (min^{-1}) values so obtained were α -HCH = 1.1×10^{-6} and γ -HCH = 2.0×10^{-6} . These are rough, because OH^- attack accounts for most of the HCH losses, even at pH 7 (which is a basic solution at 45 °C). More accurate values of k_n could be obtained by working in slightly acid media. Ellington et al. (19) carried out hydrolysis experiments at pH 3 and determined k_n (min^{-1}) for γ -HCH = 3.8×10^{-6} at 65.5 °C and 1.7×10^{-5} at 84.4 °C. Extrapolating to 45 °C by a relationship similar to eq 7 yields $k_n = 6.1 \times 10^{-7} \text{ min}^{-1}$, a factor of 3 lower than found in this work.

By similar reasoning, Wolfe et al. (25) showed that p,p' -DDT and methoxychlor were decomposed by different

routes at pH values typical of natural waters. Both compounds exhibited a change from reaction with H_2O in acidic solution to OH^- attack in strongly basic solution. However DDT was dehydrochlorinated by OH^- at pH >7, whereas methoxychlor breakdown proceeded mainly by reaction with H_2O up to pH 8–9. The products of methoxychlor reaction with water and base were also different. Breakdown of HCHs below pH 7 was not investigated in this study; however, at the slightly basic conditions typical of the Great Lakes and the oceans, reaction with OH^- dominates.

Dehydrochlorination rates of the HCHs depend strongly on temperature. This is in part due to the effect of temperature on the reaction of HCH with OH^- (k_b) and also due to the fact that water dissociation increases with temperature (higher a_{OH^-}). Values of k_b ($M^{-1} \text{ min}^{-1}$) were determined at pH 9 and four temperatures, ranging from 5 to 45 °C (Table I). Equation 7 plots of $\log k_b$ vs reciprocal temperature are shown in Figure 3. The resulting regression equations are

$$\log k_b(\alpha\text{-HCH}) = 14.151 - 4091/T \quad r^2 = 0.982 \quad (8)$$

$$\log k_b(\gamma\text{-HCH}) = 15.111 - 4417/T \quad r^2 = 0.983 \quad (9)$$

From these slopes, E_a values (kJ/mol) were 78.3 ± 7.6 and 84.6 ± 7.8 for α -HCH and γ -HCH, respectively. Ellington et al. (19) reported $E_a = 73.2 \pm 3.2 \text{ kJ/mol}$ for γ -HCH.

Values of k_b determined in this work are compared to others in Table II. All were done in buffered distilled water except for Kucklick et al. (16) (seawater) and Cristol (18) (70% ethanol-water). The former authors worked at pH 7.76, and neutral hydrolysis may have accounted for some of the breakdown of HCHs. Correction for this was made in deriving k_b from their data by assuming values of k_n estimated in this work. At 20 °C, k_b for γ -HCH ranges from 0.66 to $7.27 \text{ M}^{-1} \text{ min}^{-1}$ among six laboratories. The $k_b = 1.10 \text{ M}^{-1} \text{ min}^{-1}$ found here agrees well with Kucklick's (1.27) and Ellington's (1.53) results and is within a factor of 2 of Miller and Pedit's determination (0.66) (22). Cristol's values for k_b are 2.5 and 6.5 times higher for γ -HCH and α -HCH than found here, possibly because of the great difference in experimental media. No explanation can be given for the apparently high γ -HCH result of Saleh et al. (21).

Table II. Comparison of k_b Values for the HCHs^a

temp (°C)	k_b at exp temp (M ⁻¹ min ⁻¹)		k_b at 20 °C (M ⁻¹ min ⁻¹)		ref
	α -HCH	γ -HCH	α -HCH	γ -HCH	
5-45			1.57	1.10	this work
45	20.6	19.3	1.65	1.27	16
25		13.0		7.27	21
20	10.2	2.68	10.2	2.68	18
24-85				1.53	19
23		0.94		0.66	22

^a Values of k_b at other experimental temperatures were adjusted to 20 °C using slopes of eqs 8 and 9, except in the case of ref 19 for which their reported slope was used.

The above discussions assume that breakdown of the HCHs occurs by base and (to a slight extent) neutral hydrolysis and that catalysis by the phosphate and borate-acetate buffer components is negligible. Specific experiments were not done to verify this, but Kucklick et al. (16) obtained $k_b = 1.65$ for α -HCH and 1.27 for γ -HCH at 20 °C in artificial seawater containing a carbonate buffer. The proximity to our results (1.57 and 1.10 for α -HCH and γ -HCH, respectively) suggests that these three buffers do not contribute to HCH decomposition.

Lake Huron has a slightly alkaline pH of 7.6-7.8 (26), and the pH of seawater is about 8.1. Hydrolysis half-lives, calculated at pH 8 and 5 °C using k_b from eqs 8 and 9, are 26 and 42 yr for α -HCH and γ -HCH, respectively. By comparison, a sedimentation residence time of 10 yr has been estimated for HCHs in oligotrophic ocean waters (17). Reported photolysis half-lives are much faster: 14-150 d for γ -HCH in mid-winter (21). A 48-d photolytic half-life was found for γ -HCH in distilled water containing 5-25 mg/L fulvic acid (27). However photolysis is important only in the upper water column, whereas HCHs are uniformly mixed to 60 m in the central Arctic Ocean (12) and to at least 30 m in the Great Lakes (7). HCHs are also found down to 1200 m in the North Atlantic Ocean (1). Microbial transformation of HCHs in the North Sea water has recently been demonstrated by separation of the enantiomers of α -HCH by chiral-phase GC (28), but rates have not been determined. The relative contribution of hydrolysis to loss of HCHs in subsurface waters requires that rates be better established for sedimentation and microbial breakdown.

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