

OH Reaction Kinetics of Gas-Phase α - and γ -Hexachlorocyclohexane and Hexachlorobenzene

W. WAYNE BRUBAKER, JR. AND
RONALD A. HITES*

School of Public and Environmental Affairs and
Department of Chemistry, Indiana University,
Bloomington, Indiana 47405

Rate constants for the gas-phase reactions of the hydroxyl radical (OH) with α - and γ -hexachlorocyclohexane (α - and γ -HCH) and hexachlorobenzene (HCB) were measured over the temperature range 346–386 K. The experiments were carried out in He diluent gas at approximately 1 atm, in a 160-mL quartz chamber. OH was produced by the photolysis of ozone in the presence of H₂O, and reactants in the chamber were monitored by online mass spectrometry. The rate constants measured at elevated temperatures were extrapolated by the Arrhenius equation, and OH reaction rate constants at 298 K were estimated for each compound. These rate constants at 298 K (in units of 10⁻¹³ cm³ s⁻¹) were α -HCH, 1.4; γ -HCH, 1.9; and HCB, 0.27. Atmospheric lifetimes based on OH reactions (τ_{OH}) were also estimated (in units of days): α -HCH, 120; γ -HCH, 96; and HCB, 940. These relatively high atmospheric lifetimes indicate that these compounds can be transported great distances through the atmosphere before removal processes associated with the global distillation effect.

Introduction

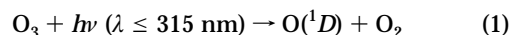
Hexachlorocyclohexanes (HCH) and hexachlorobenzene (HCB) are environmentally persistent compounds, which have been used as pesticides throughout the world. Of the five isomers found in technical-grade HCH, the γ -isomer (known as lindane) accounts for 8–15% of the mixture and is the only insecticidal ingredient; α -HCH makes up another 55–80% of technical HCH, which is still used today in developing countries (1). HCB is used in organic syntheses and as a fungicide (2). All of these compounds (see Figure 1 for structures) can undergo long-range atmospheric transport and can be deposited to remote areas of the globe, such as the Arctic and Antarctica (3–7), where they can bioaccumulate in the food chain.

In the atmosphere α - and γ -HCH and HCB are typically found in the gas phase (8), and thus, reactions with the hydroxyl radical (OH) are expected to be a significant removal pathway for these compounds (9–11). OH reaction rate constants, however, have not been measured for α - and γ -HCH and HCB, primarily due to the relatively low volatilities of these compounds at room temperature and limitations of traditional reaction systems (9). Our laboratory recently developed a reaction system that allows us to investigate the OH reaction kinetics of organic compounds of low volatility (12–14), and we have now completed such studies with these three compounds. We present here OH reaction rate

constants of gas-phase α - and γ -HCH and HCB over the temperature range 346–386 K and briefly discuss the environmental implications.

Experimental Section

The experimental setup was similar to that described in detail elsewhere (12–14). Gas-phase reactants were introduced into a 160-mL quartz chamber and monitored in real time by an online mass spectrometer. This chamber was mounted in the oven of a gas chromatograph for exact temperature control. Helium (99.999%; Gas Tech, Hillside, IL) served as the primary diluent gas for all experiments, and the pressure inside the chamber was held at approximately 1 atm. OH radicals were produced by



O₃ was generated by flowing O₂ (99.998% purity; Gas Tech, Hillside, IL) through a 12-kV discharge prior to chamber introduction. Water vapor was introduced by passing the He gas flow through H₂O (HPLC-grade; EM Science, Gibbstown, NJ) at room temperature. The O₂–O₃ mixture accounted for approximately 1% of the total gas volume in the chamber, and O₃ concentrations were approximately 10¹⁶ cm⁻³ in the chamber at about 300 K. A mercury, Pen-Ray lamp (UVP, Upland, CA) provided UV radiation centered at 254 nm. Typical OH concentrations for experiments at 347 K were approximately 2 × 10¹⁰ cm⁻³.

OH reaction rate constants were measured by the relative rate technique (15, 16), using hexafluorobenzene (HFB) as the reference compound in all experiments. HFB was typically injected into the reaction chamber in a solution of CCl₄, which is essentially nonreactive to OH (12, 16). Approximately 10–20 μg of the test compounds, α - and γ -HCH and HCB, were introduced during their respective experiments by volatilization from a heated quartz probe inserted into the chamber (14). For all experiments, the concentrations of HFB and the test compound each ranged between 1 and 3 × 10¹⁴ cm⁻³.

The reactants, excluding OH, were monitored by a Hewlett Packard 5985B mass spectrometer, which was interfaced to the reaction chamber by a 60 cm × 100 μm i.d. deactivated fused silica capillary (SGE, Austin, TX). This transfer capillary was held at approximately 100 °C. The mass spectrometer was operated in its selected ion monitoring (SIM) mode, using either electron impact (EI) positive ionization or electron capture negative ionization (ECNI) (14). HFB was monitored at m/z 186 (C₆F₆^{+/-}) for all experiments, and the test compounds were monitored at m/z 109 (C₆H₂Cl⁺) for α - and γ -HCH in the EI mode, m/z 255 (C₆H₆Cl₄³⁷Cl⁺) for γ -HCH in the ECNI mode, and m/z 284 (C₆Cl₅³⁷Cl⁺) for HCB in the EI mode. In cases where ECNI was used, it was necessary to introduce HFB via split injection (14), with the concentration of HFB ranging between 0.8 and 8 × 10¹⁴ cm⁻³.

The reaction chamber was irradiated 1–2 times during each experiment for durations of 1–5 min apiece. Assuming OH reactions were the primary loss processes during UV irradiation of the chamber, the recorded m/z signal intensities for the two compounds follow

$$\ln \frac{[\text{test}]_0}{[\text{test}]_t} = \left(\frac{k_{\text{test}}}{k_{\text{HFB}}} \right) \ln \frac{[\text{HFB}]_0}{[\text{HFB}]_t} \quad (3)$$

* Corresponding author e-mail: HITESR@INDIANA.EDU.

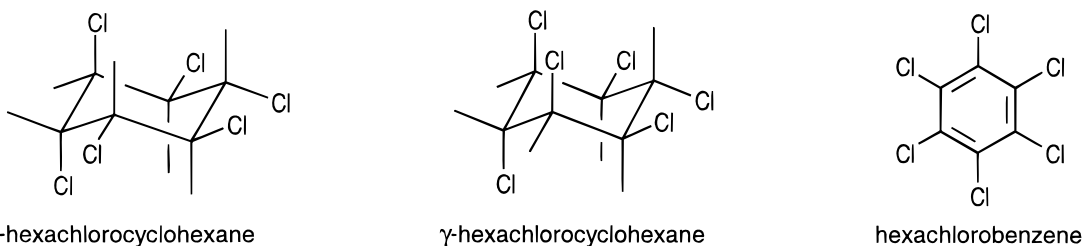


FIGURE 1. Structures of the compounds studied.

TABLE 1. Experimental Conditions, Rate Constant Ratios, and Rate Constants for OH Radical Reactions of α -Hexachlorocyclohexane, γ -Hexachlorocyclohexane, and Hexachlorobenzene

T (K)	$k_{\text{test}}/k_{\text{ref}}^a$	rate constant ($\times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$) ^b	T (K)	$k_{\text{test}}/k_{\text{ref}}^a$	rate constant ($\times 10^{-12}$ $\text{cm}^3 \text{s}^{-1}$) ^b
α -Hexachlorocyclohexane			γ -Hexachlorocyclohexane		
346	0.98 ± 0.12	0.26 ± 0.08	347	1.78 ± 0.26	0.47 ± 0.14
346	1.10 ± 0.14	0.29 ± 0.09	347	1.54 ± 0.22	0.41 ± 0.12
346	1.09 ± 0.14	0.29 ± 0.09	347	1.58 ± 0.23	0.42 ± 0.13
365	0.94 ± 0.16	0.29 ± 0.09	347 ^c	1.73 ± 0.25	0.46 ± 0.14
366	1.06 ± 0.18	0.32 ± 0.10	347 ^c	1.51 ± 0.22	0.40 ± 0.12
386	1.15 ± 0.09	0.40 ± 0.12	367	1.86 ± 0.31	0.57 ± 0.17
386	1.23 ± 0.09	0.43 ± 0.13	367	1.85 ± 0.31	0.57 ± 0.17
386	1.23 ± 0.09	0.43 ± 0.13	367	1.95 ± 0.33	0.60 ± 0.18
			367 ^c	1.91 ± 0.32	0.59 ± 0.18
			367 ^c	1.56 ± 0.26	0.48 ± 0.14
Hexachlorobenzene					
347	0.38 ± 0.05	0.10 ± 0.03	385	2.10 ± 0.20	0.73 ± 0.22
347	0.42 ± 0.05	0.11 ± 0.03	385	1.97 ± 0.18	0.68 ± 0.20
367	0.56 ± 0.04	0.17 ± 0.05			
367	0.57 ± 0.01	0.18 ± 0.05			
386	0.71 ± 0.04	0.25 ± 0.07			
386	0.68 ± 0.03	0.24 ± 0.07			

^a Reference compound was hexafluorobenzene. Stated uncertainties of the rate constant ratios are based on two relative standard deviations of the measurements at a given temperature. ^b Stated uncertainties of the experimental rate constants reflect the estimated overall uncertainty recommended for hexafluorobenzene's rate constants of $\pm 30\%$ (17). ^c Measured with ECNI.

where the signal intensities were measured at time $t = 0$ and at subsequent times t . The values k_{test} and k_{HFB} represent the OH reaction rate constants for the test and reference compounds, respectively. Values of k_{test} were calculated from the slopes of experimental plots of eq 3 and the temperature dependent expression for k_{HFB} most recently recommended by Atkinson (17):

$$k_{\text{HFB}} = (3.88_{-0.79}^{+0.98}) \times 10^{-12} e^{-(931 \pm 78\text{K})/T} \text{ cm}^3 \text{ s}^{-1} \quad (4)$$

Other potential loss processes of the reactants, which could interfere with our OH rate constant measurements, were accounted for by analysis of the signal intensities before and after the UV irradiation.

Results and Discussion

OH Reaction Rate Constants. The results for our OH reaction rate constant measurements are given in Table 1. The uncertainties stated for the rate constant ratios, $k_{\text{test}}/k_{\text{ref}}$, are based on two relative standard deviations for measurements at a given temperature, giving an indication of the variability between experiments at that temperature. These uncertainties for $k_{\text{test}}/k_{\text{ref}}$ are never larger than $\pm 30\%$, the uncertainty reported for the reference compound HFB (17); see eq 4. All measurements were made with EI ionization, except those designated for γ -HCH, which used ECNI. The EI- and ECNI-acquired data for γ -HCH were consistent with each other, demonstrating the potential of ECNI to measure the OH

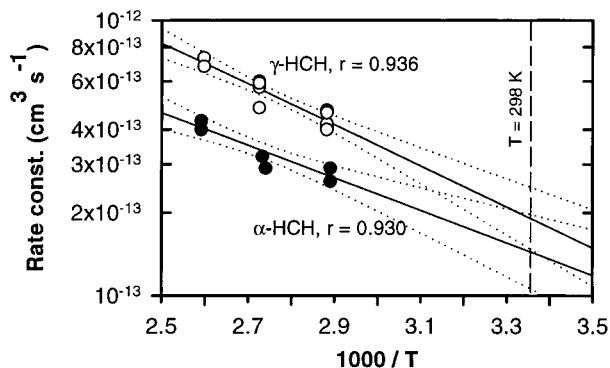


FIGURE 2. Arrhenius plot for α - and γ -hexachlorocyclohexane-OH reactions. Symbols: ●, α -HCH-OH reaction rate constants; ○, γ -HCH-OH reaction rate constants. Lines: (solid) fit to each data set; (dotted) 95% confidence limits of each fit.

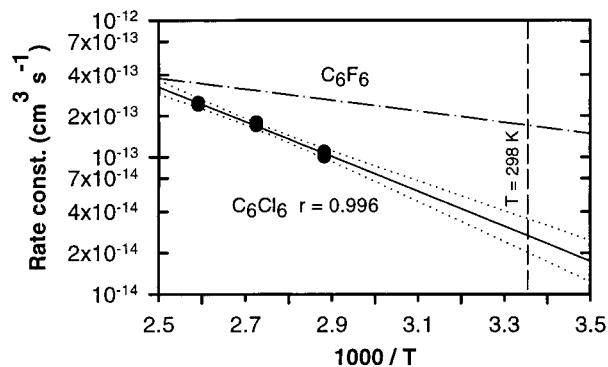


FIGURE 3. Arrhenius plot for hexachlorobenzene-OH reaction. Lines: (solid) fit to data; (dotted) 95% confidence limits of the fit; (dashed) expression recommended by Atkinson for hexafluorobenzene-OH reaction (17).

reaction rate constants of chlorinated compounds with lower volatilities (14).

The natural logarithms of the OH reaction rate constants for each compound in Table 1 were fitted by a linear regression to the reciprocal of the experimental temperature; see Figures 2 and 3. The results of these regressions are given in Arrhenius parameters (preexponential factor, A , and activation energy, E_a) in Table 2, where $k = Ae^{-E_a/RT}$. Each regression is significant at the 99.9% confidence level. For some haloalkane-OH reactions, an alternate relationship between the rate constants and temperature is $k = CT^2e^{-D/T}$, but fits of our HCH data to this other expression gave the same results as the simpler expression. With the parameters in Table 2, OH reaction rate constants were estimated at 298 K for α - and γ -HCH and HCB and compared to values predicted by the structure-reactivity method developed by Kwok and Atkinson (18). Our experimentally derived values for α - and γ -HCH are both lower than the prediction of $5.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (18) by factors of 4 and 3, respectively. Our value at 298 K for HCB is about 35% higher than Kwok and Atkinson's prediction of $0.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (18).

TABLE 2. Temperature Dependence of Experimentally Determined OH Reaction Rate Constants and Estimated Rate Constants

compound	<i>N</i>	pre-exponential factor ($\times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$)	E_a (kJ/mol) ^a	rate constant estimated at 298 K, k^{298} ($\times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$) ^b
α -hexachlorocyclohexane	8	1.4	11.2 ± 1.8	1.4 (1.1–2.0)
γ -hexachlorocyclohexane	12	6.0	14.2 ± 1.7	1.9 (1.4–2.5)
hexachlorobenzene	6	49	24.3 ± 1.5	0.27 (0.20–0.38)

^a Uncertainty in E_a is based on one standard error of the slope of the temperature dependence regression (where $k = Ae^{-E_a/RT}$). ^b Values in parentheses represent 95% confidence limits of the temperature dependence regression.

The disagreement between our HCH-OH reaction rate constants at 298 K and the values predicted by Atkinson indicates that the HCH isomers are less reactive toward OH than expected. While no other experimental rate constants exist in the peer-reviewed literature, Palm et al. recently cited a rate constant of $6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for γ -HCH present on aerosol particles (19), which was reported by Behnke and Zetzsch (20) and agrees with Kwok and Atkinson's gas-phase prediction (18). We also note that our experimental derived parameter *A* for γ -HCH is high as compared to the values for α -HCH (this study) and cyclohexane at 298 K (21). The larger *A* value for γ -HCH suggests experimental problems at the lower temperatures. Slight differences were observed in the pre- and post-UV signal trends during our γ -HCH measurements at 347 K, but this was accounted for by our background subtraction of such trends.

The hydroxyl radical is only expected to react with α - and γ -HCH by H-atom abstraction at C–H bonds (18), and our data suggest that the chlorine substituents at each carbon make such a reaction unfavorable. For example, unchlorinated cyclohexane has a higher OH reaction rate constant of $72 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 298 K (21). While Kwok and Atkinson's estimation method does not distinguish between the two HCH isomers presented here (18), our data indicate that the γ -isomer has a rate constant that is about 40% higher than that of the α -isomer (see Table 2). This difference could be attributed to the slight steric differences between the two isomers, but this explanation is unlikely given that α - and γ -HCH only differ by the position of one chlorine (see Figure 1). It is more likely that the observed differences are electronic (22). OH reacts with HCB by addition to the aromatic ring rather than H-atom abstraction (18). Note in Figure 3 that HCB reacts much slower with OH than its fluorinated counterpart, HFB. This difference may be related to the difference in the electronegativities between chlorine and fluorine.

The activation energies for α - and γ -HCH and HCB were compared to those found in our laboratory's OH reaction studies of polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (13, 14, 23). The E_a values given in Table 2 for α - and γ -HCH are similar to those measured for tetra- and pentachlorinated biphenyls (13) and 1,2,3,4-tetrachlorinated-*p*-dioxin (14) and about an order of magnitude higher than those for two- and three-ring PAH (23). HCB's E_a value, on the other hand, is at least 50% higher than those of the other compounds studied. This higher activation energy for HCB is likely due to steric considerations (a chlorine is present on each carbon). The relatively high number of chlorines, which can absorb more collisional energy in the gas phase, is an activation barrier that requires greater energy to cause a reaction between this compound and OH. Similar analogies can be made between the more and lesser chlorinated compounds mentioned above.

Atmospheric Implications. Atmospheric lifetimes were estimated for α - and γ -HCH and HCB (see Table 3) using

TABLE 3. Estimated Rate Constants and Atmospheric Lifetimes at 277 K, the Average Temperature of the Earth's Atmosphere

compound	rate constant estimated at 277 K, k^{277} ($\times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$) ^a	atmospheric lifetime, τ_{OH} (days) ^b
α -hexachlorocyclohexane	1.0 (0.6–1.6)	120
γ -hexachlorocyclohexane	1.2 (0.8–1.8)	96
hexachlorobenzene	0.13 (0.09–0.19)	940

^a Values in parentheses represent 95% confidence limits of the temperature dependence regression. ^b Calculated using $9.7 \times 10^5 \text{ cm}^{-3}$ as the global OH concentration averaged over 24 h (24).

$$\tau = \frac{1}{k_{\text{OH}}[\text{OH}]} \quad (5)$$

where k_{OH} is the OH reaction rate constant estimated from our Arrhenius parameters in Table 2 at 277 K, the average temperature of the Earth's atmosphere (24, 25), and [OH] is the global OH concentration in the atmosphere, averaged over 24 h with a value of $9.7 \times 10^5 \text{ cm}^{-3}$ (24). The atmospheric lifetimes given for the HCH isomers (120 and 96 days) are much longer than the 7–15 days previously predicted (9, 26). Given the relatively long atmospheric lifetimes (at least for reaction with OH) and given their vapor pressures, all three of these compounds are likely to move long distances through the atmosphere.

A recent study, in fact, measured the concentrations of 22 organochlorine compounds in over 200 tree bark samples collected worldwide (27). Of the 22 compounds, only the concentrations of α - and γ -HCH, HCB, and pentachloroanisole gave significant, positive correlations with absolute values of the latitude where the samples were collected (27). This observation supported the hypothesis known as "global distillation" (28), which suggests that organic pollutants will be volatilized from warmer regions of the globe where they are used and transported to colder regions where they condense. The relatively low OH reaction rates measured here for gas-phase α - and γ -HCH and for HCB clearly favor this global distillation process. For example, gas-phase PAH have estimated tropospheric lifetimes ≤ 1 day based on their OH reactions rates (23), and they would be far less likely to undergo long-range atmospheric transport. Global distillation involves a number of other factors (for example, vapor pressures and partition coefficients), and models to account for these processes are still in the early stages of development (28–30). Clearly, OH reactions should be incorporated in these models.

Acknowledgments

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