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Transformation of Hexachloroethane in a Sulfidic Natural Water

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To investigate the roles that hydrogen sulfide and polysulfides could play as reductants in natural waters, reactions of hexachloroethane and pentachloroethane were examined in samples obtained from the anoxic hypolimnion of Lower Mystic Lake, MA. Experiments were conducted by monitoring the disappearance of pentachloroethane or hexachloroethane and appearance of reaction products; measured pseudo-first-order reaction rate constants for hexachloroethane were compared to predictions based on measured polysulfide and bisulfide concentrations and second-order rate constants. For pentachloroethane, 80% of the reaction could be attributed to abiotic dehydrohalogenation. An additional 9% resulted from abiotic reductive elimination to trichloroethylene. Reaction of hexachloroethane was predominately abiotic. At least 61% occurs via reductive elimination to tetrachloroethylene; a further 7−10% involves hydrogenolysis to pentachloroethane (indicative of a free-radical pathway). More than 20% of the observed hexachloroethane disappearance in filter-sterilized samples can be attributed to reaction with H_2S and S_n^{2-} species, with the latter playing a predominant role. These (and related reductants) could promote reductive dehalogenation through dissociative electron-transfer processes involving a free radical intermediate; alternatively, they may serve as "nucleophilic reductants". Results of this study demonstrate that aqueous polysulfide species, in particular, should not be overlooked as potential "environmental reductants" in sulfate-reducing environments.

Introduction

Coastal marine environments support a wide variety of resources and are of critical importance to economic as well as cultural life. Almost half of the population of the United States lives in coastal areas, thereby placing a heavy burden on the quality of receiving waters. In addition to point sources of pollution, coastal regions are subject to nonpoint pollution via fluvial runoff (*1*) or groundwater inflow (*2*−*4*), which funnel contaminants directly into highly sensitive ecosystems. A better understanding of how contaminants interact with dissolved and suspended species present in the water column or in porewaters is a prerequisite to assessing the impact of anthropogenic activities on these important environments.

In many coastal environments, increased biological activity during warmer months leads to depletion of dissolved oxygen. Under such conditions, microbial sulfate reduction can give rise to locally high concentrations of hydrogen sulfide species (defined as H_2S and HS^-) and polysulfide ions (chiefly S_n^{2-}). H_2S species can attain levels as high as 5.6 mM in anoxic estuarine porewaters, and polysulfide concentrations as high as 200 μM have also been reported (*5*, *6*). Such species are noteworthy because HS^- and S_n^{2-} are potent nucleophiles and reductants. These features render such species capable of promoting the transformation of otherwise recalcitrant organic contaminants via nucleophilic substitution and reduction pathways.

Halogenated alkanes can, in principle, undergo reaction through several routes: nucleophilic substitution, dehydrohalogenation (loss of HX), and reductive dehalogenation. The last actually consists of two reactions: hydrogenolysis (replacement of halogen by hydrogen) and reductive elimination (loss of two vicinal or geminal halogens). Numerous studies have shown HS^- and S_n^{2-} are capable of promoting bimolecular nucleophilic substitution (S_N2) reactions of mono- and dihalogenated alkanes (*5*, *7*−*12*). For more highly halogenated alkanes, however, dehydrohalogenation and reductive dehalogenation (both of which are favored by increasing halogen substitution) are likely to predominate over S_N2 reactions.

Previous studies conducted in well-defined systems have indicated that H_2S species are insufficiently reactive to contribute significantly to the reductive dehalogenation of alkyl polyhalides. Rather, it has been suggested their role is principally one of a bulk reductant of some electron-transfer "mediator" (e.g., hydroquinones or other constituents of natural organic matter [NOM], metalloorganic complexes such as iron porphyrins, or mineral surfaces) that in turn catalyzes the actual reaction with the contaminant in question (*13*−*18*). These prior studies have, however, been conducted with model compounds or NOM isolates from aerobic environments that may or may not accurately mimic conditions in natural sulfate-reducing systems.

Preliminary experiments conducted by Roberts (*19*) suggested that polysulfides might be sufficiently abundant in a sulfidic lake water to serve as direct (as opposed to bulk) reductants, thereby accounting for a significant fraction of hexachloroethane transformation. The present investigation was initiated in order to better quantitate the role polysulfides might play as reductants in natural waters. Hexachloroethane was selected as a model contaminant because many prior studies have emphasized its reductive dehalogenation (e.g., *16*, *18*−*24*). To clarify reaction pathways, transformations of potential intermediates were also examined. Particular emphasis was placed on assessing whether pentachloroethane represented a reaction intermediate, since this compound is believed to be indicative of a free-radical pathway (*25*).

Experimental Section

Reagents. Hexachloroethane (99%), tetrachloroethylene (99%), 1,1,2,2-tetrachloroethane (99%), and trichloroethylene (99.5%) were used as obtained from Aldrich. Pentachloro-

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ethane was obtained from ICN. Standard solutions of these compounds were prepared in hexane (ultra resi-analyzed grade, J. T. Baker) for GC analysis. Stock solutions for spiking aqueous samples were prepared in methanol (ultra resi-analyzed grade, J. T. Baker).

Na_2S stock solutions were prepared under argon from $Na_2S\cdot 9H_2O$ (Baker or Mallinckrodt) using deoxygenated (argon-sparged) deionized distilled water. Before use, clear crystals were selected and rinsed free of surface oxidation products. Na_2S stock solutions were standardized via iodometric titration, and were stored in an anaerobic glovebox in crimp-sealed serum vials. Polysulfide standards were prepared by adding an excess of S_8 (>99.9%, Fluka) to HS^- solutions in serum vials under argon.

Water Samples. The natural water samples selected for investigation were obtained from the anoxic hypolimnion of Lower Mystic Lake, Arlington, MA. This meromictic lake formerly received semidiurnal tidal inflow from the Mystic River which was halted when dams were constructed in 1909 and 1966. Following dam construction, the saltwater in the density-stratified lake became anoxic, developing high levels of H_2S species comparable to those observed in anoxic estuarine or salt marsh porewaters.

Lake water samples were obtained on June 25, 1994. Samples were acquired from a depth of 20 m (5 m below the chemocline) with a peristaltic pump, collecting the water in argon-purged 1 L flasks equipped with stopcock outlets, and were stored on ice for transport to Johns Hopkins University. Flasks were subsequently stored prior to use (within 3 months) under water at 4 °C. Lake water samples (filter-sterilized) were analyzed for total organic carbon (TOC) using a Dohrmann DC-80 Total Organic Carbon analyzer. Additional analyses were also conducted to determine hydrogen sulfide species and polysulfides, as described below.

Kinetic Experiments. Aliquots of 14 mL of lake water samples were transferred under argon to 10 mL (nominal volume) glass ampules. All samples were first filtered (5 μm) to remove suspended sediment. Some lake water samples were also filter-sterilized through a 0.2 μm filter (Anotop Plus, Alltech) as they were transferred to sterile ampules. Ampules were then spiked with 5 μL of a methanol solution of individual organohalides to yield initial concentrations of approximately 5 μM and were immediately flame-sealed, shaken by hand, and transferred to a temperature-controlled water bath (25 °C) for static incubation in the dark. This technique appeared successful at maintaining the reduced character of the water: if the seal on an ampule was even slightly imperfect, the sample rapidly became turbid, attributed to oxidation of reduced sulfur species to S_8.

Experiments were sampled daily for 10 days. The headspace volume in the ampules was determined to be <0.63 mL. Calculations based on K_H values given by ref 26 indicated that, in the worst case (i.e., for tetrachloroethylene), less than 3% of the compound would be present in the gas phase. Corrections for air:water partitioning were therefore neglected. Extractions were conducted by shaking 1 mL of hexane with 10 mL of sample. Extracts were diluted 100-fold prior to GC analysis in order to obtain timecourses for parent compound transformation; solvent extracts were also run undiluted to maximize detection of minor reaction products.

Complementary kinetic experiments were conducted in clean systems, as described in ref 19. In these earlier experiments, incubations were carried out in 300 mL three-necked flasks, which were wrapped in black plastic to prevent photochemical reactions and then maintained within a water bath at 25 °C. The three-way stopcock adapters on these flasks allowed all sample manipulation steps, such as spiking with hexachloroethane or removal of aliquots for analysis, to be conducted under argon, minimizing exposure of the flask contents to the atmosphere. To begin these experiments, flasks containing either 5 mM Na_2S or 5 mM Na_2S equilibrated with S_8 at varying pH were spiked with 50 μL of a methanol stock solution of hexachloroethane to yield initial concentrations of approximately 5.5 μM. Flasks were sampled by removing 100 μL aliquots, which were extracted with 1 mL of hexane for analysis by GC.

Hexane extracts were analyzed using a Carlo Erba Mega or a Fisons Mega 2 high-resolution gas chromatograph. Separation was effected by an Rt$_x$-1 column (30 m × 0.32 mm ID × 5.0 μm film thickness; Restek), with a ^{63}Ni electron capture detector used for peak detection.

Analysis of Reduced Sulfur Species. The total hydrogen sulfide content ($[H_2S]_T$, representing the sum of $[H_2S]$ and $[HS^-]$) was measured in the lake water using the methylene blue method (*27*). Jacobs (*28*) has shown that polysulfides interfere only minimally with this reaction at low ratios of polysulfides to total hydrogen sulfide species (such as those encountered in this study). Prior to derivatization with the mixed diamine reagent according to the methylene blue method, lake water samples and Na_2S standards were diluted 10-fold with deoxygenated Q-H_2O.

Analytical techniques which would enable the determination of individual polysulfide species in environmental samples have not, to the best of our knowledge, been developed. To assess the concentrations of total polysulfides in lake water samples, the total dissolved sulfur(0) content ($[S(0)]_T$, numerically equivalent to $(n-1)\Sigma([S_n^{2-}] + [HS_n^-]) + 8[S_8(aq)]$), was determined by reacting polysulfides with sulfite to thiosulfate (*29*) after first sparging to remove H_2S species. Thiosulfate was determined according to the method of Vairavamurthy and Mopper (*30*). The HPLC system consisted of a P2000 Spectrasystems Pump and membrane degasser and A53000 Spectrasystems autosampler (Thermo Separation Products) coupled to a 759A absorbance detector (Applied Biosystems). The column used was a Bondapack C_{18} (Waters, 125 Å; 300 mm × 3.9 mm; 10 μm), and peaks were detected at $\lambda = 320$ nm with a sensitivity of 0.02 AUFS. This derivatization and analysis procedure was tested against a polysulfide standard; results indicated 75% of the $S(0)_T$ content of the polysulfides was converted to thiosulfate.

Total polysulfide concentrations $[HS_n^-]_T$, numerically equal to $[HS_4^-] + [S_4^{2-}] + [HS_5^-] + [S_5^{2-}] + [HS_6^-] + [S_6^{2-}]$ were estimated from measured $[S(0)]_T$ by subtracting out the contribution of $[S_8(aq)]$ (1.9×10^{-8} M; ref 31) and assuming that the relative abundance of S_4^{2-}:S_5^{2-}:S_6^{2-} species was governed by equilibrium constraints at a particular pH and ionic strength. The total polysulfide content was used to determine total concentration of the reactive polysulfide dianion ΣS_n^{2-} (numerically equal to $[S_4^{2-}] + [S_5^{2-}] + [S_6^{2-}]$) by assuming that the ratio of individual monoprotonated to fully deprotonated species was again dictated by equilibrium constraints.

Data Analysis. Data were analyzed using *Scientist for Windows* v. 2.01 (MicroMath Scientific Software, Salt Lake City, UT). Reaction rate constants were determined by fitting observed data for parent compounds and reaction products to numerically integrated solutions of the system of governing differential rate expressions. Rate expressions describing the observed kinetics were solved using the EPISODE package (numerical integrator for stiff systems), and rate constants were determined from least-squares fits (Powell algorithm) of the observed data to the model.

Results

Lake Water Chemistry. Table 1 summarizes data pertaining to the composition of the water in the anoxic hypolimnion of Lower Mystic Lake. The $[H_2S]_T$ and pH measurements can be used to predict the distribution of reduced sulfur

TABLE 1. Lake Water Chemistry for Anoxic Hypolimnion of Lower Mystic Lake, MA[a]

parameter	value determined
pH	6.80 (± 0.05)[b]
total organic carbon (TOC)	43 ± 1.7 mg/L
ionic strength[c]	0.40 M
$[\mathrm{H_2S}]_\mathrm{T}$	7.1 (± 0.03) × 10^{-3} M
$[\mathrm{S(0)}]_\mathrm{T}$	3.3 (± 0.1) × 10^{-4} M
$[\Sigma \mathrm{S}_n^{2-}]$	8.4 (± 0.3) × 10^{-5} M

[a] Uncertainties represent 1 standard deviation for analysis of duplicate samples, unless otherwise Indicated. [b] Based on analysis of 7 samples. [c] Calculated from major ion analyses reported by ref 32.

species that would exist in these waters through equilibration with orthorhombic $\mathrm{S_8}$ according to the reaction:

$$\mathrm{HS}^- + \frac{(n-1)}{8}\mathrm{S_8(ort)} \leftrightarrow \mathrm{S}_n^{\;2-} + \mathrm{H}^+ \qquad (1)$$

The relevant formation constants for polysulfide species, along with their ionization constants, were obtained from model-derived thermodynamic values (*33*). These constants, along with the ionization constant for $\mathrm{H_2S}$ (*34*), were corrected for ionic strength using the Davies equation.

The predicted equilibrium $[\mathrm{S(0)}]_\mathrm{T}$ in this lake water is 1.6 × 10^{-4} M, while the measured $[\mathrm{S(0)}]_\mathrm{T}$ value was 3.3 (± 0.1) × 10^{-4} M. After factoring in the derivatization efficiency, these results indicate that the lake water is approximately 2.7× supersaturated with respect to polysulfides. Substantially greater (up to 500–1000-fold; ref 29) levels of polysulfide supersaturation have been reported in salt marsh pore waters; this has been interpreted as the result of a dynamic cycling of sulfur species within such environments. For the measured lake water $[\mathrm{H_2S}]_\mathrm{T}$ and pH, the $[\mathrm{S(0)}]_\mathrm{T}$ results suggest a total reactive polysulfide $\Sigma \mathrm{S}_n^{2-}$ concentration of 8.4 × 10^{-5} M.

Pentachloroethane Transformation in Lake Water. Pentachloroethane represents one possible reduction product of hexachloroethane; careful attention was therefore paid to examining reactions of this potential intermediate by using it as a starting material. Pentachloroethane degraded in the lake water over the course of several days (Figure 1). Mass balances after 10 days were 91 and 86% for the unaltered and filter sterilized systems, respectively. Tetrachloroethylene and trichloroethylene were the only products detected. Product distribution in the unaltered samples was similar to that obtained in the filter-sterilized samples.

Tetrachloroethylene undoubtedly originates from a dehydrohalogenation pathway. In principle, trichloroethylene could be produced by one of three routes (Scheme 1): (a) reductive elimination of pentachloroethane to trichloroethylene; (b) hydrogenolysis of pentachloroethane to 1,1,2,2-tetrachloroethane, followed by dehydrohalogenation of this intermediate; (c) dehydrohalogenation of pentachloroethane to tetrachloroethylene, followed by hydrogenolysis.

To investigate the feasibility of pathway b, experiments were conducted by spiking filter-sterilized and unaltered lake water samples with 1,1,2,2-tetrachloroethane and monitoring its behavior over the course of 10 days. No parent compound disappearance was discerned, nor did any significant accumulation of trichloroethylene occur. This is consistent with the slow abiotic dehydrohalogenation of this compound, which at the pH of the lake water should proceed with a pseudo-first-order rate constant of 0.007 day^{-1} (*35*). The lack of any perceptible accumulation of 1,1,2,2-tetrachloroethane (quantitation limit ≅ 3 nM) in the experiments with pentachloroethane, coupled with its slow rate of reaction, precludes it as a significant intermediate in trichloroethylene formation. Parallel experiments similarly demonstrated the stability of tetrachloroethylene (as well as trichloroethylene) in unaltered and filter-sterilized lake water over the course of 10 days, a result inconsistent with pathway c. This suggests trichloroethylene originates from the reductive elimination of pentachloroethane (pathway a).

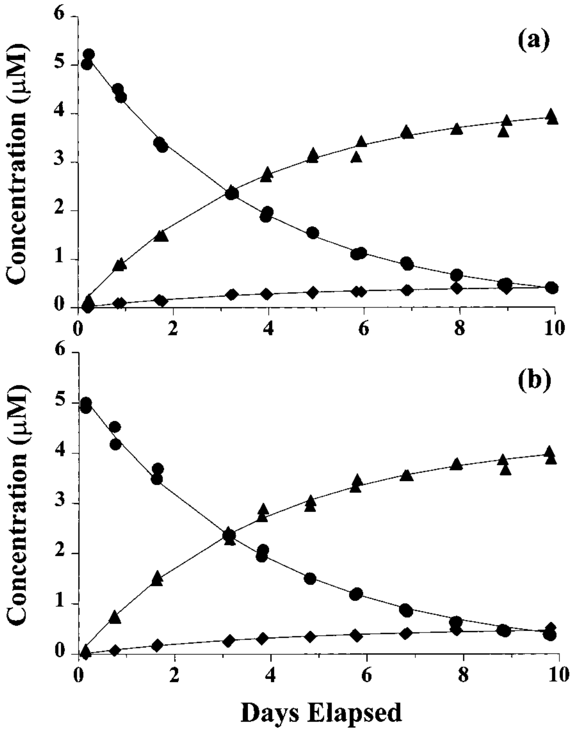
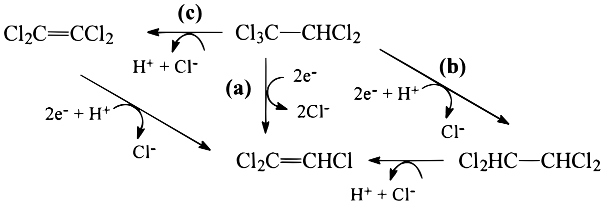


FIGURE 1. Transformation of pentachloroethane (●) to tetrachloroethylene (▲) and trichloroethylene (◆) in filter-sterilized (a) and unaltered (b) lake water samples. Solid lines represent model fits to data.

SCHEME 1



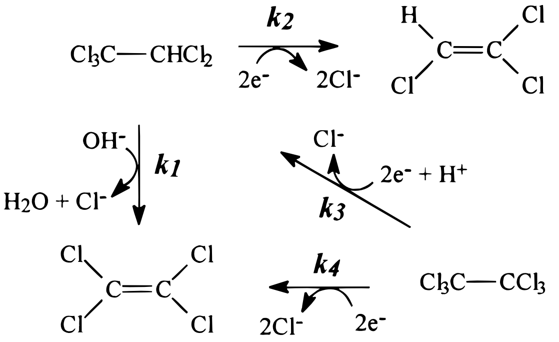
The degradation of pentachloroethane over time was modeled as a pseudo-first-order reaction with the solution:

$$[\mathrm{Cl_3C-CHCl_2}]_t = [\mathrm{Cl_3C{-}CHCl_2}]_\mathrm{o} \times \exp[-k_{\mathrm{obs}}t] \qquad (2)$$

where k_{obs} is the pseudo-first-order rate constant for pentachloroethane disappearance. Nonlinear least-squares analysis of eq 2 resulted in model fits to the pentachloroethane data shown in Figure 1, with k_{obs} values of 0.26 (±0.01) day^{-1} for both the unaltered and the filter-sterilized systems.

From the analytical results shown in Figure 1, a simple kinetic scheme was developed to model the transformation of pentachloroethane (Scheme 2). In this approach, the rate of appearance of tetrachloroethylene and trichloroethylene can be used to separate the contributions to k_{obs} that result from dehydrohalogenation (pathway 1) and reductive elimination (pathway 2). In solving the system of equations to obtain best-fit values of k_1 and k_2, it was assumed that all of the pertinent reactions were pseudo-first-order. The resulting model fits to the tetrachloroethylene and trichloroethylene data are pictured as the solid lines in Figure 1. No statistical differences were found in the resulting values of k_1 and k_2 between the filter-sterilized samples vs the unaltered lake water, indicating that abiotic reactions are responsible

SCHEME 2



for the observed transformations. Thus, values of k_1 and k_2 given in Table 2 represent averaged values.

Hexachloroethane Transformation in Lake Water. Hexachloroethane reduction proceeded over the course of days in filter-sterilized (Figure 2a) and unaltered (Figure 2b) lake water samples. Observed products were pentachloroethane, tetrachloroethylene, and trichloroethylene; no 1,1,2,2-tetrachloroethane was detected. A complete mass balance was not attained: mass balances were 71% in the unaltered lake water and 67% in the filter-sterilized water. Tetrachloroethylene was the most abundant product, accounting for approximately 70% of the initial hexachloroethane in the unaltered lake water and 62% in the filter-sterilized water after 10 days of reaction. Trichloroethylene and pentachloroethane were detected in smaller amounts and accounted for <1 and <2%, respectively, of the mass balance at this time in each system.

Overall disappearance rate constants were once again determined assuming that the parent compound underwent exponential decay; the resulting k_{obs} values were 0.33 (±0.03) day^{-1} for the unaltered water and 0.26 (± 0.02) day^{-1} for the filter-sterilized water. The reaction of hexachloroethane in the unaltered lake water was only slightly (1.3×) faster than that observed in the filter-sterilized water. This close correspondence of the k_{obs} values indicates that the bulk of the observed transformation (≥80%) in the unaltered water is abiotic in origin. Whether or not the remaining 20% is microbially mediated or whether it instead is promoted by nonbiological colloidal materials removed by the 0.2 μm filters cannot be determined from the available data.

In modeling the data, hexachloroethane was assumed to react either via hydrogenolysis to pentachloroethane (via pseudo-first-order rate constant k_3) or by reductive elimination to tetrachloroethylene (via k_4) (Scheme 2). Tetrachloroethylene was assumed to be formed by two concurrent pathways: via reductive elimination of hexachloroethane (given by k_4), and from the dehydrohalogenation of a pentachloroethane intermediate via k_1. Finally, it was assumed that all of the observed trichloroethylene resulted from reductive elimination of pentachloroethane via k_2. Results obtained from pentachloroethane experiments were used to constrain k_2, while k_1 was calculated from the product of k_{OH^-} (*25*) and lake water [OH$^-$] (see Discussion). The remaining rate constants k_3 and k_4 (Table 2) were determined through least-squares fitting of the data to numerically integrated solutions of the system of differential rate expressions. Model fits (or predictions, in the case of trichloroethylene) are shown as solid lines in Figure 2.

This modeling exercise demonstrated that at least 61% of the hexachloroethane transformation in both filter-sterilized and unaltered water samples proceeded via reductive elimination to tetrachloroethylene. The slight enhancement observed in the unaltered water relative to the results obtained in the filter-sterilized samples seems to be primarily directed toward this reaction, which increased k_4 values by a factor of approximately 1.3.

Kinetics of Sulfide and Polysulfide Reaction with Hexachloroethane. To assess whether reduced sulfur species (H_2S, HS^-, and S_n^{2-}) could play a direct role as reductants (as opposed to serving as bulk reductants of "mediator" species), second-order rate constants for reaction with hexachloroethane were needed. A few experiments in clean chemical systems were carried out by Roberts (*19*) to obtain preliminary estimates of these rate constants. Reaction rates were measured at neutral pH in the presence of H_2S species only (no polysulfides added) and at two different pH values containing varying amounts of polysulfides (computed according to eq 1). Details concerning these experiments have been summarized in ref 18.

Reaction rates obtained in the somewhat more extensive experiments conducted by Perlinger et al. (*18*) compare closely with the earlier work of Roberts (*19*). Perlinger et al. have combined both sets of data to provide estimates of second-order rate constants for reactions of hexachloroethane with H_2S, HS^-, and S_n^{2-} species of $k_{H_2S} \approx 1.1\ (\pm 0.5) \times 10^{-5}\ M^{-1}\ s^{-1}$, $k_{HS^-} \approx 1.2\ (\pm 0.7) \times 10^{-5}\ M^{-1}\ s^{-1}$, and $k_{S_n^{2-}}$ (expressed as an average for all polysulfide dianions) as 6.8 (±1.7) × $10^{-3}\ M^{-1}\ s^{-1}$, where uncertainties reflect 95% confidence limits. That is, polysulfides are approximately 600× as reactive as are hydrogen sulfide species.

Discussion

Mechanisms of Pentachloroethane Reaction in Sulfidic Lake Water. For any reaction, the contribution of any known environmental "reagent" to the total rate of disappearance can be quantified by comparing the relevant first- or pseudo-first-order rate constant for the process in question to the sum of the relevant rate constants, i.e., the k_{obs} value. Thus, for pentachloroethane, the observed rate constant can be expressed as

$$k_{obs} = k_{OH^-}[OH^-] + k_{H_2O} + \sum k_{red_i}[Red_i] + \ldots \qquad (4)$$

where k_{OH^-} is the second-order rate constant for the base-promoted dehydrohalogenation reaction, k_{H_2O} the (pseudo) first-order rate constant for the pH-independent component of hydrolysis, k_{red_i} are the second-order rate constants for any species *i* that reduce pentachloroethane to trichloroethylene, and [Red$_i$] is the concentration of each reductant.

The second-order rate constant for the base-promoted dehydrohalogenation of pentachloroethane is 27.3 $M^{-1}\ s^{-1}$ (*25*); multiplying this by [OH$^-$] for the lake water yields a predicted pseudo-first-order rate constant of 0.20 day^{-1}. This amounts to nearly 80% of the total pentachloroethane k_{obs}. The very close correspondence of the product k_{OH^-}[OH$^-$] to the model-fit pseudo-first-order rate constant for pentachloroethane dehydrohalogenation (k_1) in the lake water of 0.21 day^{-1} indicates that catalytic effects potentially introduced by dissolved or suspended species (microorganisms, inorganic particles) were insignificant. Note that, at the lake water pH, the contribution to hydrolysis involving reaction with the neutral species H_2O is negligible (*36*). At present, insufficient data are available to indicate the identity of the abiotic reductant(s) responsible for the additional 9% contribution to the rate constant pertaining to pentachloroethane removal through pathways involving reductive elimination to trichloroethylene.

Mechanisms of Hexachloroethane Reaction in Sulfidic Lake Water. In a similar fashion, the contribution of reactions with defined reduced sulfur species (polysulfides, hydrogen sulfide species) known to be present in the lake water to the total rate of hexachloroethane removal can be computed by comparing the quantity ($k_{H_2S}[H_2S] + k_{HS^-}[HS^-] + k_{S_n^{2-}}[\sum S_n^{2-}]$)

TABLE 2. Parameters Obtained from Kinetic Modeling of Lake Water Experiments According to Scheme 2[a]

parameter	pentachloroethane[b]	filter-sterilized hexachloroethane	unaltered hexachloroethane
pseudo-first-order rate constant (day^{-1})			
k_1	0.21 (± 0.01)	0.18[c]	0.18[c]
k_2	0.023 (± 0.003)	0.023[d]	0.023[d]
k_3	NA[e]	0.018 (± 0.008)	0.032 (± 0.010)
k_4	NA	0.16 (± 0.01)	0.21 (± 0.01)
R^2 of model to data set	0.999	0.996	0.994

[a] Values in parentheses represent 95% confidence limits. [b] Since no significant difference was found between rate constants in the unaltered and filter sterilized samples, the values reported for k_1 and k_2 represent averaged results. [c] Constrained to equal $k_{OH^-}[OH^-]$, with k_{OH^-} taken to equal the base-promoted dehydrohalogenation rate constant reported by ref 25. [d] Constrained to equal k_2 values obtained from lake water samples spiked with pentachloroethane. [e] NA = not applicable.

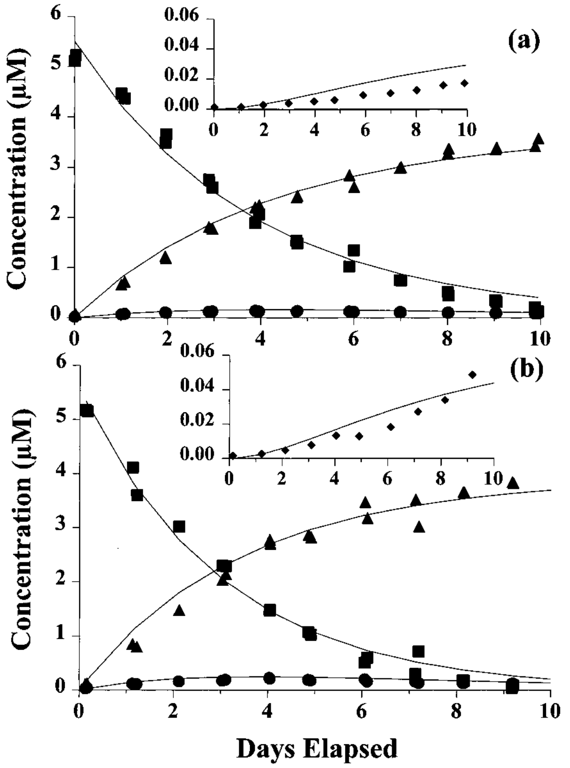


FIGURE 2. Transformation of hexachloroethane (■) to tetrachloroethylene (▲), pentachloroethane (●), and (inset) trichloroethylene (◆) in filter-sterilized (a) and unaltered (b) lake water samples. Solid lines represent model fits to experimental data with k_1 and k_2 values constrained as indicated in Table 2, or (in the case of trichloroethylene data) predicted concentrations.

to hexachloroethane k_{obs} values. The results indicate that approximately 17 (±4)% of the total hexachloroethane transformation observed in the unaltered anoxic lake water can be attributed to direct reaction with HS^-, H_2S, and S_n^{2-} species. In the filter-sterilized experiments, the contribution of these species to the overall reaction is approximately 21 (±4)%. Of these three reduced sulfur species, polysulfides play the predominant role. Despite their lesser abundance relative to H_2S and HS^-, their much greater reactivity renders them approximately 7 times as important in promoting hexachloroethane reaction.

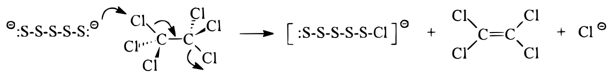
At present, little information is available concerning the mechanisms through which reduced sulfur species react with hexachloroethane. The production of tetrachloroethylene in the clean chemical experiments confirms that reaction with polysulfides takes place at least in part through a pathway involving reduction. Even though the mass balance in the clean chemical experiments is incomplete, we feel that some pathway involving reduction is likely to predominate. The inertness of hexachloroethane to hydrolysis (*36*) would tend to argue against the possibility that polysulfides could be playing the role of a nucleophile in an S_N2 attack on carbon, given what is known about the reactivity of polysulfides in other S_N2 reactions of alkyl halides (*9*, *11*).

In principle, reduced sulfur species could serve as one-electron reductants through a dissociative electron-transfer process:

$$^{-}{:}S\text{-}S\text{-}S\text{-}S\text{-}S{:}^{-} + Cl_3C\text{-}CCl_3 \rightarrow$$
$$^{-}{:}S\text{-}S\text{-}S\text{-}S\text{-}S^{\bullet} + [Cl_3C\text{-}CCl_3]^{\bullet -} \rightarrow Cl_3C\text{-}CCl_2^{\bullet} + Cl^-$$

The resulting pentachloroethyl radical could be further reduced to tetrachloroethylene, abstract a hydrogen atom from some suitable donor, couple with other radicals, or could add to unsaturated regions in the NOM present in the lake water. The coupling of the pentachloroethyl and polysulfide radicals that would result from an initial electron transfer step (possibly facilitated by the presence of a solvent "cage") would be expected to yield a sulfur-substituted product that would not have been amenable to analysis via the solvent extraction/GC method employed.

Alternatively, polysulfides could function as nucleophiles via what has been referred to as "nucleophilic elimination" (*37, 38*) to yield tetrachloroethylene plus an unstable sulfenyl halide. Such a reaction represents the group transfer of chlorine to the nucleophile, and thus could be envisioned as a two-electron transfer that does not involve a free radical intermediate:



The unstable sulfenyl halide would be expected to decompose rapidly to S(0) plus chloride ion. Numerous researchers in the past have found evidence that reduced sulfur species can promote reductive elimination through just such a nucleophilic pathway (e.g., *37–41*). Such studies have, however, generally been conducted in organic solvents and in clean systems that bear little relationship to complex natural aquatic environments. Whether the role of reduced sulfur species involves such a "nucleophilic elimination" mechanism requires further study.

In searching for clues concerning pathways through which hexachloroethane reacts with reduced sulfur species in the lake water, the extent to which pentachloroethane represents a reaction intermediate was of particular interest to this study. Previous work (*25*) had suggested that the pentachloroethyl carbanion was insufficiently stable to undergo significant protonation in aqueous solution, indicating that the appearance of pentachloroethane as a product of hexachloroethane reduction may be diagnostic of a free-radical pathway.

A pentachloroethyl radical might be expected to undergo significant trapping by scavengers present in sulfate-reducing environments. Thiols, in particular, are very effective radical scavengers, and serve as sources of extractable hydrogen atoms (*42*). For example, Hammond et al. (*43*) found that concentrations of *n*-butyl mercaptan of 0.16 M or greater were sufficient to intercept ~80% of the isobutyronitrile radicals obtained from the thermal decomposition of azobis(isobutyronitrile). The sulfidic, eutrophic lake water used in the present experiments should possess abundant free radical trapping agents (NOM, thiols, and H_2S) which are readily able to donate hydrogen atoms to a pentachloroethyl radical, thereby leading to pentachloroethane.

The modeling exercises indicated that about 7−10% of the overall hexachloroethane reaction occurred through a pentachloroethane intermediate, with the bulk of the hexachloroethane reduction circumventing such a route. If hexachloroethane reduction is in fact dominated by a free radical pathway, this poor yield may simply reflect a low trapping efficiency for $H^\bullet$ abstraction, possibly because of competition introduced by coupling of pentachloroethyl radicals with polysulfide radicals or addition of pentachloroethyl radicals to unsaturated sites in the NOM. Alternatively, this could reflect a pathway that does not involve a free radical intermediate, such as a nucleophilic elimination pathway. Additional studies will be required to assess whether reduction of *vic*-dihaloalkanes by reduced sulfur species proceeds via nucleophilic vs radical pathways.

The overall importance of polysulfides as reductants of anthropogenic contaminants depends on their abundance relative to other reductants. Even higher concentrations of polysulfides have been measured in anoxic estuarine and salt marsh waters than in Lower Mystic Lake water, potentially enabling polysulfides to play an important part elsewhere. Although Perlinger et al. (*18*) found that polysulfides were not significant reductants of hexachloroethane in relatively well-defined systems containing high (up to 450 μM) concentrations of mercaptojuglone (a model electron-transfer mediator), this does not necessarily denote a similarly negligible role for polysulfides in natural waters. Little is known about the concentrations or reactivity of electron-transfer mediators in sulfate-reducing environments, or the extent to which NOM in such environments possesses moieties structurally analagous to mercaptojuglone. Although the dominant pathway for hexachloroethane reaction in Lower Mystic Lake water may well represent reduction by some electron-transfer mediator, we nevertheless believe that polysulfide species merit further scrutiny as environmental "reagents" in complex natural systems.

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