

# Nucleophilic Substitution Reactions of Dihalomethanes with Hydrogen Sulfide Species

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■ Measurements of  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{BrCl}$ , and  $\text{CH}_2\text{Cl}_2$  reaction kinetics as a function of pH and temperature indicate that  $\text{HS}^-$ -promoted reactions exceed hydrolysis rates at  $\text{HS}^-$  concentrations greater than 2–17  $\mu\text{M}$ , well within ranges common in sulfate-reducing environments. Experiments suggest that polysulfide-mediated reaction rates may exceed  $\text{HS}^-$ -mediated rates in waters in equilibrium with orthorhombic  $\text{S}_8$  at pH values greater than 7.0. The Swain-Scott model of nucleophilic reactivity underestimates rates at which these dihalomethanes react with  $\text{HS}^-$ . For  $\text{CH}_2\text{Cl}_2$ , the observed reaction rate is 5 times the predicted rate; greater discrepancies are observed with the "softer" substrates  $\text{CH}_2\text{BrCl}$  and  $\text{CH}_2\text{Br}_2$ , for which ratios of  $k_{\text{obs}}/k_{\text{pred}}$  are approximately 10–30. Examination of reaction products by FT-IR, solid-state  $^{13}\text{C}$  NMR, GC-MS, and elemental analysis indicates the major product to be poly(thiomethylene), although minor amounts of dithiomethane were also observed. Published data suggest such thiols possess toxic properties. Reactions of dihalomethanes with  $\text{HS}^-$  may thus yield products of greater toxicological significance than the parent compounds.

## Introduction

Dihalomethanes are widely used as organic solvents, degreasing agents, and chemical intermediates. Owing to their popularity in industrial applications, they are ubiquitous pollutants in aquatic systems. Existing information suggests these compounds are only slowly transformed by abiotic processes under aerobic conditions. Estimated half-lives for reactions with water at pH 7, 25 °C, are 704, 44, and 183 years for  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{BrCl}$ , and  $\text{CH}_2\text{Br}_2$ , respectively (1), much greater than the corresponding values for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$ . These half-lives are believed to reflect bimolecular nucleophilic substitution ( $\text{S}_{\text{N}}2$ ) reactions, as dehydrohalogenation reactions do not occur readily for dihalomethanes (2), and reactivity trends are not consistent with an  $\text{S}_{\text{N}}1$  mechanism.

Under aerobic conditions, dihalomethanes are readily degraded by microorganisms or cell extracts thereof (3–14). In contrast, a number of studies have found dihalomethanes to be relatively stable in cultures of anaerobic microorganisms (15–18). If biological transformation is slow under anoxic conditions, abiotic  $\text{S}_{\text{N}}2$  pathways may be of considerable environmental significance, provided suitable nucleophiles exist.

One nucleophile of potential importance in anoxic systems is the bisulfide ion  $\text{HS}^-$ , produced by the microbially mediated dissimilatory reduction of sulfate. Total  $\text{H}_2\text{S}$  concentrations  $[(\text{H}_2\text{S})_{\text{T}}]$  as high as 470  $\mu\text{M}$  to 12 mM have been encountered in landfill-contaminated groundwater (19) and thermal springs and subsurface brines (20), and concentrations on the order of tens of micromolar are quite common. Several researchers have studied the reactions of hydrogen sulfide species with primary alkyl monohalides and *vic*-dihalides (21–24). These investigations have confirmed that hydrogen sulfide species can promote the

transformations of primary alkyl halides. Such reactions may be of considerable significance because of the potential toxicity of the organic sulfide reaction products. It is essential to obtain reliable estimates of reaction rates of halogenated organic contaminants with hydrogen sulfide species under environmental conditions in order to incorporate these processes into fate and hazard assessment models. One problem with previous studies is the absence of data such as mass balances or detailed kinetic measurements to substantiate that observed transformations are solely attributable to reactions with hydrogen sulfide species. Aqueous solutions of hydrogen sulfide are sensitive to oxygenation, and several partially oxidized sulfur species may be more reactive than the bisulfide ion  $\text{HS}^-$ . The products of dihalomethane reaction with these different species undoubtedly differ substantially in their toxicity and mobility in the environment. A major purpose of the present study was to extend previous work to investigate the reactions of hydrogen sulfide species with *gem*-dihalides. In so doing, we have taken pains to verify that our observed rates are for reactions solely with  $\text{HS}^-$ . We have also endeavored to characterize reaction products, both to confirm our proposed reaction mechanisms and to provide information required in assessing the toxicological significance of these reactions.

A final purpose of the present study was to examine the effect of alkyl halide structure on reactivity. The bisulfide ion  $\text{HS}^-$  is chemically analogous to the hydroxide ion  $\text{OH}^-$ ; reaction rates for the latter nucleophile are available from the literature. By comparing the reactivity of these two environmental reagents within a series of dihalomethanes, we can begin to assess the utility of models which have been proposed to explain structure-reactivity relationships.

## Materials and Methods

**Reagents.** Reaction kinetics were measured under pseudo-first-order conditions in solutions containing  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (Mallinckrodt);  $\text{HCl}$  (Mallinckrodt) was used to adjust the pH to the desired value and  $\text{NaCl}$  (Mallinckrodt) to adjust ionic strength to 0.05 equiv/L. When the reaction kinetics of  $\text{CH}_2\text{Br}_2$  and  $\text{CH}_2\text{BrCl}$  were measured, ratios of alkyl halide to hydrogen sulfide species were such that supplemental pH buffering was unnecessary. Additional buffering in the form of  $(\text{NH}_4)_2\text{HPO}_4$  (Mallinckrodt) was used for experiments with  $\text{CH}_2\text{Cl}_2$ , owing to the higher ratios of  $\text{CH}_2\text{Cl}_2$  to  $(\text{H}_2\text{S})_{\text{T}}$ . All aqueous solutions were prepared using high-purity (>15 M $\Omega$ /cm) deionized distilled water prepared with a Milli-Q water system (Millipore Corp., Bedford, MA).

Determinations of pH were performed at the appropriate temperature with an Orion Model SA 720 pH/ISE meter and an Orion Ross combination pH electrode. Bisulfide ion concentrations were determined from  $(\text{H}_2\text{S})_{\text{T}}$  and pH from the expression for the  $\text{pK}_{\text{a}}$  (at zero ionic strength) of  $\text{H}_2\text{S}$  as a function of temperature given in the review by Millero (25), correcting for ionic strength according to the expression  $K_{\text{a}}' = K_{\text{a}}\gamma_{\text{H}_2\text{S}}/\gamma_{\text{HS}^-}$ . Activity coefficients  $\gamma_{\text{HS}^-}$  for  $\text{HS}^-$  were estimated from the extended Debye-Hückel relationship, and activity coefficients  $\gamma_{\text{H}_2\text{S}}$

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for the neutral species  $\text{H}_2\text{S}$  were assumed equal to 1.

Stock solutions of  $\text{CH}_2\text{BrCl}$  (99%, Aldrich),  $\text{CH}_2\text{Br}_2$  (99+%, Aldrich), and  $\text{CH}_2\text{Cl}_2$  (99.99%; Omnisolv, EM Science) were prepared in methanol (99.9%; Omnisolv) for spiking experimental flasks. For most experiments with  $\text{CH}_2\text{BrCl}$  and  $\text{CH}_2\text{Br}_2$ ,  $\text{Cl}_2\text{C}=\text{CHCl}$  (Mallinckrodt) was included in the spiking solution to establish the integrity of our glass reaction vessels against losses of volatile compounds. Standards were prepared by diluting alkyl halides directly into hexane (85% *n*-hexane; Baker Capillary-Analyzed grade). All organic solvents were used as received without further purification. Gas chromatographic (GC) analysis indicated the hexane contained traces of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{BrCl}$ ; corrections were made by subtracting peak areas for these compounds in solvent blanks from peak areas for standards or samples.

Reagents used for measuring sulfite, thiosulfate, and polysulfides via reversed-phase high-pressure liquid chromatography (HPLC) included sodium acetate (Fisher), tetrabutylammonium hydrogen sulfate (>99%, Fluka), 2,2'-dithiobis(5-nitropyridine) (98%, Aldrich), and acetonitrile (HPLC grade, Fisher). Standards were prepared with  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (Mallinckrodt) and anhydrous  $\text{Na}_2\text{SO}_3$  (Mallinckrodt). Polysulfide solutions were prepared by adding excess  $\text{S}_8$  (sublimed, Mallinckrodt) to aqueous solutions containing hydrogen sulfide species.

Thiol products were methylated by adding aliquots of a solution containing  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (Fluka) and  $\text{CH}_3\text{I}$  (Mallinckrodt) to samples of the reaction media. Standards were prepared by diluting  $\text{H}_3\text{CSCH}_2\text{SCH}_3$  (99%, Aldrich) directly into  $\text{CH}_2\text{Cl}_2$ .

Reagents used for measuring formaldehyde included 2,4-pentanedione (acetylacetone) (99+%, Aldrich), ammonium acetate (99%, Aldrich), and glacial acetic acid (Mallinckrodt). Formaldehyde standards were prepared by diluting a 0.6 M stock solution prepared from commercial formaldehyde solution (Mallinckrodt). The stock formaldehyde solution was standardized by the sodium sulfite method described by Walker (26).

To obtain FT-IR spectra of potential reaction products, 1,3,5-trithiane (97%) was purchased from Aldrich and was purified via sublimation. Spectra were measured using KBr (Mallinckrodt) disks after drying the KBr at 100 °C.

**Hydrogen Sulfide Solutions.** All glassware used to prepare hydrogen sulfide solutions was cleaned by washing with alcoholic KOH to remove sulfur(0) species, followed by soaking in 4 N  $\text{HNO}_3$  and rinsing with Milli-Q water to remove trace metals. Stock sodium sulfide solutions (0.125–0.375 M) were prepared by rinsing clear crystals of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  with deoxygenated Milli-Q water to remove surface deposits of oxidized sulfur species, blotting them with a cellulose wipe, and transferring them (after weighing) to a closed system consisting of a volumetric flask, a Milli-Q water reservoir/gas washing bottle, a reagent storage flask/reaction vessel (consisting of a three-necked flask equipped with stopcock adapters), a tank of compressed argon, and ancillary tubing and stopcocks. The closed system could be purged with argon by adjusting stopcocks, and solutions could be prepared and transferred to reagent storage/reaction vessels using argon pressure to minimize contamination with atmospheric oxygen; details are given in Roberts (27). Sodium sulfide concentrations were determined by iodometric titration using a starch end point.

Anoxic stock solutions of HCl (0.19–0.54 M) were also prepared using this closed system, after first bubbling concentrated HCl with argon. HCl concentrations were measured via potentiometric titration against  $\text{Na}_2\text{CO}_3$ , with

the end point determined via the Gran function.

Anoxic working solutions of  $\text{HS}^-$  (1.5–22.5 mM) were prepared by adding weighed amounts of required salts [ $\text{NaCl}$  and  $(\text{NH}_4)_2\text{HPO}_4$ ] to the closed system before purging with argon. Aliquots of stock solutions of  $\text{Na}_2\text{S}$  and HCl were transferred from reagent storage flasks using glass syringes equipped with Teflon needles and nylon stopcocks; all manipulations were performed via stopcocks under a stream of argon gas. After being mixed, the working solutions were transferred under argon pressure to the reaction vessel, leaving no or very little headspace to prevent volatilization (generally <1-mL headspace to 300-mL total volume). Aliquots of the excess working solution were then removed under argon pressure for measurement of pH and to check total hydrogen sulfide concentrations via iodometric titration.

**Kinetic Experiments.** Vessels used for studying rates of  $\text{CH}_2\text{BrCl}$  and  $\text{CH}_2\text{Br}_2$  reaction were wrapped in several layers of black plastic to minimize exposure to light and were placed in a water bath to reach thermal equilibrium at  $25.01 \pm 0.02$  or  $35.00 \pm 0.02$  °C. Flasks were then spiked (under a stream of argon gas) with 50- $\mu\text{L}$  aliquots of a methanol solution containing  $\text{CH}_2\text{BrCl}$ ,  $\text{CH}_2\text{Br}_2$ , and  $\text{Cl}_2\text{C}=\text{CHCl}$  to give initial concentrations of approximately 17  $\mu\text{M}$   $\text{CH}_2\text{BrCl}$ , 5  $\mu\text{M}$   $\text{CH}_2\text{Br}_2$ , and 19  $\mu\text{M}$   $\text{Cl}_2\text{C}=\text{CHCl}$ . After an initial mixing period and sampling, reaction vessels were returned to the water baths for incubation. At 1- or 2-day intervals, 100- $\mu\text{L}$  aliquots were removed (under argon) via a glass syringe and were extracted with 1 mL of hexane for analysis via GC.

Because of the relative insensitivity of our analytical method for  $\text{CH}_2\text{Cl}_2$ , a somewhat different technique was adopted for investigating its reaction rates. After working solutions were transferred to reagent storage flasks, 20-mL aliquots were removed using a Teflon needle connected to an all-glass syringe containing several glass beads to aid in mixing. The syringes were spiked with a 5- $\mu\text{L}$  aliquot of a methanol solution containing  $\text{CH}_2\text{Cl}_2$  to give initial concentrations of 150  $\mu\text{M}$ , and after mixing, the contents were transferred under argon to 10-mL (nominal volume) glass ampules (type I borosilicate glass, Wheaton) that were sealed with a minimum amount of headspace ( $\approx 0.5$  mL of headspace to 17 mL of solution). The ampules were incubated in a water bath at either  $50.0 \pm 0.2$  or  $63.9 \pm 0.6$  °C. Ampules were periodically sacrificed for analysis by removing them from the water bath, chilling them to quench the reaction, and extracting 0.75-mL aliquots with 1 mL of hexane for analysis via GC. An experiment conducted with  $\text{CH}_2\text{Br}_2$  via this ampule technique yielded a rate constant which was not significantly different from rates obtained from incubations conducted in three-necked glass reaction vessels.

Rate constants were obtained by performing a linear regression of  $\ln$  concentration vs time. For each dihalomethane, some experiments were conducted at each temperature over sufficient time (>3–4 half-lives) to verify clean pseudo-first-order kinetics.

**Gas Chromatography.** GC analyses were performed with a Carlo-Erba HRGC 5160 unit equipped with a cold on-column injector, a 30 m  $\times$  0.32 mm i.d. thick film (5- $\mu\text{m}$   $\text{Rt}_x$ -1 cross-linked 100% dimethylpolysiloxane stationary phase) fused-silica capillary column (Restek Corp., Bellefonte, PA), and a  $^{63}\text{Ni}$  electron capture detector. Concentrations were determined by comparing peak areas for samples to those measured for external standards (after correction for traces of contamination in solvent blanks). Because the detector response was nonlinear, standards were analyzed each day, generally at five or six concen-

trations spanning the ranges measured in the samples, and a calibration curve was obtained by fitting the responses to a curve of the form (area) =  $a(\text{picomoles})^b$ . Multiple injections of standards indicated that this GC technique provided highly reproducible results (typically  $\leq 2\text{--}3\%$  relative standard deviation).

**Analysis of Reduced Sulfur Species (Sulfite, Thiosulfate, Polysulfides).** At the end of the incubation periods, sulfite and thiosulfate concentrations were determined in several samples containing 4.5 mM  $(\text{H}_2\text{S})_{\text{T}}$ , pH 7.2–8.4, by a modification of the HPLC method described by Valravamurthy and Mopper (28). We used an HPLC system consisting of a Waters 501 HPLC pump with a Waters 484 tunable absorbance detector and a reversed-phase  $\text{C}_{18}$  column (3.9 mm  $\times$  300 mm) with a 4- $\mu\text{M}$  packing (Novapak, Waters). Separations were obtained with isocratic elution with a 60% aqueous buffer consisting of 0.05 M sodium acetate and 7.5 mM tetrabutylammonium hydrogen sulfate (pH adjusted to  $3.5 \pm 0.05$  with HCl) and 40% acetonitrile.

We also attempted to determine polysulfide concentrations in the same experimental media by converting polysulfide sulfur(0) [equivalent to  $\sum (n-1)(\text{S}_n^{2-} + \text{HS}_n^-)$ ] to thiosulfate via reaction with sulfite as described by Luther et al. (29), carrying out the reaction in 10-mL glass ampules. Results indicated polysulfide S(0) concentrations of 3.8–4.0 mM, which represents a substantial fraction of the sulfur initially present (84–89%). We do not believe this accurately reflects the polysulfide concentrations present in the samples. Spectrophotometric scans of underivatized samples in the UV–visible range (200–800 nm) failed to indicate any absorbance that would be expected of polysulfides at this concentration (30). A positive interference in our polysulfide measurements from hydrogen sulfide species could result from  $\text{H}_2\text{S}$  oxygenation stemming from limitations of our ampule filling or sealing technique. Alternatively, a positive interference could be produced by reaction of  $\text{H}_2\text{S}$  species with sulfite; reactions of hydrogen sulfide species in aqueous solutions of sulfur dioxide have been reported to result in formation of elemental sulfur, polythionates, thiosulfate, and dithionate, depending on reaction conditions (31).

**Solid Reaction Product Studies.** A preliminary product study was conducted in a pH 6.8 solution containing 0.15 M  $(\text{H}_2\text{S})_{\text{T}}$  and 5 mM  $\text{CH}_2\text{Br}_2$ . After 2 weeks of incubation at 35 °C, the resulting precipitate was transferred to a centrifuge tube and was centrifuged and rinsed five times with deoxygenated Milli-Q water. Acetone was then added to facilitate removal of residual water, and the product was dried under a stream of argon gas over a warm (35–40 °C) water bath. Attempts were made to recrystallize the reaction product with a 1:3 benzene–dioxane mixture, which earlier studies had indicated worked well for the cyclic trisulfide 1,3,5-trithiane. The reaction product, however, exhibited at best limited solubility in this solvent mixture, nor was it appreciably soluble in benzene, dioxane, *n*-pentane, cyclohexane, acetone, isobutyl alcohol, chlorobenzene, toluene, nitromethane, dimethyl sulfoxide, dimethyl sulfide, tetrahydrofuran, carbon disulfide, or dimethylformamide. Attempts were made to identify this product via combined gas chromatography–mass spectrometry (GC–MS) by analyzing a suspension in benzene, but either it was too insoluble or it did not chromatograph well, because chromatograms failed to reveal anything other than traces of a compound with major ions at  $m/e$  124 (100), 78 (49), and 45 (35) and isotope peaks suggestive of an empirical formula of  $\text{C}_2\text{H}_4\text{S}_3$ ; this may reflect the oxidation product of the dithiomethane

dimer  $\text{HSCH}_2\text{SCH}_2\text{SH}$ . In contrast, GC–MS analysis of a benzene solution of the cyclic trimer 1,3,5-trithiane yielded a sharp peak with a spectrum consistent with published mass spectra.

Subsequent product studies were conducted using a solution containing 0.15 M  $(\text{H}_2\text{S})_{\text{T}}$  at pH 7.6, spiked with  $\text{CH}_2\text{Br}_2$  to give an initial concentration of 0.01 M. A parallel study was conducted with a 0.15 M  $(\text{H}_2\text{S})_{\text{T}}$ , pH 7.6, solution spiked with commercial formaldehyde to give an initial concentration of 0.01 M. Flasks were incubated at 35 °C for 1 week. The sample spiked with formaldehyde became turbid after 1 h, while no evidence of precipitate formation was observed in the sample spiked with  $\text{CH}_2\text{Br}_2$  until the following morning. Over time, a white flocculent precipitate developed in both flasks. After 1 week, the contents of each flask were vacuum-filtered in a Büchner funnel through filter paper (Schleicher & Schuell No. 595). Filters were rinsed with 125 mL of hot Milli-Q water, followed by 60 mL of ethanol. After drying, a total of 0.27 g of product was obtained from the sample spiked with formaldehyde, and 0.23 g of product was obtained from the sample spiked with  $\text{CH}_2\text{Br}_2$ . Actual precipitate yields were undoubtedly greater, as part of the product in each case broke through or around the filter.

A sample of the  $\text{CH}_2\text{Br}_2$  reaction product was sent to Schwarzkopf Microanalytical Laboratory (Woodside, NY) for elemental analysis and melting point determination. FT-IR spectra of both reaction products were obtained (using KBr disks, and correcting for background absorbance from traces of water still present in the KBr) on a Mattson Cygnus 100 FT-IR instrument that was purged with dry air. A solid-state  $^{13}\text{C}$  NMR spectrum of the  $\text{CH}_2\text{Br}_2$  reaction product was recorded on an IBM NR/200 AF (4.7 T) spectrometer operating at 50.3 MHz using a cross-polarization pulse sequence and dipolar decoupling in conjunction with magic angle spinning. The sample was packed into an aluminum oxide rotor and spun at ca. 3.9 kHz. A cross-polarization contact time of 1 ms was used, with a 5.0- $\mu\text{s}$  90° proton pulse and a 3.0-s recycle time. Spectra were referenced to the methyl resonance of *p*-di-*tert*-butylbenzene (31.0 ppm from TMS). For purposes of comparison, spectra were also recorded of unrecrystallized 1,3,5-trithiane.

**Dissolved-Phase Product Studies.** A product study at a lower initial  $\text{CH}_2\text{Br}_2$  concentration (75  $\mu\text{M}$ ) was conducted with a solution containing 5 mM  $(\text{H}_2\text{S})_{\text{T}}$ , pH 8.15, and ionic strength 0.05 equiv/L (adjusted with NaCl). Aliquots of this solution were transferred to 10-mL ampules and were incubated at 35 °C. Ampules were sacrificed each day, and a 4-mL aliquot was transferred via syringe to a second 10-mL ampule containing 9.5 mL of an anoxic aqueous solution consisting of 0.0125 M  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and 0.01 M  $\text{CH}_3\text{I}$  in order to methylate any thiols present. A 100- $\mu\text{L}$  aliquot of the remaining solution from the first ampule was also extracted with a 1-mL sample of hexane for GC analysis of  $\text{CH}_2\text{Br}_2$ . Methylation was carried out by incubating the ampule containing the reaction mixture at 67 °C for 1 h. After being cooled to room temperature, 10 mL of the reaction mixture was extracted with 1 mL of  $\text{CH}_2\text{Cl}_2$  containing 1,1,1,2-tetrachloroethane as an internal standard for analysis via GC–MS. Tests extracting aqueous solutions of authentic  $\text{H}_3\text{CSCH}_2\text{SCH}_3$  with  $\text{CH}_2\text{Cl}_2$  at this solvent to water ratio indicated good extraction efficiencies (>95% based on GC–MS analysis), and tests of this methylation procedure using anoxic solutions of 1,2-ethanedithiol (99%, Aldrich) in a 5 mM  $(\text{H}_2\text{S})_{\text{T}}$  matrix resulted in good yields [78–103%, based on GC–MS total ion chromatogram using bis-

(methylthio)methane as an external standard].

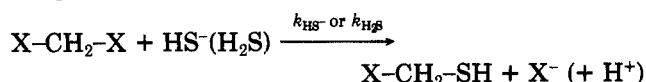
A second set of low initial  $\text{CH}_2\text{Br}_2$  concentration product studies was conducted to examine whether a significant amount of formaldehyde was produced. At the completion of time courses, selected samples that had been spiked with  $17 \mu\text{M}$   $\text{CH}_2\text{BrCl}$  plus  $5 \mu\text{M}$   $\text{CH}_2\text{Br}_2$  were assayed for formaldehyde. Measurements were performed via a modification of the spectrofluorometric method described by Belman (32). Aliquots (3 mL) of a reagent containing 2 M ammonium acetate, 0.05 M acetic acid, and 0.02 M acetylacetone were transferred to 5-mL glass ampules. An equal volume of a formaldehyde standard solution (containing 1.5–24  $\mu\text{M}$  formaldehyde) or a sample was added to the ampule, which was sealed under argon and incubated for 1 h at  $37^\circ\text{C}$ . After cooling to room temperature, fluorescence measurements were conducted on a Perkin-Elmer LS-5 fluorescence spectrophotometer at an excitation wavelength of 409 nm (slit width 3 nm) and an emission wavelength of 510 nm (slit width 5 nm). Absorbance readings at 409 and 510 nm were recorded on a Beckman DU-7 spectrophotometer to correct for the inner-filter effect (33). The detection limit for this method is approximately  $1.5 \mu\text{M}$  (based on an absorbance reading equal to twice the blank). Tests conducted by spiking a 15 mM  $(\text{H}_2\text{S})_{\text{T}}$ , pH 7, solution with formaldehyde and immediately sealing it in an ampule with acetylacetone reagent indicated that  $\text{H}_2\text{S}$  does not significantly interfere with the analysis.

**GC-MS Analyses.** GC-MS analyses of benzene suspensions of  $\text{CH}_2\text{Br}_2$  solid reaction products, of benzene solutions of 1,3,5-trithiane, and of  $\text{CH}_2\text{Cl}_2$  extracts obtained from the product methylation experiment, were conducted with a Hewlett-Packard benchtop gas chromatograph-mass spectrometer (Model 5995b, modified as described by ref 34) equipped with a Teknivent Vector/One controller/data system. Separations were achieved with a 30-m, thin-film ( $0.25 \mu\text{m}$ ) fused-silica capillary column with a nonpolar DB-5 cross-linked phase (J&W Scientific, Folsom, CA). Helium was used as a carrier gas. The mass spectra were recorded under electron impact ionization at 70 eV. For the analyses of the benzene extracts, ions  $m/e$  30–31 and 35–275 were monitored, while for the methylation experiment, masses were acquired from  $m/e$  45–160.

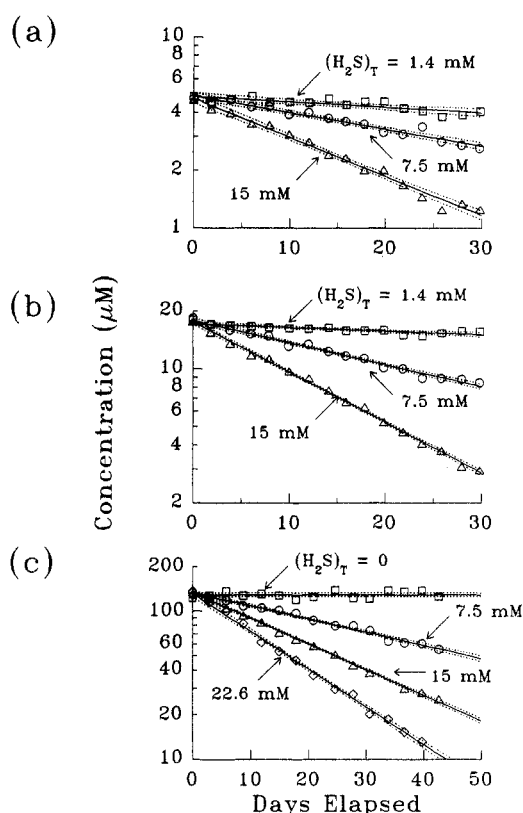
## Results

**Reaction Kinetics.** Example results of our experiments are shown in Figure 1. As indicated by the good linearity of the plots of log concentration vs time, reaction rates display pseudo-first-order kinetics. There is no evidence of any downward curvature of the experimental data that might result from reactions with other sulfur species potentially formed during the course of an experiment, such as organic thiol products of dihalomethane reactions or hydrogen sulfide oxidation products (such as sulfite, thiosulfate, or polysulfides). Nor is there any evidence of upward curvature that might result from losses of volatile hydrogen sulfide species from solution. Details of the solution compositions and pseudo-first-order rate constants obtained in each experiment are provided in Roberts (27).

At a given pH, the results in Figure 1 indicate that reaction rates are clearly dependent on  $(\text{H}_2\text{S})_{\text{T}}$ . This is consistent with an initial, rate-limiting step involving nucleophilic attack of the dihalomethane by  $\text{HS}^-$  (or  $\text{H}_2\text{S}$ ):



If the combined effects of  $(\text{H}_2\text{S})_{\text{T}}$  and pH on reaction kinetics are investigated, the relevant rate constants for



**Figure 1.** Example time courses showing dihalomethane transformation at different  $(\text{H}_2\text{S})_{\text{T}}$  concentrations and constant temperature and approximately constant pH: (a) reaction of  $\text{CH}_2\text{Br}_2$  at pH 7,  $25^\circ\text{C}$ ; (b) reaction of  $\text{CH}_2\text{BrCl}$  at pH 7,  $25^\circ\text{C}$ ; (c) reaction of  $\text{CH}_2\text{Cl}_2$  at pH 8,  $50^\circ\text{C}$ .

the  $\text{H}_2\text{S}$ -promoted and the  $\text{HS}^-$ -promoted reactions can be extracted. The overall rate constant for the reaction of a dihalomethane with hydrogen sulfide species can be given by the expression (neglecting reaction with  $\text{S}^{2-}$ )

$$k_{\text{obs}} = \frac{-1}{(\text{CH}_2\text{X}_2)} \frac{d(\text{CH}_2\text{X}_2)}{dt} = k_{\text{H}_2\text{S}}(\text{H}_2\text{S}) + k_{\text{HS}^-}(\text{HS}^-) \quad (1)$$

Substituting expressions for  $\text{H}_2\text{S}$  and  $\text{HS}^-$  concentrations as a function of  $(\text{H}_2\text{S})_{\text{T}}$

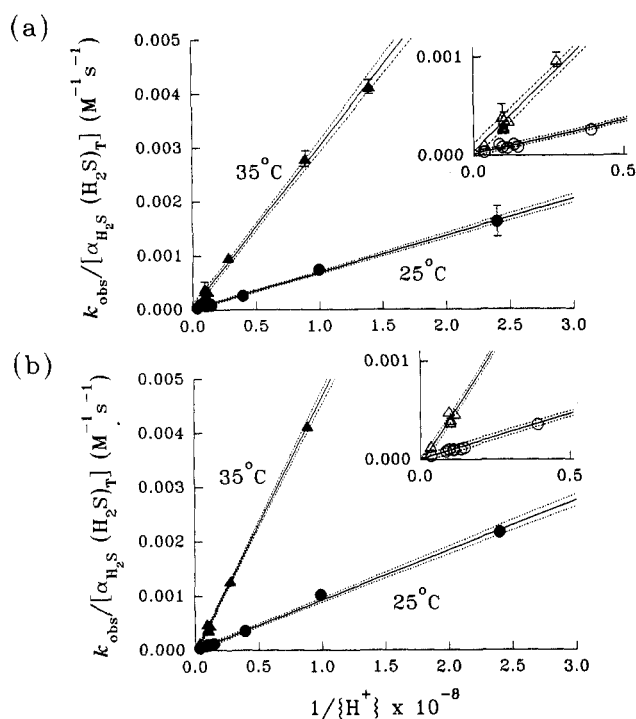
$$\alpha_{\text{H}_2\text{S}} = (\text{H}_2\text{S})/(\text{H}_2\text{S})_{\text{T}} = [1 + K_a'/[\text{H}^+]]^{-1} \quad (2)$$

$$\alpha_{\text{HS}^-} = (\text{HS}^-)/(\text{H}_2\text{S})_{\text{T}} = [1 + \{\text{H}^+\}/K_a']^{-1} \quad (3)$$

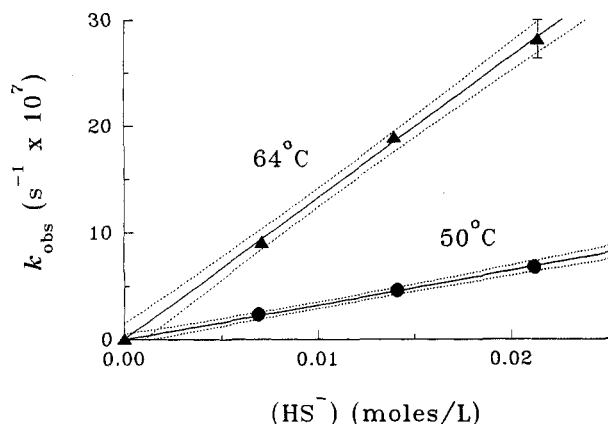
where  $K_a'$ , the apparent ionization constant, is ca.  $10^{-7}$  (25). After rearranging, the observed rate constant can be given in terms of  $(\text{H}_2\text{S})_{\text{T}}$  and  $[\text{H}^+]$  as

$$k_{\text{obs}}/[\alpha_{\text{H}_2\text{S}}(\text{H}_2\text{S})_{\text{T}}] = k_{\text{H}_2\text{S}} + k_{\text{HS}^-}K_a'/[\text{H}^+] \quad (4)$$

Plots of  $k_{\text{obs}}/[\alpha_{\text{H}_2\text{S}}(\text{H}_2\text{S})_{\text{T}}]$  vs  $1/[\text{H}^+]$  are given for  $\text{CH}_2\text{Br}_2$  and  $\text{CH}_2\text{BrCl}$ , respectively, in parts a and b of Figure 2. The slope at each temperature is equivalent to the product of the second-order rate constant  $k_{\text{HS}^-}$  and the apparent ionization constant  $K_a'$ , while the intercept is equivalent to the second-order rate constant  $k_{\text{H}_2\text{S}}$ . The intercepts of the fits are not significantly different from 0, indicating that the  $\text{H}_2\text{S}$ -promoted reaction occurs at a rate too slow to measure in our experiments. If the relative reactivity of  $\text{H}_2\text{S}:\text{HS}^-$  in  $\text{S}_{\text{N}}2$  reactions of dihalomethanes parallels that of  $\text{H}_2\text{O}:\text{OH}^-$  with chloromethane and bromomethane [ $1:10^{4.2}$ – $10^{4.3}$  (35–37)], then  $\text{H}_2\text{S}$  (as distinct from  $\text{HS}^-$ ), with its limited aqueous solubility [0.1 M at 1 atm  $P_{\text{H}_2\text{S}}$  (25)], is unlikely to compete effectively with  $\text{H}_2\text{O}$  or to be of importance as an environmental reagent in nucleophilic substitution reactions.



**Figure 2.** Plot of  $k_{\text{obs}}/[\alpha_{\text{H}_2\text{S}}(\text{H}_2\text{S})_T]$  vs  $1/[\text{H}^+]$ : (a) for reactions of  $\text{CH}_2\text{Br}_2$  and (b) for reactions of  $\text{CH}_2\text{BrCl}$ . Insets represent blowups of lower left portions of graphs. Dashed lines reflect 95% confidence intervals obtained from linear regressions.



**Figure 3.** Plot of pseudo-first-order rate constant  $k_{\text{obs}}$  vs  $[\text{HS}^-]$  for reactions of dichloromethane. Error bars correspond to 95% confidence limits in  $k_{\text{obs}}$  values; dashed lines reflect 95% confidence limits obtained in linear regression.

Owing to concerns that significant amounts of the volatile species  $\text{H}_2\text{S}$  could be lost at neutral pH to the headspace in the reagent storage vessel during ampule filling, we did not investigate the effect of pH on the kinetics of  $\text{CH}_2\text{Cl}_2$  reaction. Rate constants for  $\text{CH}_2\text{Cl}_2$  reaction as a function of  $\text{HS}^-$  concentration and temperature are shown in Figure 3. Under the conditions we investigated, the rates of the  $\text{OH}^-$ - and the  $\text{H}_2\text{O}$ -promoted reactions are both negligible (38), and so no correction is required for concurrent hydrolysis; rates observed in the absence of  $\text{HS}^-$  were not significantly different from 0.

Values of  $k_{\text{HS}^-}$  were calculated from  $k_{\text{obs}}$  values by performing regressions on  $k_{\text{obs}}$  vs  $[\text{HS}^-]$ , neglecting any contribution from the  $\text{H}_2\text{S}$ -promoted reaction. Values of  $k_{\text{obs}}$  were weighted according to their estimated uncertainty in performing these regressions. The results for  $\text{CH}_2\text{Br}_2$  and  $\text{CH}_2\text{BrCl}$  are given in Table I, along with estimates of the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the  $\text{HS}^-$ -promoted reaction and  $k_{\text{OH}^-}$  values obtained from the literature.

**Table I. Rate Constants and Activation Parameters for Dibromomethane and Bromochloromethane**

	rate constant ( $\text{M}^{-1} \text{s}^{-1}$ )		$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger(25^\circ \text{C})$ (J/(mol deg))
	25 °C	35 °C		
$\text{CH}_2\text{Br}_2$				
$k_{\text{HS}^-}$	$5.25 (\pm 0.34) \times 10^{-6}$	$1.74 (\pm 0.10) \times 10^{-4}$	89.0	-28
$k_{\text{OH}^-}$ <sup>a</sup>	$6.1 (\pm 0.6) \times 10^{-7}$			
$\text{CH}_2\text{BrCl}$				
$k_{\text{HS}^-}$	$7.29 (\pm 0.46) \times 10^{-6}$	$2.42 (\pm 0.20) \times 10^{-4}$	89.2	-25
$k_{\text{OH}^-}$ <sup>a</sup>	$2.5 (\pm 0.3) \times 10^{-6}$			

<sup>a</sup> Rates measured in 66.7% dioxane–water at 35.7 °C; data from ref 39.

**Table II. Rate Constants and Activation Parameters for Dichloromethane**

	rate const ( $\text{M}^{-1} \text{s}^{-1}$ )		$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger(50^\circ \text{C})$ (J/(mol deg))
	50 °C	64 °C		
$k_{\text{HS}^-}$	$3.27 (\pm 0.14) \times 10^{-6}$	$1.35 (\pm 0.05) \times 10^{-4}$	88.9	-56
$k_{\text{OH}^-}$ <sup>a</sup>	$6.8 \times 10^{-7}$	$3.7 \times 10^{-6}$	107.0	-32
$k_{\text{H}_2\text{O}}$ <sup>a</sup>	$3.0 \times 10^{-11}$	$2.0 \times 10^{-10}$	119.3	-78

<sup>a</sup> Rate constants from expressions for log  $k$  as a function of temperature given by ref 38; activation parameters estimated from calculated second-order rate constants at 50 and 64 °C.

Similarly, Table II summarizes results obtained for  $\text{CH}_2\text{Cl}_2$ . Activation enthalpies are very similar for all three dihalomethanes despite differences in dissociation energies of C–Br and C–Cl bonds. The  $\Delta H^\ddagger$  value obtained for  $\text{CH}_2\text{Cl}_2$  reaction with  $\text{HS}^-$  is substantially smaller than the values calculated for its reactions with the “harder” nucleophiles  $\text{H}_2\text{O}$  and  $\text{OH}^-$ . The  $\Delta S^\ddagger$  value for  $\text{CH}_2\text{Cl}_2$  reaction with  $\text{HS}^-$  appears more negative than the corresponding values for the brominated dihalomethanes; this result is counter to what would be anticipated if activation entropy were dominated by steric factors.

#### Potential Reactions with Other Sulfur Species.

Any system containing hydrogen sulfide species may also contain a host of more oxidized sulfur species. Elemental sulfur ( $\text{S}_8$ ), sulfite ( $\text{SO}_3^{2-}$ ) [and its conjugate acid species bisulfite ( $\text{HSO}_3^-$ )], thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ), tetrathionate ( $\text{S}_4\text{O}_6^{2-}$ ), sulfate ( $\text{SO}_4^{2-}$ ), and polysulfide ions (predominately  $\text{S}_n^{2-}$ ,  $n = 4-6$ ) have all been reported as products of the reaction of hydrogen sulfide species with  $\text{O}_2$  (40–42). The interrelationships between these species can be complex and are still not fully understood. Elemental sulfur combines readily (30, 43) with  $\text{HS}^-$  to form polysulfides, especially at high pH. In aqueous solution, polysulfide ions are known to disproportionate rapidly [ca.  $10^{-2} \text{s}$  (43, 44)] to an equilibrium distribution of polysulfides. Hence, any system containing any given polysulfide will inevitably contain other polysulfide species. Although polysulfides should disproportionate to thiosulfate and bisulfide, the rate at which this occurs has been shown to be slow at 25 °C (45), and thus polysulfide solutions are kinetically stable at room temperature, at least within the time frame of 1 year or so (46).

Evidence suggests several of these partially oxidized sulfur species can be at least as reactive in  $\text{S}_\text{N}2$  reactions as  $\text{HS}^-$ . Elemental sulfur and  $\text{S}_4\text{O}_6^{2-}$  characteristically behave as electrophiles and so would not be expected to interact with dihalomethanes. Conversely,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{S}_n^{2-}$  are all powerful nucleophiles and, if present in appreciable quantities in our reaction media, could con-

tribute to observed rates. An estimate of the relative reactivity of various sulfur species can be obtained from their nucleophilicity constants in the Swain-Scott expression (47):

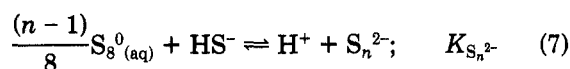
$$k_{\text{nuc}}/k_{\text{H}_2\text{O}} = 10^{sn} \quad (5)$$

where  $s$  is a substrate constant and  $n$  reflects the nucleophilicity of the species in question. Nucleophilicity parameters for sulfur species given by Wells (48) for reactions in water and aqueous organic solvents are  $n_{\text{SO}_3^{2-}} = 2.5$ ,  $n_{\text{HS}^-} = 5.1$ ,  $n_{\text{SO}_3^{2-}} = 5.1$ , and  $n_{\text{S}_2\text{O}_3^{2-}} = 5.35$ . According to this model, the relative reactivity of different sulfur species with substrates having  $s$  values of 1 would be expected to follow the ratio  $k_{\text{SO}_3^{2-}}:k_{\text{HS}^-}:k_{\text{SO}_3^{2-}}:k_{\text{S}_2\text{O}_3^{2-}}$  of  $2.5 \times 10^{-3}:1:1:1.8$ . Haag and Mill (23) measured reaction rates of a variety of sulfur nucleophiles with hexyl bromide in aqueous solution and found relative reactivities  $k_{\text{HS}^-}:k_{\text{SO}_3^{2-}}:k_{\text{S}_2\text{O}_3^{2-}}:k_{\text{S}_n^{2-}}$  of 1:0.97:0.5:60. That is,  $\text{SO}_3^{2-}$  is approximately as reactive as  $\text{HS}^-$ , while  $\text{S}_2\text{O}_3^{2-}$  is somewhat less reactive and  $\text{S}_n^{2-}$  is substantially more reactive. The polysulfide rate constants reported by Haag and Mill represent apparent rate constants based on the total amount of polysulfide present and do not indicate the reactivity of individual polysulfide species.

According to these estimates of relative reactivity, the  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_3^{2-}$  concentrations we measured in our reaction media [ $(\text{H}_2\text{S})_T:\text{S}_2\text{O}_3^{2-}:\text{SO}_3^{2-} \approx 1:0.01:0$ ;  $(\text{HS}^-) \geq 0.3(\text{H}_2\text{S})_T$ ] are too small to contribute significantly to observed rates. Difficulties in direct measurement of polysulfide ions in our experiments complicate similar arguments for polysulfides, whose molar absorptivities (30) are too low to allow them to be measured spectrophotometrically at levels at which they might be kinetically competent. By measuring reaction rates as a function of pH, however, we can show that they are unlikely to have contributed to rates observed in our experiments. The good linearity of the results shown in Figure 2 actually indicates that polysulfide-mediated reactions are not significant in our experimental media. This becomes apparent if expressions for polysulfide-mediated reactions are incorporated into the expression for the observed rate constant:

$$k_{\text{obs}} = k_{\text{HS}^-}(\text{HS}^-) + \sum [k_{\text{S}_n^{2-}}(\text{S}_n^{2-})] \quad (6)$$

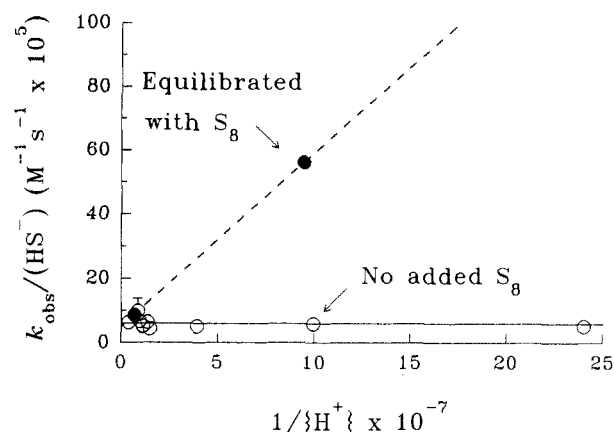
Equation 6 neglects (for simplicity) reactions with the monoprotonated species  $\text{HS}_n^-$ , which are less abundant and in all probability less reactive than their conjugate base species, and it also neglects reactions with the neutral species  $\text{H}_2\text{S}$  and  $\text{H}_2\text{S}_n$ . If expressions for polysulfide formation are written in terms of dissolved  $\text{S}_8^{0(\text{aq})}$  rather than the more conventional crystalline form of elemental sulfur



and the results substituted into eq 6, the observed rate constant in the presence of polysulfides (regardless of their degree of saturation) can be expressed as

$$k_{\text{obs}}/(\text{HS}^-) = k_{\text{HS}^-} + \{\text{H}^+\}^{-1} \sum [k_{\text{S}_n^{2-}} K_{\text{S}_n^{2-}} (\text{S}_8^{0(\text{aq})})^{(n-1)/8}] \quad (8)$$

A plot of  $k_{\text{obs}}/(\text{HS}^-)$  vs  $1/\{\text{H}^+\}$  for our experiments with  $\text{CH}_2\text{Br}_2$  at 25 °C is shown in Figure 4. For purposes of comparison, Figure 4 also indicates results we obtained in solutions saturated with elemental sulfur, for which  $\text{HS}^-$  values were estimated from measured pH, known  $\text{S}(-\text{II})_T$ , and polysulfide equilibrium constants reported by Boulègue and Michard (49), neglecting ionic strength corrections for polysulfide species. Details of these and other experiments with polysulfides are presented in

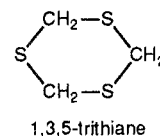


**Figure 4.** Plot of  $k_{\text{obs}}/(\text{HS}^-)$  vs  $1/\{\text{H}^+\}$  for reaction of dibromomethane at 25 °C. Open symbols indicate systems with no added  $\text{S}_8$ ; solid symbols indicate solutions equilibrated with elemental sulfur to produce polysulfides.

Roberts (27). As indicated by eq 8,  $k_{\text{obs}}/(\text{HS}^-)$  values should increase with  $1/\{\text{H}^+\}$  in systems containing kinetically significant concentrations of polysulfides. The results for our experimental systems in the absence of added  $\text{S}_8$  display a slope not significantly different from 0, from which it can be inferred that our experimental systems lacked kinetically significant polysulfide concentrations.

Data from the two experiments conducted with polysulfides (solid symbols, Figure 4) yield an estimate for  $\sum [k_{\text{S}_n^{2-}} K_{\text{S}_n^{2-}} (\text{S}_8^{0(\text{aq})})^{(n-1)/8}]$  of approximately  $5.4 \times 10^{-12} \text{ s}^{-1}$ . If we compare this estimate with our  $k_{\text{HS}^-}$  value for  $\text{CH}_2\text{Br}_2$  ( $5.25 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ ), we predict that polysulfide-mediated reactions for this alkyl halide will dominate in systems saturated with polysulfides at pH values above 7.0. This compares very well with results for hexyl bromide, for which Haag and Mill (23) determined that polysulfide-mediated reactions would predominate above pH 7.2 in systems saturated with  $\text{S}_8$ . Available data, however, suggest that many natural waters are substantially [up to 500–1000-fold (29)] supersaturated with polysulfides, which thus may represent important environmental reagents in sulfide-rich systems at still lower pH values.

**Solid Reaction Product Studies.** A number of polymers have been reported to result from reactions of dihalomethanes or formaldehyde with hydrogen sulfide species. Early studies conducted in Germany in the late 1800s (50–52) indicated that  $\text{CH}_2\text{I}_2$  reacts with  $\text{Na}_2\text{S}$  in aqueous solution or  $\text{NaHS}$  in alcohol solution to form the cyclic thioformaldehyde trimer 1,3,5-trithiane [mp 220 °C (53)]:



This also represents the major product of the reaction of  $\text{H}_2\text{S}$  with formaldehyde in aqueous solution under acidic conditions (54). Other polymers identified from the reaction of dihalomethanes or formaldehyde with hydrogen sulfide species include the linear polymer poly(thiomethylene)  $[\text{HS}(\text{CH}_2\text{S})_n\text{H}, n > 1]$  and minor amounts of the cyclic thioformaldehyde tetramer 1,3,5,7-tetrathiocane [mp 48–49 °C (55, 56)] and pentamer 1,3,5,7,9-pentathia-cyclodecane [mp 120–123 °C (56, 57)], as well as copolymers of poly(oxymethylene)/poly(thiomethylene) (58, 59).

Unlike the cyclic thioformaldehyde polymers, which are all reported as soluble in benzene, poly(thiomethylene) is



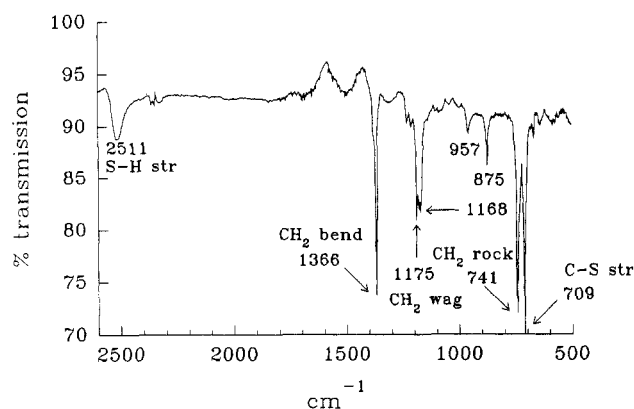


Figure 5. FT-IR spectrum of solid dibromomethane reaction product.

regarded as insoluble in common organic solvents at temperatures below  $\sim 200^\circ\text{C}$  (58), although Gipstein et al. (60) noted it is soluble in " $\alpha$ -bromonaphthalene and a solvent mixture of tetramethylene sulfone and  $\alpha$ -chloronaphthalene above  $210^\circ\text{C}$ " (but not at lower temperatures), and Lal (61) reported it to be soluble in " $o$ -phenylphenol and mixed tetrachlorobiphenyl" (Aroclor 1254) at  $\sim 230^\circ\text{C}$ . Melting points reported for poly(thiomethylene) vary widely, presumably reflecting differences in polymer chain length related to different methods of preparation: ca. 80, 123–124, 160–205, 175–176, 220–230, 220–245, 220–248, 220–255, and 245–260  $^\circ\text{C}$  have all been reported (56, 58–63).

All available evidence indicates that the solid reaction products we obtained consist largely, if not entirely, of poly(thiomethylene). The absence of appreciable solubility in benzene (as well as a large number of other organic solvents) of the  $\text{CH}_2\text{Br}_2$  and formaldehyde reaction products demonstrates that they do not contain significant proportions of any of the cyclic thioformaldehyde polymers. No traces of trithiane or higher molecular weight analogs were observed in GC-MS analyses of 0.7 mg/mL suspensions of reaction products in benzene, indicating any cyclic polymers must at best be present in very small quantities.

Further evidence as to product composition was obtained from the melting behavior we observed for the  $\text{CH}_2\text{Br}_2$  product, which conflicts with the distinct melting points reported for the cyclic polymers. The reaction product we obtained began to melt in the range  $68.8$ – $70.2^\circ\text{C}$  and completely melted at  $129.0$ – $137.0^\circ\text{C}$ . Given the undoubted dependence of melting point on chain length (which in turn reflects the method of synthesis and reaction conditions), we do not perceive any inconsistency between this melting behavior and melting points reported in the literature for poly(thiomethylene).

Microanalysis results indicate an elemental composition consistent with poly(thiomethylene), one that differs slightly from cyclic thioformaldehyde polymers. The observed results were C, 23.23%; H, 4.27%; N, 0%; O,  $<0.2\%$ ; S, 72.72%; and Br,  $<0.2\%$ . These results yield an empirical formula of  $\text{C}_1\text{H}_{2.19}\text{S}_{1.17}$ , which corresponds closely to  $\text{HS}(\text{CH}_2\text{S})_{10}\text{H}$ . If this empirical formula accurately reflects the average structure of the product we synthesized, then we should be able to find evidence that significant numbers of sulfhydryl end groups are present. From the microanalysis results, we can calculate a yield of  $>76\%$  for the precipitate we obtained for  $\text{CH}_2\text{Br}_2$  reaction, indicating it represents the major reaction product.

The FT-IR spectrum we obtained (Figure 5) differs from the published FT-IR spectrum for trithiane (64) and closely resembles the published IR spectrum for poly-

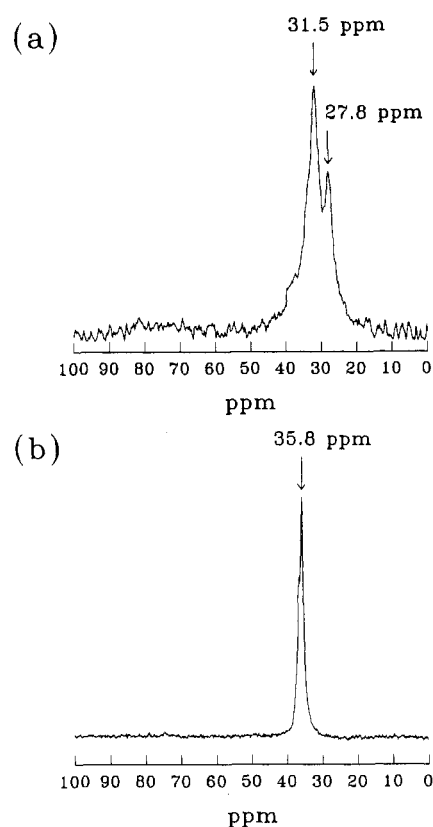


Figure 6. Solid-state  $^{13}\text{C}$  NMR spectra of (a) solid dibromomethane reaction product and (b) 1,3,5-trithiane.

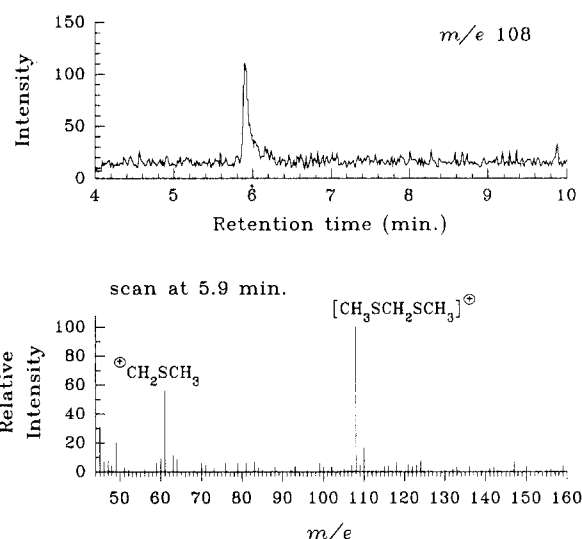
(thiomethylene) (65). Although an exact comparison is complicated by the poor quality of the published spectrum, for which methods of poly(thiomethylene) synthesis and purification were not indicated, our product certainly possesses all of the major features of this spectrum. It also shares the major IR absorbance bands previously reported for poly(thiomethylene) (66–68). The broad band at  $2511\text{ cm}^{-1}$  (not reported by earlier investigators) may be of particular note. We believe it represents an S-H stretching frequency from the terminal thiol groups. S-H stretching bands are typically weak and may go undetected in KBr pellets containing small amounts of sample. Few other functional groups, however, show absorption in this region. A spectrum similar to that shown in Figure 5 was also obtained for the product of formaldehyde reaction with  $\text{HS}^-$ , indicating that the two starting materials react to the same product under equivalent reaction conditions.

Solid-state  $^{13}\text{C}$  NMR spectra for the  $\text{CH}_2\text{Br}_2$  reaction product and for trithiane are shown in parts a and b of Figure 6, respectively. The broad peak obtained for the  $\text{CH}_2\text{Br}_2$  reaction product is characteristic of linear polymers, in which similarly substituted carbon atoms which occupy different positions within the polymer experience slightly different electronic environments. The spectrum displays two peaks with shifts at 27.8 and 31.5 ppm, both of which are within the range representative of methylene carbon bonded to sulfur [25–45 ppm (69)]. We believe the smaller peak at 27.8 ppm may reflect the carbon atoms bonded to the terminal thiol substituents, by analogy to the  $^{13}\text{C}$  NMR shifts of oxygen-substituted compounds; the  $\alpha$ -carbon signals of ethers are characteristically shifted downfield from the corresponding signals of alcohols (69). Alternatively, the second peak could represent a defect in the polymer chain, for example, substitution of O for S. This explanation is not however supported by the microanalysis results, nor are there any peaks in the region characteristic of methylene groups  $\alpha$  to ethers (40–70 ppm).

If we assume that the peak at 27.8 ppm represents the carbon  $\alpha$  to the sulfhydryl end groups, we can estimate a molecular weight from the relative areas of the two peaks; such calculations yield a formula of  $\text{HS}(\text{CH}_2\text{S})_{5.4}\text{H}$ . Because solid-state  $^{13}\text{C}$  NMR data obtained with polarization techniques are usually not amenable to precise quantitative analysis (70), this composition should be viewed as approximate. In contrast to the spectrum obtained for the  $\text{CH}_2\text{Br}_2$  reaction product, the trithiane spectrum displays a single sharp peak at 35.8 ppm.

**Dissolved-Phase Product Studies.** Formaldehyde analyses conducted at the completion of 35 °C time courses exhibited a maximum formaldehyde concentration of only 2  $\mu\text{M}$ , which is not sufficiently above our detection limit (1.5  $\mu\text{M}$ ) for us to feel confident that formaldehyde was indeed being produced. This suggests that, at relatively low initial dihalomethane concentrations [but  $(\text{H}_2\text{S})_{\text{T}}$  concentrations that are higher than normally encountered under environmental conditions], formaldehyde (or rather, methylene glycol) is not formed or is not a stable species. It is uncertain whether the derivitization method we used for formaldehyde measurement would detect other low molecular weight hydroxy or thiol compounds; the answer undoubtedly depends on the rate at which equilibrium is attained between different species. We attempted to measure formaldehyde in a suspension of 8 mg/L poly-(thiomethylene) and obtained a result identical to our blanks, indicating that depolymerization is slow at 37 °C. Evidence that formaldehyde is not a stable species in our experimental systems was obtained by an experiment at 35 °C in which we spiked a flask containing 7.5 mM  $(\text{H}_2\text{S})_{\text{T}}$  with 20  $\mu\text{M}$  formaldehyde and monitored concentrations over the course of 9 h. Formaldehyde concentrations underwent exponential decay, with a half-life on the order of 0.24 h. Although formaldehyde is not stable under our reaction conditions, we cannot rule out the possibility that it might still represent the major product of dihalomethane reaction with  $\text{HS}^-$  under conditions of low  $(\text{H}_2\text{S})_{\text{T}}$ . Unfortunately, these conditions are not experimentally accessible at temperatures of environmental relevance for the dihalomethanes we investigated, owing to the slow rate of reaction with  $\text{HS}^-$ . Experiments could be conducted at higher temperatures, but [by analogy with the pronounced effects of temperature on equilibria in the formaldehyde-dihydroxymethane-poly(oxyethylene) system (26)] this would be expected to shift the position of the complex equilibria between formaldehyde, dithiomethane, and poly(thiomethylene), limiting the applicability of the results to environmental conditions.

We also investigated whether low molecular weight thiols were produced in a separate experiment at 35 °C that was spiked to give a moderate initial  $\text{CH}_2\text{Br}_2$  concentration (75  $\mu\text{M}$ ). Traces of the methylated derivative of  $\text{CH}_2(\text{SH})_2$  (Figure 7) were observed to increase over time, which to the best of our knowledge is the first time that  $\text{CH}_2(\text{SH})_2$  has ever been detected from the reaction of a dihalomethane with hydrogen sulfide species. Observed concentrations, however, were only ~7% of what would be anticipated if  $\text{CH}_2(\text{SH})_2$  were the sole reaction product. This might indicate that some other monomer such as hydroxythiomethane is the major product or that polymerization is proceeding effectively even at low initial dihalomethane concentrations. Given that we have noted turbidity developing in preliminary experiments spiked to give 300  $\mu\text{M}$  initial  $\text{CH}_2\text{Br}_2$  concentration, we feel that polymerization may well proceed at relatively low dihalomethane concentrations, even if the amount of polymer produced is too small to permit its visual detection.



**Figure 7.** GC-MS trace of  $m/e$  108 and mass spectrum of bis-(methylthio)methane obtained by methylating dibromomethane reaction product with  $\text{CH}_3\text{I}$ .

## Discussion

**Proposed Reaction Pathways.** The major pathways we believe to be important in the nucleophilic substitution reaction of a dihalomethane with  $\text{HS}^-$  are illustrated in Figure 8. The products we have observed are consistent with a bimolecular ( $\text{S}_{\text{N}}2$ ) mechanism, as is the observed dependence of reaction rate on  $\text{HS}^-$  concentration. The initial, rate-determining step in the reaction of a dihalomethane thus undoubtedly involves the nucleophilic attack by  $\text{HS}^-$  to form an  $\alpha$ -halothiomethane, liberating a halide ion in the process.

By analogy with reactions of  $\alpha$ -halo alcohols and ethers, this slow step should be followed by a fast  $\text{S}_{\text{N}}1$  step to produce thioformaldehyde. Although  $\alpha$ -halo thioethers react more slowly than their oxygen-substituted analogs,  $\alpha$ -halo ethers (71, 72), reactions are still rapid in absolute terms: Bordwell et al. (71) noted that  $\text{CH}_3\text{SCH}_2\text{Cl}$  reacted at a rate too rapid to measure. Because such evidence indicates destruction of an  $\alpha$ -thiomethane should be many orders of magnitude faster than its rate of formation from the reaction of a dihalomethane with  $\text{HS}^-$ , an  $\alpha$ -halothiomethane intermediate would not be expected to accumulate to detectable concentrations.

The next product, thioformaldehyde, is also highly unstable, and does not appear to have ever been isolated in aqueous solution. The instability of thioformaldehyde can be rationalized in terms of the reluctance of sulfur to form double bonds with carbon, which in turn results from the larger size of sulfur's p orbital and thus weaker  $\pi$  overlap with the adjacent carbon atom. Even in the case of aqueous solutions of formaldehyde, in which relatively more stable carbon-oxygen double bonds are possible, the aldehyde form is only present at a fraction of the  $\text{CH}_2(\text{OH})_2$  concentration [approximately  $1:1.9 \times 10^3$  (73)]. Any thioformaldehyde formed is thus likely to rapidly add either hydrogen sulfide or water to form dithiomethane or hydroxythiomethane. Both of these latter products have been reported from the reaction of hydrogen sulfide species with formaldehyde (74, 75). Which of these will predominate is undoubtedly dependent on reaction conditions such as  $(\text{H}_2\text{S})_{\text{T}}$ , pH, and temperature.

All of these factors, plus the initial concentration of dihalomethane and the reactivity of the dihalomethane in question, will affect the rate of production of polymer precursors. This in turn will dictate whether cyclic poly-



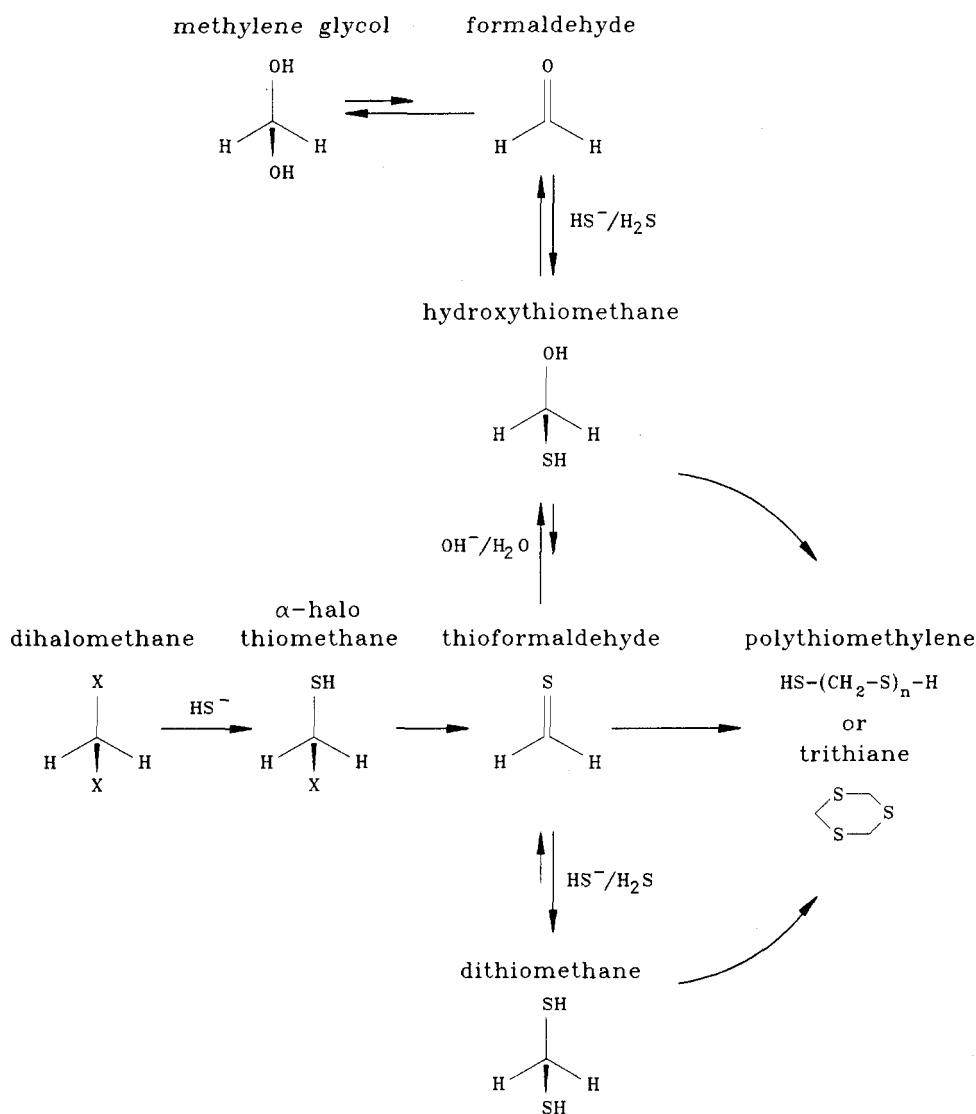


Figure 8. Proposed pathways for reactions of dihalomethanes and formaldehyde initiated by  $\text{S}_\text{N}2$  reaction with  $\text{HS}^-$ .

mers such as thioformaldehyde trimers, tetramers, or pentamers, linear polymers such as poly(thiomethylene), or monomers such as dithiomethane or formaldehyde will represent the major products of dihalomethane reaction with  $\text{HS}^-$  under environmental conditions. Many of the steps following thioformaldehyde production are likely to be freely reversible, and the positions of the competing equilibria are also undoubtedly dependent on solution conditions. Unraveling all of the steps involved and determining their reaction rates represents a complex problem, one beyond the scope of the present study, which is further complicated by the instability of many of the reaction intermediates and the relative insensitivity of available analytical techniques.

**Significance of  $\text{HS}^-$ -Promoted Reactions with Dihalomethanes.** Under environmental conditions, the overall rate of dihalomethane transformation will equal the sum of the contributing abiotic and microbially mediated processes, i.e.:

$$\frac{-d(\text{CH}_2\text{X}_2)}{dt} = [k_{\text{H}_2\text{O}}(\text{H}_2\text{O}) + k_{\text{OH}^-}(\text{OH}^-) + k_{\text{HS}^-}(\text{HS}^-) + \sum k_{\text{S}_n^{2-}}(\text{S}_n^{2-})](\text{CH}_2\text{X}_2) + k_{\text{bio}} \quad (9)$$

where we have assumed a zero-order rate expression for biotransformation. Focusing on the abiotic processes, we can now identify which will be the key terms in eq 9 under

various solution conditions. At  $\text{pH} < 10$ , the  $\text{OH}^-$ -promoted rate is negligible in comparison to the  $\text{H}_2\text{O}$ -promoted rate, at least for  $\text{CH}_2\text{Cl}_2$ . By comparing our measurements of  $k_{\text{HS}^-}$  with estimates of  $k_{\text{H}_2\text{O}}$  at  $25^\circ\text{C}$ , we can calculate the minimum concentration of  $\text{HS}^-$  required for the  $\text{HS}^-$ -promoted reaction to equal the  $\text{H}_2\text{O}$ -promoted rate. We have been unable to locate any measurements of  $k_{\text{H}_2\text{O}}$  in the literature for  $\text{CH}_2\text{Br}_2$  and  $\text{CH}_2\text{BrCl}$ , but if we assume that these correspond to half-lives at  $\text{pH} 7$ ,  $25^\circ\text{C}$ , reported by Mabey and Mill (1), we can infer that 2.3 and  $6.9 \mu\text{M}$   $\text{HS}^-$  is required for the  $\text{HS}^-$ -promoted rate to equal the  $\text{H}_2\text{O}$ -promoted rate at  $25^\circ\text{C}$  for  $\text{CH}_2\text{Br}_2$  and  $\text{CH}_2\text{BrCl}$ , respectively. By extrapolating our measurements of  $\text{CH}_2\text{Cl}_2$  reaction at 50 and  $64^\circ\text{C}$ , we can estimate a  $k_{\text{HS}^-}$  value of  $1.9 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  at  $25^\circ\text{C}$ ; comparing this to the  $k_{\text{H}_2\text{O}}(\text{H}_2\text{O})$  value of  $3.2 \times 10^{-11} \text{ s}^{-1}$  obtained from the results of Fells and Moelwyn-Hughes (38), we can calculate that  $17 \mu\text{M}$  ( $\text{HS}^-$ ) is required for the  $\text{HS}^-$ -promoted rate to equal the  $\text{H}_2\text{O}$ -promoted rate. These concentrations are well within  $\text{HS}^-$  concentration levels encountered in anoxic waters [ $\leq 700$ – $5000 \mu\text{M}$  (76)], indicating that  $\text{HS}^-$ -promoted reactions may be of considerable significance in dictating the environmental fate of dihalomethanes in anoxic systems. The activation energy we obtained for the  $\text{HS}^-$ -promoted reaction of  $\text{CH}_2\text{Cl}_2$  is significantly less than that of the  $\text{OH}^-$ -promoted reaction, as predicted by Schwarzenbach et al. (21); thus, even lower  $\text{HS}^-$  concentrations

will be required at lower temperatures for the HS<sup>-</sup>-promoted reaction to compete with CH<sub>2</sub>Cl<sub>2</sub> hydrolysis.

Our results are consistent with those of Haag and Mill (23) in indicating that polysulfide species are substantially more reactive than HS<sup>-</sup>. In systems saturated with elemental sulfur, our experiments with CH<sub>2</sub>Br<sub>2</sub> show that polysulfide-mediated reactions may dominate abiotic transformation processes at pH values greater than 7.0; such reactions may be even more important if polysulfide supersaturation is indeed as common as the results of Luther et al. (29) suggest.

Abiotic reactions with reduced sulfur species similar to the bisulfide ion may also be of considerable toxicological significance, especially in marine environments. Dibromomethane and diiodomethane are known to be released to seawater by marine macroalgae (77) and may therefore be present in or near marine sediments where sulfate-reducing conditions may prevail. Reactions of naturally occurring or anthropogenic dihalomethanes with HS<sup>-</sup> would give rise to toxic products that may diffuse back into overlying oxic waters, thereby entering the human food chain. Although poly(thiomethylene) is highly insoluble and thus may have limited access to the biosphere, relatively low molecular weight polymers of HS(CH<sub>2</sub>S)<sub>n</sub>H (*n* = 3–4) are known to be toxic to rats, with an LD<sub>50</sub> of 365 mg/kg (78). Poly(thiomethylene) has also been reported to give rise to skin "allergies" in humans (59). Moreover, Fielding (79) noted that dithiomethane and low molecular weight variants of HS(CH<sub>2</sub>S)<sub>n</sub>H, *n* = 2–4, are effective nematocides. Such products may thus be considerably more toxic than at least some of the parent dihalomethanes; for example, the LD<sub>50</sub> (for rats, administered orally) of CH<sub>2</sub>Cl<sub>2</sub> is 2100 mg/kg (80), and that for CH<sub>2</sub>BrCl is 5000 mg/kg (81).

**Structure-Reactivity Relationships.** Effects of structure on reactivity are often rationalized in terms of steric and inductive factors. Steric effects are generally considered to greatly retard S<sub>N</sub>2 reaction rates, while inductive effects can either enhance or diminish S<sub>N</sub>2 reactivity, depending on the substrate-nucleophile pair in question. Effects of alkyl substituents are believed to be expressed primarily through steric factors, polar effects of alkyl substituents being much too small to account for observed reactivity trends (82). A comparison of *k*<sub>H<sub>2</sub>O</sub> or *k*<sub>OH<sup>-</sup></sub> values for methyl vs ethyl halides indicates that adding one methyl-sized substituent to a methyl halide does not in fact greatly affect S<sub>N</sub>2 reactivity. The value of *k*<sub>H<sub>2</sub>O</sub> reported for CH<sub>3</sub>Br at 25 °C (83) is only 6% faster than the value given for CH<sub>3</sub>–CH<sub>2</sub>Br. Reaction rates reported for the H<sub>2</sub>O-promoted reaction of CH<sub>3</sub>Cl range from 2.0 × 10<sup>-8</sup> to 3.1 × 10<sup>-8</sup> s<sup>-1</sup> (35–37, 83–84), if anything slightly slower than the rate for CH<sub>3</sub>–CH<sub>2</sub>Cl of 3.1 × 10<sup>-8</sup> s<sup>-1</sup> (84). From this it might be concluded that steric effects on S<sub>N</sub>2 reactivity are quite modest, at least at this level of substitution.

Bromine substituents provide approximately the same steric hindrance as a methyl substituent (85). In contrast to the negligible difference in reactivity between CH<sub>3</sub>–CH<sub>2</sub>–Br and CH<sub>3</sub>–Br, Br–CH<sub>2</sub>–Br is markedly less reactive than CH<sub>3</sub>–Br [*k*<sub>OH<sup>-</sup></sub> for CH<sub>2</sub>Br<sub>2</sub> at 35 °C ≈ 6.1 × 10<sup>-7</sup> vs 1.4 × 10<sup>-4</sup> M<sup>-1</sup> s<sup>-1</sup> for CH<sub>3</sub>Br (36, 39)]. From this result, it might be concluded that inductive factors should dictate the S<sub>N</sub>2 reactivity of dihalomethanes, larger inductive effects being associated with less-reactive substrates. This simple prediction does not, however, fit the observed reactivity sequence for both *k*<sub>OH<sup>-</sup></sub> and *k*<sub>HS<sup>-</sup></sub> of CH<sub>2</sub>Br<sub>2</sub> < CH<sub>2</sub>BrCl, especially when rate constants for CH<sub>2</sub>Br<sub>2</sub> are divided by a statistical factor of 2. Similar reactivity se-

quences have been noted for the reactions of several other nucleophiles (I<sup>-</sup>, CH<sub>3</sub>O<sup>-</sup>, and thiophenolate) with brominated dihalomethanes, i.e., CH<sub>2</sub>Br<sub>2</sub> < CH<sub>2</sub>BrCl < CH<sub>2</sub>BrF (86, 87). The increasing ability of larger halogens to delocalize an incipient three-electron bond, thereby slowing reactivity, may explain these reactivity patterns (88, 89). Clearly, a simple model based solely on steric and inductive factors has limitations with respect to S<sub>N</sub>2 reactions.

Perhaps the best-known model relating structure to S<sub>N</sub>2 reactivity is that of Swain and Scott (47) given by eq 5. This model can be used to predict reaction rates of substrates for which some data are already available (thereby allowing calculation of the substrate susceptibility parameter *s*) with reactants of known nucleophilicity (*n* value). It has been applied with reasonable success to the reactions of halogenated alkanes with nucleophilic species under environmental conditions (23, 90).

A value of 1.09 for the substrate constant *s* in eq 5 for CH<sub>2</sub>Cl<sub>2</sub> can be calculated by extrapolating reported *k*<sub>OH<sup>-</sup></sub> and *k*<sub>H<sub>2</sub>O</sub> values (38) to 35 °C. With these *s* and *k*<sub>H<sub>2</sub>O</sub> values, a value of 1.2 × 10<sup>-6</sup> M<sup>-1</sup> s<sup>-1</sup> can be predicted for *k*<sub>HS<sup>-</sup></sub>. Similar calculations of *s* for CH<sub>2</sub>Br<sub>2</sub> and CH<sub>2</sub>BrCl are complicated by the absence of rate data in a common solvent system. If substrate constants for CH<sub>2</sub>Br<sub>2</sub> and CH<sub>2</sub>BrCl are assumed to equal the value for CH<sub>2</sub>Cl<sub>2</sub>, and if *n* values of 4.2 and 5.1 are assumed for OH<sup>-</sup> and HS<sup>-</sup>, respectively (47), then we can predict *k*<sub>HS<sup>-</sup></sub> values from *k*<sub>OH<sup>-</sup></sub> values measured in 67% dioxane–water at 35 °C (39) of 2.4 × 10<sup>-5</sup> and 5.8 × 10<sup>-6</sup> M<sup>-1</sup> s<sup>-1</sup> for CH<sub>2</sub>BrCl and CH<sub>2</sub>Br<sub>2</sub>, respectively. These predicted values are all less than observed values: *k*<sub>obs</sub>/*k*<sub>pred</sub> = 5.5, 10, and 30, for CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>BrCl, and CH<sub>2</sub>Br<sub>2</sub>, respectively. Note that these discrepancies are sensitive to the choice of *s*, smaller values resulting in larger discrepancies; moreover, including solvent effects on *k*<sub>OH<sup>-</sup></sub> values measured for the two brominated substrates would undoubtedly increase the discrepancy between observed and predicted rates, S<sub>N</sub>2 rates for reactions of this charge type being slower in more polar solvents (82).

Ratios of observed *k*<sub>HS<sup>-</sup></sub>/*k*<sub>OH<sup>-</sup></sub> increase in the order CH<sub>2</sub>Cl<sub>2</sub> < CH<sub>2</sub>BrCl < CH<sub>2</sub>Br<sub>2</sub>, that is, as the halogen substituents become "softer". This is precisely the effect noted by Bunnett (91), which gave rise to attempts to describe S<sub>N</sub>2 reactivity in terms of the principle of hard and soft acids and bases (HSAB). Pearson and Songstad (92) described how this principle applies to S<sub>N</sub>2 reactions; as relatively soft acids, alkyl substrates would be expected to react more readily with soft bases such as HS<sup>-</sup> than with the hard base OH<sup>-</sup>, particularly if leaving groups are soft (such as I<sup>-</sup>) or borderline (such as Br<sup>-</sup>) rather than hard (Cl<sup>-</sup> and F<sup>-</sup>). This tendency can be even greater if the alkyl substrate contains additional "soft" substituents, even if they are not being displaced in the rate-determining step (described by Pearson and Songstad as a "sympiotic effect"). Factors such as this clearly complicate attempts to predict reaction rates based solely on characteristics of the attacking nucleophile. Attempts have recently been made to quantitatively relate HSAB effects to nucleophilic reactivity (93), although to date with only limited success.

## Conclusions

Our results indicate that abiotic S<sub>N</sub>2 reactions of dihalomethanes with the bisulfide ion HS<sup>-</sup> may be of considerable environmental significance in sulfate-reducing environments, conditions not believed to be conducive to rapid biological transformation. Bisulfide-promoted rates will exceed hydrolysis rates for HS<sup>-</sup> concentrations above 2–17 μM, well within ranges commonly encountered in anoxic aquatic systems. Analogous reactions with poly-

sulfide species  $S_n^{2-}$  are likely to be more important than  $HS^-$ -promoted reactions in waters with pH values above 7 that are in equilibrium with orthorhombic  $S_8$ . Because available evidence indicates many sulfate-reducing environments are in fact supersaturated with polysulfides, such reactions may be of even greater environmental significance than indicated by our results.

Products observed from the reaction of dihalomethanes with  $HS^-$  consisted primarily of poly(thiomethylene) and minor amounts of dithiomethane. These products, along with the observed first-order dependence of the rate expression on  $HS^-$  and dihalomethane concentrations, show that these reactions occur through bimolecular nucleophilic substitution ( $S_N2$ ). No formaldehyde was detected during the reaction of dihalomethanes with millimolar levels of hydrogen sulfide species, although we cannot rule out the possibility that this product may be formed at low hydrogen sulfide concentrations, conditions that currently are not experimentally accessible. Available evidence indicates the products of dihalomethane reaction possess toxic properties.

Applying the Swain-Scott model to predicting rates of  $HS^-$  reaction with dihalomethanes leads to underestimates of  $k_{HS^-}$ , with observed values being 5 times higher than predicted values for  $CH_2Cl_2$ . Somewhat greater discrepancies are obtained for  $CH_2Br_2$  and  $CH_2BrCl$ , for which ratios of observed to predicted rates may be greater than 10–30. This may reflect hard-soft interactions, as suggested by previous researchers, although alternative models of nucleophilic reactivity such as that of Shaik (88, 89) also qualitatively agree with observed effects of structural changes on reactivity. Structure-reactivity relationships for  $S_N2$  reactions are complex and are not amenable to a simple treatment in terms of inductive and steric effects.

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