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Dechlorination of Chloropicrin and 1,3-Dichloropropene by Hydrogen Sulfide Species: Redox and Nucleophilic Substitution Reactions

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The chlorinated fumigants chloropicrin (trichloronitromethane) and 1,3-dichloropropene (1,3-D) are extensively used in agricultural production for the control of soilborne pests. The reaction of these two fumigants with hydrogen sulfide species (H_2S and HS^-) was examined in well-defined anoxic aqueous solutions. Chloropicrin underwent an extremely rapid redox reaction in the hydrogen sulfide solution. Transformation products indicated reductive dechlorination of chloropicrin by hydrogen sulfide species to produce dichloro- and chloronitromethane. The transformation of chloropicrin in hydrogen sulfide solution significantly increased with increasing pH, indicating that H_2S is less reactive toward chloropicrin than HS^- is. For both 1,3-D isomers, kinetics and transformation products analysis revealed that the reaction between 1,3-D and hydrogen sulfide species is an S_N2 nucleophilic substitution process, in which the chlorine at C3 of 1,3-D is substituted by the sulfur nucleophile to form corresponding mercaptans. The 50% disappearance time (DT_{50}) of 1,3-D decreased with increasing hydrogen sulfide species concentration at a constant pH. Transformation of 1,3-D was more rapid at high pH, suggesting that the reactivity of hydrogen sulfide species in the experimental system stems primarily from HS^-. Because of the relatively low smell threshold values and potential environmental persistence of organic sulfur products yielded by the reaction of 1,3-D and HS^-, the effects of reduced sulfide species should be considered in the development of alternative fumigation practices, especially in the integrated application of sulfur-containing fertilizers.

KEYWORDS: Fumigant; dechlorination; chloropicrin; 1,3-dichloropropene; hydrogen sulfide species

INTRODUCTION

The chlorinated aliphatic fumigants chloropicrin and 1,3-dichloropropene (1,3-D) have been widely applied in crop production for several decades. Although these two fumigants are not recognized as stratospheric ozone-depleting substances such as methyl bromide, their rapid volatilization causes air pollution (*1*−*3*) that is a public health concern. They may also contaminate subsurface aquatic environments through leaching (*4*), particularly in sensitive regions with shallow groundwater tables.

Research has indicated that many dehalogenation reactions produce transformation products that may be less toxic, less likely to bioaccumulate, and more susceptible to further biodegradation than the parent compounds (*5*−*8*). Generally, halogenated organic compounds undergo three types of dehalogenation via biotic or abiotic transformation: reductive dehalogenation, nucleophilic substitution, and dehydrodehalogenation. Because of their high oxidation state, highly halogenated compounds are subject to reductive dehalogenation in the presence of appropriate reductants, as in hydrogenolysis (the replacement of a halogen with a hydrogen), dihaloelimination (elimination of vicinal halides to form a C−C double bond), and radical coupling (*9*). For example, biotransformations of tetrachloroethylene (*5*) and chloropicrin (*10*) in the environment are recognized as sequential reductive dehalogenation processes. In several cases, some halogenated intermediates resulting from the reductive dehalogenation of polyhalogenated chemicals may be more toxic and persistent than the parent compounds. For example, tetrachloroethylene and trichloroethylene can be sequentially dechlorinated to a more toxic vinyl chloride (*11*,

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12). For mono- and dihalogenated compounds (e.g., primary alkyl halides), the dehalogenation process is mainly associated with the nucleophilic substitution reaction, especially in the presence of strong nucleophiles. The fumigant methyl bromide and chloroacetanilide herbicides, for instance, can be dehalogenated by the fertilizers ammonium thiosulfate and thiourea via an S_N2 nucleophilic reaction (*6*, *13*, *14*). The hydrolysis of halogenated aliphatic compounds in aquatic ecosystems is also often a nucleophilic dehalogenation process.

Some nucleophilic transformations may be exploited for the remediation of halogenated organic contaminants. For example, glutathione conjugation, an important natural detoxification reaction involving the nucleophilic removal of a halogen through an enzyme-mediated reaction, can potentially be used for in situ bioremediation and phytoremediation of halogenated contaminants (*8*). Some glutathione nucleophilic metabolites, such as ethane sulfonic acids of chloroacetanilide herbicides, have been frequently detected in groundwater (*15*−*17*). To provide a more complete risk assessment, it is of vital importance to determine the environmental toxicity, distribution, and fate of pesticide transformation products. Many nucleophilic transformation products are relatively persistent and mobile, although their toxicity may be decreased as compared to the parent compounds.

In hypoxic environments, many environmentally relevant nucleophiles, such as reduced sulfur species, play a crucial role in the abiotic dehalogenation process (*18*−*23*). Bisulfide (HS^-), a potential electron donor (reductant) and nucleophile that can react with a wide array of halogenated organic compounds, occurs ubiquitously in well water, salt marshes, anoxic bottom layers of estuaries, and hypoxic soils at levels ranging from 0.2 μM to 5 mM. HS^- is produced by anaerobic microbial reduction of sulfate associated with the decomposition of organic matter. Another important source of HS^- in agricultural soils results from the application of sulfur-containing agrochemicals. Elemental sulfur is an essential nutrient in soils and is also used as a pesticide. Sulfur is currently the most heavily used pesticide in California at 24 million kg of active ingredient in 2003. Under hypoxic conditions, elemental sulfur can undergo reduction by soil microorganisms to generate HS^- (*23*). HS^- and other reduced sulfur species often occur in fumigated soil, especially in soil treated with metam sodium (currently the most heavily used soil fumigant in the United States) because metam sodium rapidly decomposes to methyl isothiocyanate (MITC) and HS^- in soil (*24*). HS^- was also detected as one of the main degradation products of MITC in soil and aquatic media (*25*). Hence, the study of the effect of HS^- on the fate of halogenated fumigants may be of considerable environmental significance, particularly in soils treated previously with metam sodium or sulfur-containing fertilizers.

The primary objective of this study was to investigate the potential impact of hydrogen sulfide species (H_2S and HS^-) on the abiotic transformation of the halogenated fumigants chloropicrin and 1,3-D by determining the mechanism and kinetics of reaction in aqueous solution. These studies not only provide important insights into the transformation and fate of the fumigants but also provide useful information for further evaluation of the potential environmental effects of degradation products.

MATERIALS AND METHODS

Reagents. Standards of chloropicrin (99%) were obtained from Chem Service (West Chester, PA), and 1,3-D (Telone II, 50.5% cis and 46.9% trans isomer) was donated by Dow AgroSciences LLC (Indianapolis, IN). Chloronitromethane (95%) and dichloronitromethane (>95%) standards were purchased from Cansyn Chemical Corp. (New Westminster, BC, Canada). Sodium sulfide ($NaS\cdot 9H_2O$, ACS reagent grade) and flake sulfur (S, 99.99%) were purchased from Sigma-Aldrich Co. (St. Louis, MO). All chemicals were used as received.

Experimental Systems. All aqueous solutions were prepared using high-purity deionized water (E-pure, Barnstead, Dubuque, IA). All glassware used with hydrogen sulfide solutions was washed with alcoholic potassium hydroxide (KOH) to remove traces of sulfur species, followed by soaking in 10% nitric acid (HNO_3) and rinsing with deionized water. The glassware was autoclaved prior to use to inhibit microbial growth.

Buffer solutions of pH 6−8 were prepared by mixing phosphate buffer (0.1 M KH_2PO_4) and different amounts of sodium hydroxide (NaOH) according to ref *26*. A buffer solution of pH 9 (0.1 M, Fisher Scientific) consisted of boric acid (H_3BO_3) and NaOH. Sufficient NaCl was added to buffer solutions to establish an ionic strength of 0.15 equiv/L. All buffer solutions were deoxygenated by purging with argon for 1 h. Stock sulfide solutions (~0.1 M) were prepared by rinsing $NaS\cdot 9H_2O$ crystals with deoxygenated water to remove the surface-oxidized products, wiping them dry with a cellulose tissue, and then dissolving in deoxygenated water. Serum bottles (55 mL) sealed with Teflon-faced butyl rubber septa served as reactors. The sealed reactor may avoid losses of fumigant by volatilization and prevent the oxidation of hydrogen sulfide species by adventitious O_2. Fumigant solutions of chloropicrin (0.5 mM) and 1,3-D (1.0 mM) were prepared by spiking the liquid fumigant standards to deoxygenated buffer solutions (50 mL) in reactors. Kinetics experiments were initiated by spiking stock sulfide solutions to fumigant solutions. Experimental processes were conducted within an anaerobic glovebag enriched with 5% H_2/95% N_2 to maintain anoxic conditions. All reactors were vigorously shaken and then incubated in the dark at 21 ± 0.5 °C for chloropicrin and 25 ± 0.5 °C for 1,3-D. At regular time intervals, a 0.5 mL aliquot of reaction solution was withdrawn from each reactor using a gastight syringe and transferred into a sealed glass vial containing ethyl acetate (3.0 mL) and anhydrous sodium sulfate (2.5 g). Simultaneously, 0.5 mL of N_2 was injected into the reactor to avoid the introduction of headspace. The sealed vials were shaken for 5 min, and then, an aliquot of the ethyl acetate extract was transferred to a gas chromatography (GC) vial for fumigant concentration determination by GC/electron capture detection (ECD). Preliminary experiments revealed that the reaction was quenched immediately when ethyl acetate was used as an extraction solvent because chloropicrin or 1,3-D was efficiently extracted into the organic phase, while hydrogen sulfide species remained in the aqueous phase. Control experiments were concurrently performed in deoxygenated buffer solutions containing only chloropicrin or 1,3-D to measure their hydrolysis. The recovery of two fumigants ranged from 95 to 105% using the above-described procedures.

To identify primary reaction products and to propose the transformation pathway, 10 mM chloropicrin or 1,3-D and 10 mM hydrogen sulfide species were mixed in buffer solution (pH 9). Aliquots of the reaction solution were periodically extracted according to the above extraction procedure and analyzed by GC/mass spectrometry (MS).

Fresh stock sulfide solutions were prepared daily. The total concentration of hydrogen sulfide species $[H_2S]_T$ was determined by iodometric titration, representing the sum of all hydrogen sulfide species ($[H_2S]_T = [H_2S] + [HS^-] + [S^{2-}]$). The exact pH values in the reaction sulfide solutions were measured using an Accumet pH meter (Fisher Scientific).

GC/ECD and GC/MS Analysis. Ethyl acetate extracts were analyzed for chloropicrin and 1,3-D using a Hewlett-Packard HP 6890 GC equipped with an on-column injector, a micro-ECD, and a 30 m DB-VRX, 0.25 mm i.d. × 1.4 μm film thickness fused silica capillary column (J&W, Folsom, CA). The GC conditions were 1.4 mL min^{-1} carrier gas flow rate (He), 240 °C inlet temperature, and 290 °C detector temperature. The initial oven temperature was 45 °C for 1 min and the temperature was increased to 80 °C at 2.5 °C/min, then increased to 120 °C at 30 °C/min, and held for 2 min. Under these conditions, the retention times for *cis*-1,3-D, *trans*-1,3-D, chloropicrin, chloronitromethane, and dichloronitromethane were 10.9, 12.2, 13.6, 10.1, and 11.3 min. Data were subjected to analysis of variance, and means were compared by least significant difference.

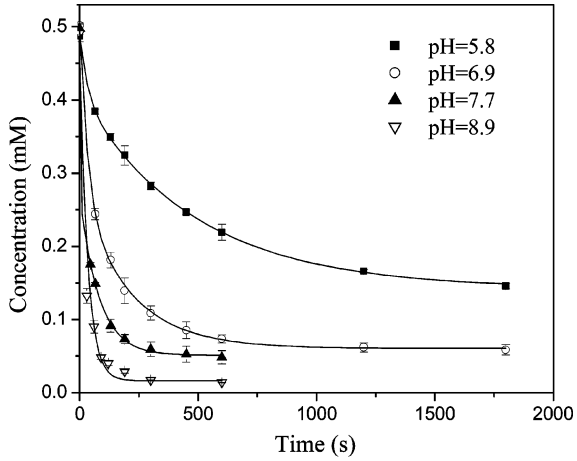


Figure 1. Dissipation of chloropicrin (0.5 mM) in hydrogen sulfide solutions (0.5 mM) at different pH values at 21 ± 0.5 °C. Error bars represent standard deviation of triplicate samples.

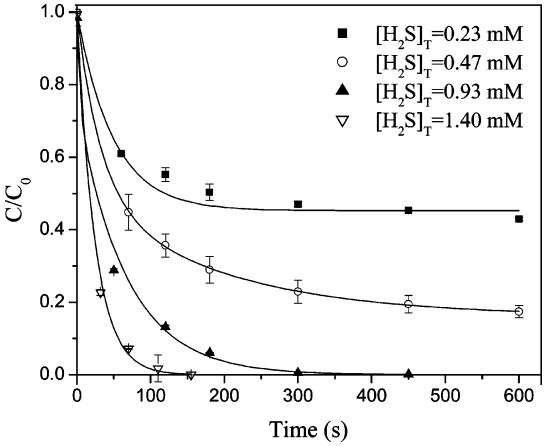


Figure 2. Example time courses for dissipation of chloropicrin in different initial $(H_2S)_T$ concentration solutions at constant temperature (21 ± 0.5 °C) and approximately constant pH (6.9 ± 0.1). C_0 is the initial concentration of chloropicrin (0.5 mM) in the solutions.

Chloropicrin and 1,3-D transformation products were analyzed using an HP 5890 GC in tandem with an HP 5971 quadrupole mass selective detector equipped with an on-column injector. Chloropicrin transformation products were separated using a 30 m DB-VRX, 0.25 mm i.d. × 1.4 μm film thickness fused silica capillary column; 1,3-D transformation products were separated using a 30 m HP-5MS (Wilmington, DE), 0.25 mm i.d. × 0.25 μm film thickness fused silica capillary column. The EI mass spectra were generated using an electron energy of 70 eV and were monitored for ions *m*/*z* 10−150 for chloropicrin and *m*/*z* 50−300 for 1,3-D transformation products.

RESULTS AND DISSCUSSION

Chloropicrin Transformation by Hydrogen Sulfide Species. The reaction of chloropicrin with hydrogen sulfide in buffer solution was assessed at different pH values. **Figure 1** illustrates the disappearance of chloropicrin in the presence of 0.5 mM hydrogen sulfide species at pH 5.8−8.9. Chloropicrin dissipated rapidly (within <1 h) when in contact with hydrogen sulfide species at all pH values and within a couple of minutes at high pH (**Figure 1**). No discernible fumigant degradation occurred in the control buffer solutions containing only chloropicrin at these short time scales. This observation is consistent with previous reports that chloropicrin undergoes extremely slow hydrolysis in the absence of light and microorganisms (*24*, *27*).

The dissipation of chloropicrin in hydrogen sulfide solutions follows an exponential decay (**Figure 1**). The dissipation half-life of the fumigant was approximated based on the description of chloropicrin reduction by iron-bearing clay minerals (*28*, *29*). A similar calculation was utilized to describe the reductive dehalogenation of polyhalogenated hydrocarbons (*30*, *31*). The dissipation half-lives ($t_{1/2}$) of chloropicrin in solutions containing 0.5 mM hydrogen sulfide species decreased with increasing pH. For example, the half-life of chloropicrin decreased by more than a factor of 20 when hydrogen sulfide solution pH increased from 5.8 to 8.9 ($t_{1/2}$ decreased from approximately 10 to 0.45 min). In these experimental systems, the total hydrogen sulfide $(H_2S)_T$ concentration represents the sum of three hydrogen sulfide species (H_2S, HS^-, and S^{2-}). The proportion of these individual species in hydrogen sulfide solution is pH-dependent (*18*, *32*). At pH < 6, H_2S is the predominating sulfide species. As the pH increases, the proportion of H_2S that dissociates to HS^- gradually increases, and HS^- accounts for 99% of the total at pH 9 (*33*). At the pH range used in these experiments (5.8−8.9), the concentration of S^{2-} is very small ($pK_2 = 14.6$) (*32*). The dissipation kinetics of chloropicrin in solutions of different pH (**Figure 1**) clearly indicates that the reactivity of chloropicrin with H_2S is much lower than that with HS^-.

Figure 2 depicts chloropicrin dissipation at different $(H_2S)_T$ concentrations at a pH of 6.9 ± 0.1. The rate of chloropicrin dissipation in buffer solutions at constant pH increased with increasing total hydrogen sulfide concentration. These results show that, at a given pH, the rate of reaction between chloropicrin and hydrogen sulfide species is clearly dependent on $(H_2S)_T$ concentration.

Transformation Mechanism of Chloropicrin and Hydrogen Sulfide Species. A precipitate was immediately formed when chloropicrin was mixed with hydrogen sulfide in the buffer solutions (pH 6−8). The elemental composition of the solid reaction product was analyzed using an elemental analyzer (CE-ELANTECH Flash 1112, Thermo) after separating the precipitate from the reaction solution. Microanalysis results showed that the contents of both C and N were <0.3% and that the major constituent of the solid product was S (>85.0%), which is close to the microanalysis of the standard sulfur.

The reaction solution was periodically extracted and analyzed by GC/MS to monitor the progress of the reaction. Two reaction products were detected and identified as dichloronitromethane (Cl_2CHNO_2; **Figure 3a**) and chloronitromethane ($ClCH_2NO_2$; **Figure 3b**) according to the analysis of their mass spectra (*27*). These two reaction products were further verified using authentic standards. The products dichloronitromethane and chloronitromethane were also detected as the reduction products of chloropicrin in aqueous solution containing metam sodium (*24*).

On the basis of these identified reaction products, chloropicrin is believed to react via a redox reaction mechanism in hydrogen sulfide solution. The major transformation pathways of chloropicrin in the presence of hydrogen sulfide species are proposed in **Scheme 1**. Chloropicrin, as an electron acceptor, initially obtains an electron (*9*), resulting in the formation of a carbon-centered radical ($Cl_2C{\cdot}NO_2$), which would further transform to Cl_2CHNO_2 (**Scheme 1a**). Simultaneously, the reductive dechlorination of chloropicrin may be initiated by a two-electron transfer, which liberates two chlorine ions and produces a carbene(oid) intermediate ($ClC{:}NO_2$) (*34*). Subsequent reaction of this radical intermediate would lead to the formation of $ClCH_2NO_2$ (**Scheme 1b**). The proposed mechanism is similar to the reduction of chloropicrin by ferruginous smectite (*28*, *29*) and zerovalent iron (*34*) to simultaneously produce Cl_2CHNO_2 and $ClCH_2NO_2$ via parallel reaction pathways. In this

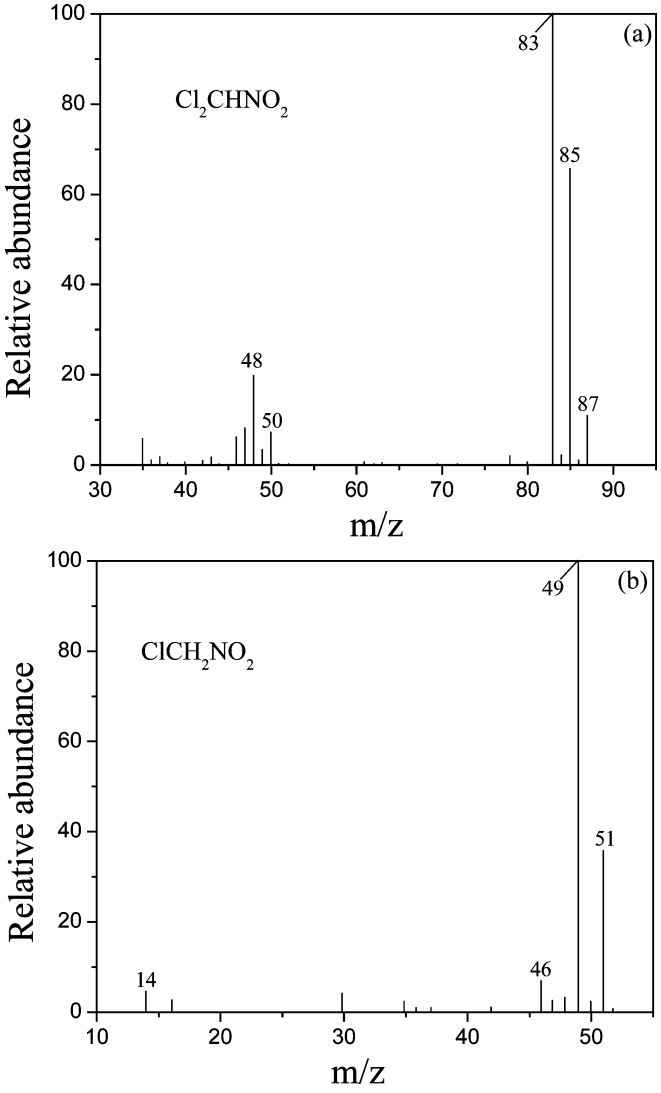


Figure 3. Mass spectra (EI) of transformation products obtained from the reaction of chloropicrin with hydrogen sulfide species: (**a**) dichloronitromethane (Cl_2CHNO_2) and (**b**) chloronitromethane ($ClCH_2NO_2$).

Scheme 1

$$Cl_3CNO_2 + HS^- (H_2S) \rightarrow Cl_2CHNO_2 + S + Cl^- (+ H^+) \quad (a)$$

$$Cl_3CNO_2 + 2HS^- (H_2S) \rightarrow ClCH_2NO_2 + 2S + 2Cl^- (+ 2H^+) \quad (b)$$

$$Cl_2CHNO_2 + HS^- (H_2S) \rightarrow ClCH_2NO_2 + S + Cl^- (+ H^+) \quad (c)$$

$$ClCH_2NO_2 + HS^- (H_2S) \rightarrow CH_3NO_2 + S + Cl^- (+ H^+) \quad (d)$$

redox reaction system, hydrogen sulfide species (HS^- and H_2S) serve as electron donors and are oxidized to elemental sulfur (S) (**Scheme 1**), in agreement with the microanalysis of the solid precipitate.

The concentrations of Cl_2CHNO_2 and $ClCH_2NO_2$ monitored by GC are shown in **Figure 4** along with the loss of chloropicrin (0.5 mM) in solutions containing excess hydrogen sulfide (2.0 mM). Results indicate that Cl_2CHNO_2 and $ClCH_2NO_2$ were immediately yielded when chloropicrin was mixed with hydrogen sulfide species. The simultaneous formation of Cl_2CHNO_2 and $ClCH_2NO_2$ supports the proposed reaction mechanism in which the reduction of chloropicrin involves the formation of radicals prior to homolysis. The formation of Cl_2CHNO_2 achieved a maximum when chloropicrin was completely reduced by hydrogen sulfide species. The concentration of Cl_2CHNO_2

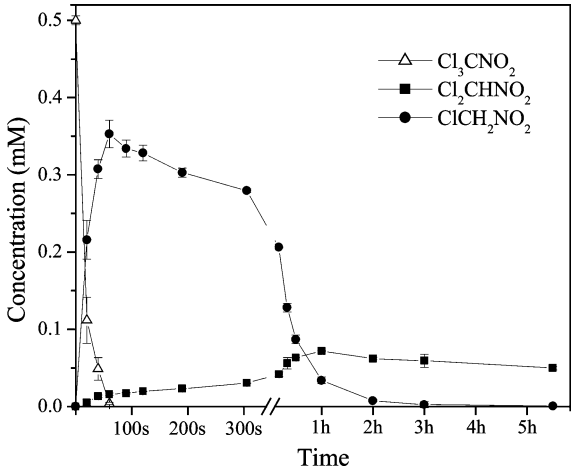


Figure 4. Dissipation of chloropicrin (0.5 mM) and formation of dichloronitromethane (Cl_2CHNO_2) and chloronitromethane ($ClCH_2NO_2$) in hydrogen sulfide solutions (2.0 mM) at 21 ± 0.5 °C (pH 7.0 ± 0.1).

then decreased gradually, with a concurrent gradual increase in $ClCH_2NO_2$ concentration (**Figure 4**), inferring that Cl_2CHNO_2 was further reduced by hydrogen sulfide species via a redox reaction to yield $ClCH_2NO_2$ (**Scheme 1c**). The latter would further transform to the nonhalogenated product nitromethane (CH_3NO_2) in hydrogen sulfide solution (**Scheme 1d**), which could also be reduced to methylamine (CH_3NH_2) (*34*). Because the oxidation potential of chloronitromethane compounds decreases with an increasing number of hydrogen atoms in the molecule, a reactivity trend of $Cl_3CNO_2 > Cl_2CHNO_2 > ClCH_2NO_2$ is expected for hydrogen sulfide species in the reaction system. This is similar to the degradation of chloropicrin in the presence of zerovalent iron (*34*).

The experimental results presented in **Figure 4** clearly indicate a lack of mass balance among the chloronitromethane compounds after the initial reaction time, which suggests that chloropicrin and dichloronitromethane might also directly reduce to nitromethane via the involvement of a series of carbene(oid) intermediates (such as $ClC{:}NO_2$ and $HC{:}NO_2$). The occurrence of these intermediates species in the process of chloropicrin reduction had been verified by using a carbene(oid) trapping agent as performed by Pearson et al. (*34*).

Previous research has shown that elemental sulfur can readily combine with HS^- to form polysulfides (*19*, *20*). Polysulfides are considered to be substantially more reactive than other reduced sulfide species such as HS^-. Additional experiments, in which reaction solutions of chloropicrin and hydrogen sulfide were immediately mixed with excess S_8, did not produce an increase in the rate of chloropicrin dissipation (data not shown). These results suggest that the effect of polysulfide on chloropicrin reduction was negligible in the anaerobic experimental system because of rapid reaction of chloropicrin with hydrogen sulfide species (occurring within minutes) and the relatively slow formation of polysulfide from S_8 and HS^- (*31*).

1,3-D Transformation by Hydrogen Sulfide Species. The reaction of 1,3-D with hydrogen sulfide was investigated at different pH values and different $(H_2S)_T$ concentrations. An example for 1,3-D dissipation of 1,3-D in hydrogen sulfide solution at pH 7.9 ± 0.1 is shown in **Figure 5**. As compared to the rate of 1,3-D hydrolysis [0 mM $(H_2S)_T$], the dissipation of both 1,3-D isomers was significantly accelerated in all anoxic aqueous solutions containing hydrogen sulfide species. At a given pH, the rate of 1,3-D dissipation increased with increasing initial total concentration of hydrogen sulfide (**Figure 5**),

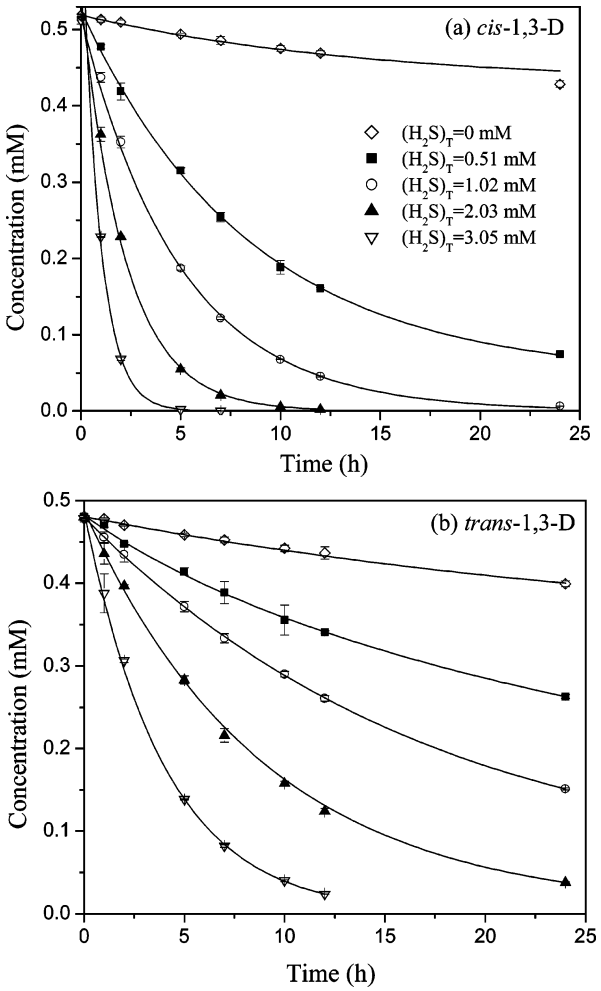


Figure 5. Dissipation of 1,3-D (1.0 mM) in different $(H_2S)_T$ concentration solutions at 25 ± 0.5 °C and pH 7.9 ± 0.1. Error bars represent standard deviations of triplicate samples. Lines indicate fit to a second-order kinetic model.

suggesting that the reaction rate of 1,3-D with hydrogen sulfide species is clearly dependent on the their initial concentrations.

The experimental results indicate that the reaction mechanism between 1,3-D and hydrogen sulfide species is consistent with an S_N2 nucleophilic substitution reaction, which follows second-order kinetics. In these experimental systems, the disappearance of 1,3-D is mainly attributed to the reaction with hydrogen sulfide species and hydrolysis. Therefore, the overall 1,3-D dissipation rate in hydrogen sulfide solution would be the sum of two concurrent reactions, which may be expressed as

$$\frac{-\mathrm{d}[1,3\text{-D}]}{\mathrm{d}t} = (k_a[H^+] + k_N + k_b[OH^-])C + k_2CX = k_hC + k_2CX \quad (1)$$

where k_a, k_N, and k_b represent the rate constants for acid-catalyzed, neutral, and base-catalyzed hydrolysis (*35*), k_h is the overall hydrolysis rate constant, k_2 is the second-order rate constant, and C and X are the concentrations of 1,3-D and hydrogen sulfide species, respectively. Because the reaction between 1,3-D and hydrogen sulfide species is much faster than 1,3-D hydrolysis (**Figure 4**), the equation may be simplified to a second-order reaction.

$$\frac{-\mathrm{d}[1,3\text{-D}]}{\mathrm{d}t} = k_2'CX = k_2'C(C - C_0 + X_0) \quad (2)$$

Upon rearrangement and integration, a solution of eq 2 is obtained

$$C = C_0\frac{(X_0 - C_0)\exp[-k_2'(X_0 - C_0)t]}{X_0 - C_0\exp[-k_2'(X_0 - C_0)t]} \quad (3)$$

where k_2' is the apparent second-order rate constant and C_0 and X_0 are the initial concentrations of 1,3-D and hydrogen sulfide species, respectively. Note that eq 3 is valid only if $C_0 \neq X_0$. The second-order rate constant (k_2') may be obtained from nonlinear least-squares fit of the experimental data to eq 3 (**Table 1**). If one inserts $C_0/2$ for C in eq 3, one obtains

$$\mathrm{DT}_{50} = \frac{\ln(2 - C_0/X_0)}{k_2'X_0(1 - C_0/X_0)} \quad (4)$$

where DT_{50} represents the 50% disappearance time of pesticide under a given set of reaction conditions (*6*, *35*).

To distinctly compare the rate of 1,3-D dissipation in buffer solutions in the presence and absence of hydrogen sulfide species, 50% disappearance times of both 1,3-D isomers at different pH values are summarized in **Table 1**. The half-life of 1,3-D hydrolysis was calculated according to pseudo-first-order kinetics, whereas the DT_{50} for 1,3-D in hydrogen sulfide solution was obtained from eq 4. **Table 1** shows that the DT_{50} of 1,3-D decreased with increasing initial hydrogen sulfide concentration at a constant pH. The reaction rate constants of both 1,3-D isomers with hydrogen sulfide species increased with increasing pH values (**Table 1**). As observed for chloropicrin, these results indicate that HS^- is more reactive toward 1,3-D than H_2S in the pH range investigated (5.9−8.9). Note that the reported rate of hydrolysis of both 1,3-D isomers in neutral buffer solution is much faster than that in previous reports (*36*, *37*) because the phosphate buffer (in solutions of pH 6−8) can accelerate the hydrolysis of 1,3-D. A similar phosphate-catalyzed hydrolysis of 1,2-dichloroethane and 1,2-dibromoethane has been reported (*38*). Because no phosphate anion was present in the pH 8.9 buffer solution, the hydrolysis rates of 1,3-D isomers were lower than those at pH 6.9 or 7.9 (**Table 1**).

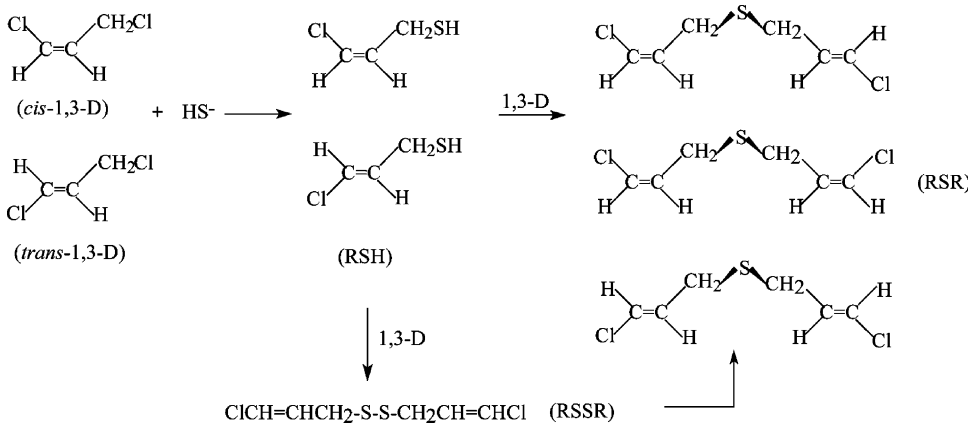
Transformation Mechanism of 1,3-D and HS^-. To elucidate the pathway of 1,3-D reaction with hydrogen sulfide, aliquots of the reaction mixture at pH 8.9 ± 0.1 were periodically extracted and analyzed by GC/MS. Six reaction products were characterized based on their mass spectra and retention times. The reaction of 1,3-D and HS^- is proposed as a bimolecular nucleophilic substitution (S_N2) mechanism. HS^- as a "soft" nucleophile attacks 1,3-D to form a RSH mercaptan, liberating a chlorine at C3 in the initial process (**Scheme 2**). Because 1,3-D is a mixture of cis and trans isomers, two corresponding mercaptans (RSH) were detected with the same mass spectrum (**Figure 6a**) but at different retention times on the total ion chromatograms. These two mercaptan isomers may convert to related mercaptides (RS^-) in aqueous solution, which should further react with any remaining 1,3-D to yield thioethers $ClCH{=}CHCH_2{-}S{-}CH_2CH{=}CHCl$ (RSR). Consistent with the stereochemistry of the reaction between the mercaptides and the 1,3-D isomers, three thioether isomer products were observed that had different retention times but the same mass spectrum (**Figure 6b**). Additionally, small amounts of dialkyl disulfide (RSSR) were also detected (**Figure 6c**), which stemmed from the oxidation combination of partial mercaptans (RSH). However, the dialkyl disulfide (RSSR) gradually degraded with increasing incubation time. The final reaction products observed in the reaction mixture of 1,3-D and HS^- were thioether isomers (RSR).

Table 1. Pseudo-First-Order Hydrolysis Rate Constants and Half-Lives ($t_{1/2}$) of 1,3-D and Second-Order Reaction Rate Constants and 50% Disappearance Times (DT_{50}) of 1,3-D (1.0 mM) with Hydrogen Sulfide Species at 25 ± 0.5 °C

		cis-1,3-D				*trans*-1,3-D			
ppH	initial $[H_2S]_T$ (mM) [a]	k_h (h^{-1})	$t_{1/2}$ (h)	k_2' ($mM^{-1}h^{-1}$)	DT_{50} (h)	k_h (h^{-1})	$t_{1/2}$ (h)	k_2' ($mM^{-1}h^{-1}$)	DT_{50} (h)
5.9 ± 0.1[b]	0	5.26×10^{-3}	131.7			5.43×10^{-3}	127.7		
	1.01 (1:1)			3.22×10^{-2}	24.96			1.16×10^{-2}	68.55
	2.03 (1:2)			3.06×10^{-2}	12.06			0.88×10^{-2}	41.49
	3.04 (1:3)			3.68×10^{-2}	6.50			0.97×10^{-2}	24.70
	4.05 (1:4)			4.51×10^{-2}	3.93			1.06×10^{-2}	16.74
	average			$3.62\ (\pm0.65)\times10^{-2}$				$1.02\ (\pm0.12)\times10^{-2}$	
6.9 ± 0.1[b]	0	7.36×10^{-3}	94.22			7.54×10^{-3}	91.92		
	0.97 (1:1)			1.39×10^{-1}	5.92			3.34×10^{-2}	25.01
	1.94 (1:2)			1.23×10^{-1}	3.13			2.75×10^{-2}	13.98
	2.91 (1:3)			1.17×10^{-1}	2.16			2.73×10^{-2}	9.14
	3.88 (1:4)			1.41×10^{-1}	1.31			2.86×10^{-2}	6.48
	average			$1.30\ (\pm0.11)\times10^{-1}$				$2.92\ (\pm0.28)\times10^{-2}$	
7.9 ± 0.1[b]	0	7.68×10^{-3}	90.24			7.61×10^{-3}	91.10		
	0.51 (2:1)			3.73×10^{-1}	5.33			6.71×10^{-2}	28.57
	1.02 (1:1)			3.06×10^{-1}	2.58			5.97×10^{-2}	13.25
	2.03 (1:2)			2.92×10^{-1}	1.26			6.24×10^{-2}	5.87
	3.05 (1:3)			4.30×10^{-1}	0.56			8.41×10^{-2}	2.83
	average			$3.50\ (\pm0.63)\times10^{-1}$				$6.83\ (\pm1.09)\times10^{-2}$	
8.9 ± 0.1	0	7.10×10^{-3}	97.60			7.26×10^{-3}	95.44		
	0.51 (2:1)			6.01×10^{-1}	3.28			7.32×10^{-2}	26.01
	1.02 (1:1)			4.05×10^{-1}	1.97			8.33×10^{-2}	9.44
	1.53 (2:3)			4.04×10^{-1}	1.24			8.17×10^{-2}	6.08
	2.04 (1:2)			3.85×10^{-1}	0.96			8.02×10^{-2}	4.52
	average			$4.49\ (\pm1.01)\times10^{-1}$				$7.96\ (\pm0.44)\times10^{-2}$	

[a] Values in parentheses are approximate initial molar ratios of 1,3-D to $[H_2S]_T$ in solutions. [b] Phosphate buffer may have catalyzed 1,3-D hydrolysis.

Scheme 2



It was apparent that the transformation of *cis*-1,3-D by hydrogen sulfide species was significantly faster than that of *trans*-1,3-D (**Figure 5** and **Table 1**). In 1,3-D, the C═C bond and four connected single bonds are all in the same plane, suggesting that the spatial hindrance for approach of hydrogen sulfide species such as HS^- should be similar for both isomers. When HS^- attacks 1,3-D isomers, a crowded transition state will be formed. In the transition state, the potential rotation around the C−C bond of *cis*-1,3-D may be hindered by the chlorine attached at the C═C bond. The greater steric hindrance facilitates breakage of the C−Cl bond in *cis*-1,3-D, yielding a corresponding RSH mercaptan. This reaction mechanism is consistent with those proposed for nucleophilic reaction processes between 1,3-D and metam sodium (*24*) or thiourea (*39*).

Environmental Implications. Our study of the rapid reaction of chloropicrin and 1,3-D with hydrogen sulfide species indicates that the abiotic transformation of halogenated fumigants by HS^- may be of considerable environmental significance in fumigated soil. To reduce fumigant volatilization, application of soluble formulations of fumigants through drip irrigation systems is being proposed to replace the conventional shank method (*40*). This approach may alleviate some environmental risks of fumigant applications by reducing atmospheric emissions and may improve pest control efficacy by extending the fumigant residence time in soil. However, drip fumigation may impose an increased risk for groundwater contamination, as leaching of water may facilitate the downward transport of fumigants to groundwater, particularly in regions with shallow aquifers and sandy soils. Fumigant application with large volumes of water by drip application increases the potential of fumigant occurrence in hypoxic environments. In anoxic aquatic and soil systems, hydrogen sulfide species such as HS^- are ubiquitous and are commonly present at sufficiently high concentrations (*32*) to undergo the abiotic reactions indicated by our results.

As illustrated in the major transformation pathways of chloropicrin and 1,3-D with HS^- (**Schemes 1** and **2**), the reaction mechanisms and products are dependent on the individual fumigant properties. The concentration of chloropicrin

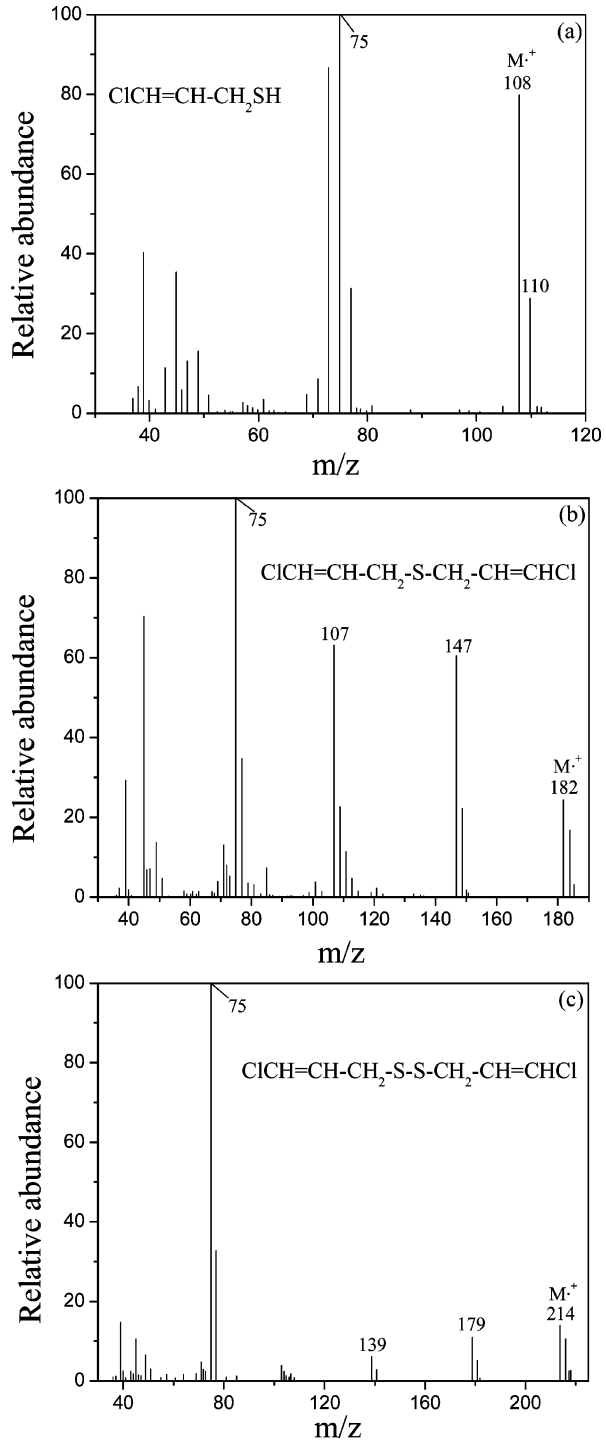


Figure 6. Mass spectra (EI) of transformation products obtained from the reaction of 1,3-D with HS^-: (**a**) mercaptan (RSH), (**b**) thioether (RSR), and (**c**) disulfide product (RSSR).

would be considerably decreased in the presence of hydrogen sulfide species, potentially resulting in diminished pest control efficacy, via a reduction mechanism similar to the environmental degradation of chloropicrin itself (*10*). The reaction of 1,3-D with hydrogen sulfide species follows a different transformation pathway than that which occurs for 1,3-D itself in soil and aquatic environments. The nucleophilic substitution reaction of 1,3-D with hydrogen sulfide species in hypoxic soil and groundwater could produce some organic sulfur compounds, such as 1,3-D thiol (RSH), thioether (RSR), and disulfide (RSSR). These organic sulfide products, in particular those containing chlorine atoms, may be hazardous to public health because of their potential toxicity and also be more persistent than the parent compounds (*9*, *21*, *41*). In addition, these low molecular weight organic sulfur compounds have relatively low smell threshold values and have great potential to enter the air through gradual volatilization from soil and aquatic systems. This may limit the potential for many other inorganic sulfur nucleophiles (such as thiosulfate, polysulfide, and sulfite) to be used as chemical remediation reagents to control fumigant emissions. For example, the fertilizer ammonium thiosulfate may react rapidly with the volatile halogenated fumigants 1,3-D (*36*) and methyl bromide (*14*). However, these reaction products may further degrade to volatile organic sulfur contaminants in soils. The results of these studies indicate that the environmental benefits of integrated fumigation practices in which inorganic sulfur chemicals serve as amendment reagents may be limited by the volatilization and toxicity of the reaction products liberated.

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