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Dehalogenation of Halogenated Fumigants by Polysulfide Salts

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Halogenated fumigants are among the most heavily used pesticides in agriculture. Because of their high mobility and toxicological characteristics, the contamination of air or groundwater by these compounds has been a great environmental concern. In this study, we investigated dehalogenation of several halogenated fumigants by polysulfides. The reaction of polysulfides and methyl iodide (MeI), 1,3-dichloropropene (1,3-D), and chloropicrin (CP) was very rapid. When the initial fumigant and polysulfide concentrations were both 0.2 mM, the observed 50% disappearance time values (DT_{50}) of MeI, *cis*-1,3-D, and *trans*-1,3-D were 27.2, 29.6, and 102 h, respectively. When the initial polysulfide concentration was 1.0 mM, the corresponding DT_{50} values were only 2.2, 1.6, and 3.8 h. Under similar conditions, the reaction with CP was even more rapid than with the other fumigants. In 0.2 mM polysulfide solution, more than 90% of the spiked CP disappeared in 1 h after the initiation of the reaction. The reaction between fumigants and polysulfides also progressed at enhanced rates when the polysulfide solution was initially purged with nitrogen. Analysis of reaction kinetics and initial products suggests that the reaction is S_N2 nucleophilic substitution for MeI and 1,3-D but likely reductive dehalogenation for CP. Given the high reactivity of polysulfide salts toward halogenated fumigants, this reaction may be used as a pollution mitigation strategy, such as for disposal of fumigant wastes, treatment of fumigant-containing wastewater, and cleanup of fumigant residues in environmental media.

KEYWORDS: Halogenated fumigants; polysulfide salts

INTRODUCTION

Halogenated organic compounds (HOCs) have a multitude of uses in modern society. They are widely used in the chemical industry as degreasing, cleaning, and refrigerating solvents, in manufacturing as raw materials for plastics and dyestuffs, and in agriculture as the active ingredients of pesticides. Consequently, many of these compounds have been found in the environment as contaminants (*1*−*3*). Among the commonly used HOCs, halogenated fumigants have been used extensively for several decades in agricultural production to control soil-borne pests. In the United States, the use of fumigants is concentrated in just a few areas, such as California and Florida. One of the most striking characteristics about fumigant uses is the high application rate (100−300 kg ha^{-1}), which is usually many times that of conventional pesticides (*4*). On the other hand, some halogenated fumigants are considered a toxicological threat to public health, often due to their acute toxicity or potential carcinogenicity. Therefore, fumigant contamination to air and/or water resources associated with the widespread use is of environmental concern (*5*−*6*). For example, the groundwater contamination by 1,2-dibromo-3-chloropropane (DBCP) and ethylene dibromide (EDB) have led to the ban of these two chemicals in the United States. Another fumigant, methyl bromide (MeBr), is currently undergoing phase out in the industrialized countries because of its potential for depleting stratosphere ozone.

A HOC-containing sp^3-hybridized carbon-halogen bond can undergo dehalogenation transformation via several routes: nucleophilic substitution, dehydrohalogenation, and reductive dehalogenation (*7*). Mono- and dihalogenated organic compounds, which contain sp^3-hybridized carbon−halogen bonds, are capable of bimolecular nucleophilic substitution (S_N2) reactions in the presence of nucleophiles (*8*−*10*). Polyhalogenated alkanes with high oxidation states are subject to dehydrohalogenation and/or reductive dehalogenation (*7*). We previously discovered that thiosulfate ($S_2O_3^{2-}$) may react effectively with a variety of halogenated fumigants such as MeBr, 1,3-dichloropropene (1,3-D), chloropicrin (CP), methyl iodide (MeI), and propargyl bromide (*11*−*13*). Recently, Zheng et al. observed rapid nucleophilic substitution reaction of MeI with thiourea in solutions and soils (*14*). Also, other researchers have shown that polysulfides are highly reactive toward chlorinated compounds such as chloroacetanilide and chloroazine herbicides at environmentally relevant concentrations (*9*, *10*).

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The primary objective of this study was to investigate reaction kinetics and mechanisms between polysulfides and three halogenated fumigants, i.e., MeI, 1,3-D, and CP, and to compare their reactivity between polysulfides and other sulfur-containing nucleophiles. Both 1,3-D and CP are important alternatives to MeBr, while MeI is currently being developed as a potential MeBr replacement (*15*, *16*).

EXPERIMENTAL PROCEDURES

Chemicals. Standards of 1,3-D (48% cis and 49% trans isomers) and CP (99%) were purchased from Chem Service (West Chester, PA). MeI (99.5%) was obtained from Aldrich (St. Louis, MO). Sodium tetrasulfide (99.0%) was purchased from Great Western Inorganics (Arvada, CO). Polysulfide solutions were prepared by dissolving sodium tetrasulfide crystals in a deoxygenated borate buffer (pH 9.0) under nitrogen. The stock solution of polysulfides was stored in a nitrogen atmosphere to prevent oxidation.

Stability of Sulfur Species. Multiple polysulfide dianions (S_n^{2-}, $n = 2-5$) are present in the aqueous sodium tetrasulfide solution (*17*−*21*). Previous studies indicated that polysulfides are thermodynamically unstable (*17*−*21*). To better characterize the reaction between polysulfides and fumigants, we first conducted experiments to investigate the stability of polysulfide dianions in solutions prepared in ambient atmosphere or purged with nitrogen. Analysis of polysulfide dianions was carried out by gas chromatography (GC) after methylation using the method of Lippa and Roberts (*9*). The initial sodium tetrasulfide concentration was either 0.2 or 1.0 mM in the aqueous phase. After different time intervals elapsed, a 1.0 mL aliquot (three replicates) was withdrawn from the reaction mixture vial using a syringe and transferred to a 20 mL borosilicate glass vial containing 200 μL of MeI. The glass vials were immediately capped with Teflon-faced silicone septa and seals and then heated in a water bath at 60 °C for 1 h. After they were cooled to room temperature, all treated samples were extracted with 4.0 mL of pentane and 3 g of anhydrous sodium sulfate. An aliquot of the solvent extract was immediately transferred to a GC vial for analysis of individual polysulfides by a GC-mass selective detector (MSD).

Methylated polysulfide derivatives were analyzed on an Agilent 6890N GC (Agilent, Wilmington, DE) equipped with an Agilent 5973 MSD in the electron impact ionization mode. Separation was achieved on a DB-1701 capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness; Agilent) with a flow rate of 1.0 mL min^{-1} (helium). To prevent sample decomposition and desulfurization in the inlet, pulsed splitless injection mode was used with the pressure set at 25 psi for 0.4 min. The total splitless time was 0.5 min. The oven temperature was initially set at 45 °C for 2.0 min, ramped to 170 °C at 20 °C min^{-1}, then to 240 °C at 30 °C min^{-1}, and finally to 280 °C at 30 °C min^{-1}. Ion source and quadrupole temperatures were 230 and 150 °C, respectively. The inlet temperature was 210 °C, and the temperature of the transfer line between GC and MSD was maintained at 280 °C. The mass spectrometer analysis was performed with a full scan mode from 50 to 500 amu. The ions used for quantitation were *m*/*z* 94 and 79 for the S_2^{2-} derivative, *m*/*z* 126, 111, and 79 for the S_3^{2-} derivative, and *m*/*z* 158, 111, and 94 for the S_4^{2-} derivative. Under the given conditions, the retention times of S_2^{2-}, S_3^{2-}, and S_4^{2-} derivatives were 4.1, 6.4, and 8.6 min, respectively. As standards of these sulfur dianions were not available, peak areas were used directly to calculate the first-order half-life ($T_{1/2}$) of the different polysulfide dianions. The total concentration of the sulfur anions, representing the sum of all reduced sulfur species (H_2S, HS^-, S^{2-}, S_n^{2-}, HS_n^-, and H_2S_n), was determined by the iodometric titration method (*22*). The sodium thiosulfate solution was standardized against potassium iodate.

Kinetics Experiments. Transformation of the three fumigants by polysulfides was studied in aqueous solutions with different initial concentrations of sodium tetrasulfide. The reaction was initiated by adding 0.2 mL of fumigant stock solution (10 mM, in acetone) into 9.8 mL of borate buffer solution containing sodium tetrasulfide at different concentrations in 20 mL crimp-top glass vials. The initial concentration of fumigant in the reaction mixture was 0.2 mM, and that of sodium tetrasulfide was 0 (blank), 0.2, 0.5, or 1.0 mM. The vials were immediately sealed with Teflon-faced butyl rubber septa and aluminum caps and incubated at room temperature (20 ± 1 °C). To evaluate the effect of oxygen in the reaction, a similar experiment was conducted in oxygen-free solutions. The overall experimental procedure was similar to that described above, but sodium tetrasulfide solution was purged with nitrogen and fumigant spiking was preformed in nitrogen in a gastight inflatable glove chamber (Cole Parmer, Vernon Hills, IL).

After different time intervals from the initiation of the reaction, a 1.0 mL aliquot of reaction solution (triplicate) was withdrawn from each treated vial using a gastight syringe (Hamilton, Reno, NV) and immediately transferred into a glass vial containing 4.0 mL of hexane and 3 g of anhydrous sodium sulfate. All sample vials were mixed vigorously for 2 min, and then, an aliquot of the hexane extract was transferred into GC vials for measurement of fumigant concentration on an Agilent 6890N GC equipped with a micro-ECD. A pulsed splitless mode was used for injection with splitless pressure at 25 psi for 0.4 min, and the total time was 0.5 min. Separation was carried out on a RTX-624 capillary column (30 m × 0.53 mm i.d. × 3.0 μm film thickness; Restek, Bellefonte, PA) with a flow rate of 5.0 mL min^{-1} (helium). The inlet temperature was 210 °C, and the detector temperature was 260 °C. The oven temperature was initially set at 45 °C for 2.0 min, ramped to 170 °C at 20 °C min^{-1}, then to 240 °C at 40 °C min^{-1}, and finally held at 240 °C for 4.45 min. Under these conditions, the retention times of MeI, *cis*-1,3-D, *trans*-1,3-D, and CP were 2.9, 7.2, 7.6, and 7.7 min, respectively. The recovery was >95% for all fumigants using the above extraction and analytical procedure.

Identification of Reaction Products. To understand the reaction mechanisms, reaction products between sodium tetrasulfide and the fumigants were tentatively identified using a protocol similar to that of Lippa and Roberts (*9*). In brief, 5.0 mM fumigant and 50 mM sodium tetrasulfide were mixed for 60 min at room temperature. Aliquots (1.0 mL) of the reaction solutions were transferred into a 20 mL glass vial and methylated with 200 μL of MeI. The treated sample vial was incubated in a water bath at 60 °C for 1 h. After it was cooled to room temperature, the aqueous sample was extracted using a procedure similar to that given for polysulfide dianions. The same analytical conditions for the GC and MSD analysis, as described above, were used to identify the methylated reaction products.

Kinetics Evaluation. The rate of reaction of fumigants with polysulfide species may be expressed by a second-order kinetic equation:

$$\frac{dC}{dt} = -k_s XC \tag{1}$$

where C is the concentration of fumigant (M), X is the concentration of polysulfide (M), t is the elapsed time (s), and k_s is the second-order rate constant (M^{-1} s^{-1}). Upon rearrangement and integration, a solution of eq 1 is

$$C = C_0 \frac{(X_0 - C_0)\exp[-k_s(X_0 - C_0)t]}{X_0 - C_0\exp[-k_s(X_0 - C_0)t]} \tag{2}$$

where C_0 and X_0 are the initial concentrations of fumigant and polysulfides, respectively (*23*). The second-order rate constant (k_s) may be obtained from nonlinear least-squares fit of the experimental data to eq 2. The 50% disappearance time DT_{50} may be estimated from eq 3 (*23*):

$$DT_{50} = \frac{\ln(2 - C_0/X_0)}{kX_0(1 - C_0/X_0)} \tag{3}$$

RESULTS AND DISCUSSION

Stability of Tetrasulfide Solution. Sodium tetrasulfide solution is known to contain a host of sulfur species including H_2S, HS^-, S^{2-}, S_2^{2-}, S_3^{2-}, S_4^{2-}, and S_5^{2-} (*17*−*21*). Through semiquantitative analysis of individual polysulfide species, S_2^{2-}, S_3^{2-}, S_4^{2-}, and S_5^{2-} were found to be the most abundant polysulfide dianions in the tetrasulfide solution at pH 9. This

Table 1. First-Order Half-Life $T_{1/2}$ (h^{-1}) and Correlation Coefficient r^2 of Sulfur Species in Borate Buffer Solution under Different Conditions

sulfur dianion	tetrasulfide concn (mM)	tetrasulfide concn (mM) based on titration	air-exposed		nitrogen-purged	
			$T_{1/2}$ [a]	r^2	$T_{1/2}$	r^2
S_2^{2-}	0.2	0.16	10.5	0.93	866	0.10
	1.0	0.80	126.0	0.49	3300	0.82
S_3^{2-}	0.2	0.16	2.4	0.70	22.2	0.77
	1.0	0.80	25.7	0.83	∞	
S_4^{2-}	0.2	0.16	1.6	0.92	4.7	0.90
	1.0	0.80	8.7	0.60	12.8	0.77

[a] Half-life values for sulfur species were calculated using a pseudo first-order model, $T_{1/2} = \ln 2/k_f$.

observation was similar to the findings of previous studies (*9*, *25*), in which S_4^{2-} was found to be the most abundant polysulfide dianion based on the equilibrium speciation diagram of polysulfide species, followed by S_5^{2-} and S_3^{2-}. Licht and Davis (*17*, *20*) reported that in highly alkaline solution, S_5^{2-} had a lower concentration relative to the other polysulfide species due to its rapid decomposition by hydroxide.

Polysulfides in the sodium tetrasulfide solution were found to be unstable, and the stability varied with the conditions under which the reaction solution was prepared. Dissipation of polysulfide dianions over time was fitted to a first-order decay model to estimate their half-life $T_{1/2}$ (h) (**Table 1**). Among the three polysulfide dianions investigated, the stability decreased in the order $S_2^{2-} > S_3^{2-} > S_4^{2-}$. For instance, in the tetrasulfide solution (0.2 mM) prepared in ambient air, dissipation $T_{1/2}$ of S_2^{2-}, S_3^2, and S_4^{2-} was 10.5, 2.4, and 1.6 h, respectively. The $T_{1/2}$ values were 126, 25.7, and 8.7 h, respectively, in the nitrogen-purged solution. Previous studies showed that tetrasulfide (S_4^{2-}) readily underwent disproportionation to an equilibrium mixture of polysulfides in the tetrasulfide solution at pH 9 (*9*).

The polysulfide dianions were more stable in high-concentration tetrasulfide solutions and in nitrogen (**Table 1**). For instance, when the initial tetrasulfide concentration was increased from 0.2 to 1.0 mM, the $T_{1/2}$ of S_2^{2-}, S_3^{2-}, and S_4^{2-} increased by 12, 11, and 5 times, respectively (**Table 1**). Further improvement in stability occurred when the solution was purged with nitrogen to eliminate oxygen. For example, when the initial tetrasulfide concentration was 0.2 mM, $T_{1/2}$ values of the polysulfide dianions increased by 2.9−82-fold after nitrogen purge as compared to the air-exposed solutions (**Table 1**). In the tetrasulfide solution with high initial concentration (e.g., 1.0 mM), $S_2^{2-}$and S_3^{2-} became highly stable in nitrogen (**Table 1**). These results suggest that polysulfides undergo oxidation by molecular oxygen. Steudel (*21*) reported that aqueous polysulfide ions rapidly took up molecular oxygen to produce thiosulfate and elemental sulfur. The dependence of stability of polysulfide dianions on its concentrations was in agreement with Licht and Davis (*17*). Therefore, the variation in instability of polysulfide species under different conditions should be considered when evaluating the reaction kinetics of fumigants with polysulfides.

Fumigant Transformation Kinetics. In the borate buffer solution (pH 9), the hydrolysis $T_{1/2}$ of MeI, *cis*-1,3-D, *trans*-1,3-D, and CP was estimated to be 204, 161, 165, and 1155 h, respectively. The persistence of these compounds in the borate solution was generally less than that in the neutral water, where the corresponding $T_{1/2}$ values were 7250, 330, 216, and 2009 h (*13*, *24*). The enhanced hydrolysis of fumigants in the borate buffer may be attributed to the high pH, as the hydroxyl group is known to be a stronger nucleophile than water in leading to an increased hydrolysis of alkyl halides (*25*).

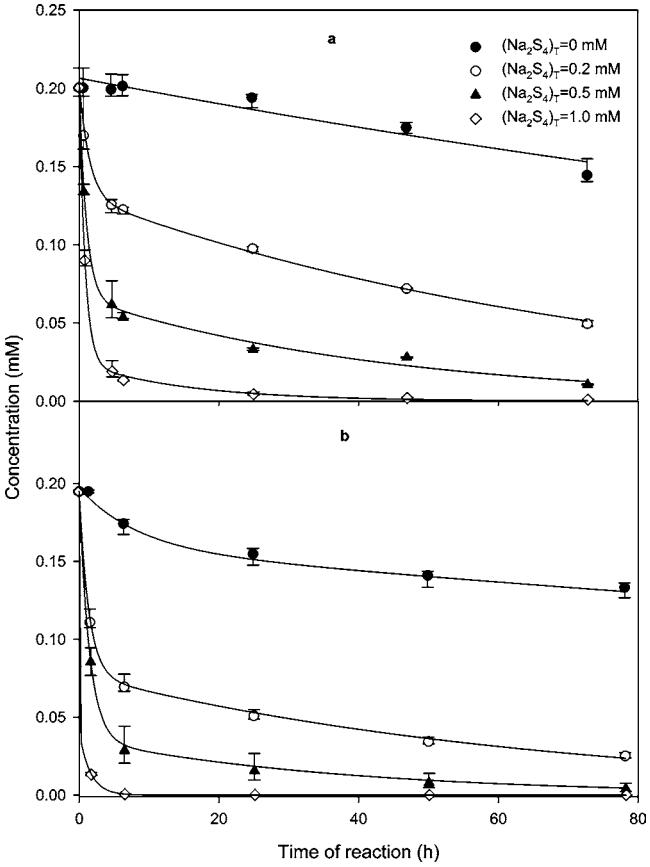

Figure 1. Dissipation of *cis*-1,3-D (0.2 mM) (**a**) in air-exposed solutions of sodium tetrasulfide and (**b**) in nitrogen-purged solutions of sodium tetrasulfide.

Table 2. Second-Order Dissipation Rate Constant k_s (M^{-1} s^{-1}), 50% Disappearance Time DT_{50} (h), and Correlation Coefficient of Fumigants (0.2 mM) in Sodium Tetrasulfide Solutions[a]

fumigant	initial Na_2S_4 (mM)	air-exposed			nitrogen-purged		
		k_s	DT_{50}	r^2	k_s	DT_{50}	r^2
MeI	0	0.0033	210.04	0.52	0.0014	495.10	0.45
	0.2	0.0506	27.44	0.83	0.0189	73.47	0.83
	0.5	0.1176	3.70	0.97	0.0850	5.12	0.90
	1.0	0.0906	2.23	0.98	0.2647	0.77	0.93
cis-1,3-D	0.0	0.0043	161.20	0.59	0.0051	135.91	0.88
	0.2	0.0469	29.61	0.92	0.1378	10.08	0.84
	0.5	0.1367	3.18	0.95	0.1964	2.22	0.91
	1.0	0.1311	1.56	0.96	0.2739	0.74	0.96
trans-1,3-D	0	0.0042	165.03	0.31	0.0072	96.27	0.81
	0.2	0.0136	102.10	0.80	0.0578	24.02	0.76
	0.5	0.0492	8.84	0.90	0.0869	5.01	0.95
	1.0	0.0533	3.83	0.98	0.1308	1.56	0.97
CP	0.0	0.0006	1155.24	0.89	0.0007	990.21	0.55
	0.2	0.6790	7.4	0.34	–	–	–
	0.5	1.2866	0.34	0.53	–	–	–

[a] k_s and DT_{50} for the control (0 mM) were estimated using a first-order relationship.

Polysulfides consistently enhanced fumigant disappearance in the borate buffer solution. The decline of *cis*-1,3-D concentration over time is shown in **Figure 1a** for air-exposed solutions and in **Figure 1b** for nitrogen-purged solutions. The dissipation of fumigant as a function of time was modeled using eqs 2 and 3 to derive k_s and DT_{50} (**Table 2**). Under similar conditions, transformation of CP by polysulfides was much more rapid than

MeI or 1,3-D isomers. For instance, when the initial tetrasulfide concentration was 0.2 mM, the DT_{50} of CP was only ~3 h in air-exposed solutions, which was many times shorter than that for MeI or 1,3-D. The reaction of polysulfides with CP in nitrogen-purged solutions proceeded so rapidly that an accurate measurement of the reaction kinetics was impossible. This implies that the reaction mechanism with polysulfides may be different for CP than for MeI or 1,3-D.

The dissipation rates of the fumigants consistently increased with increasing initial tetrasulfide concentration (**Table 2**). For instance, in air-exposed solutions, the DT_{50} of *cis*-1,3-D was 29.6 h when the initial concentration of tetrasulfide was 0.2 mM and decreased to 3.2 and 1.6 h, respectively, in 0.5 and 1.0 mM tetrasulfide solutions (**Table 2**). After nitrogen purge, the DT_{50} of *cis*-1,3-D was 10.1, 2.2, and 0.7 h, respectively, in tetrasulfide solutions at 0.2, 0.5, and 1.0 mM. Similar trends were observed also for MeI and *trans*-1,3-D.

Between the two isomers of 1,3-D, the cis isomer dissipated more rapidly than the trans isomer in either air-exposed or nitrogen-purged solutions (**Table 2**). The relative reactivity of 1,3-D isomers with polysulfides may be explained by the steric hindrance of the substituted groups on the primary carbon (C3). The stereostructure of 1,3-D suggests that the spatial hindrance for polysulfide to approach C_3 should be similar for both isomers. However, in a nucleophilic attack by polysulfide dianions, the nucleophile and 1,3-D form a crowded transition state. In the transition state, the potential rotation of the C2−C3 bond of *cis*-1,3-D will be hindered by the chlorine at C1, which destabilizes the transition complex, leading to its more rapid dissociation relative to that for the trans isomer.

At the same initial concentration, the persistence of each fumigant was consistently shortened when the tetrasulfide solutions were first purged with nitrogen (**Table 2**). As compared to the air-exposed treatments, the rate constant of reaction, k_s, in the nitrogen-purged treatments (1.0 mM) increased by 3.0-, 2.1-, and 2.5-fold for MeI, *cis*-1,3-D, and *trans*-1,3-D, respectively. The faster reaction in nitrogen may be attributed to the elimination of oxygen and the improved stability of the polysulfide dianions in the solution. Because the stability of polysulfide dianions was closely dependent on the initial tetrasulfide concentration and oxygen status, the observed k_s values were only approximate values. Consequently, measurements made with nitrogen and high polysulfide concentrations should give a more accurate description of the actual reaction kinetics.

The reactivity between the fumigants and the polysulfides is generally greater than that of the fumigant dehalogenation reaction with thiosulfate observed in previous studies (*13*, *24*). In air-exposed solutions, the second-order rate constant for thiosulfate and fumigants was 0.019, 0.017, and 0.002 $M^{-1}\ s^{-1}$ for MeI, *cis*-1,3-D, and *trans*-1,3-D, respectively (*13*). Under comparable conditions, the reaction of these fumigants with polysulfides was 5−22 times faster than that with thiosulfate. In Zheng et al. (*14*), the second-order rate constant for the reaction of MeI and thiourea in pH 9.0 buffer solution was 1.98 $\times 10^{-2}\ mM^{-1}\ h^{-1}$ ($5.5 \times 10^{-3}\ M^{-1}\ s^{-1}$). Therefore, the reaction of MeI with polysulfides was ~14 times faster than that with thiourea under similar conditions. Lippa and Roberts (*9*) noted that the nucleophilicity of polysulfide dianions S_n^{2-} was greater than HS^- toward chlorozaines. The rapid reaction of polysulfides and halogenated fumigants suggests that polysulfide salts may be even a better choice than thiosulfate salts or thiourea for decontaminating fumigant residues in various environmental media.

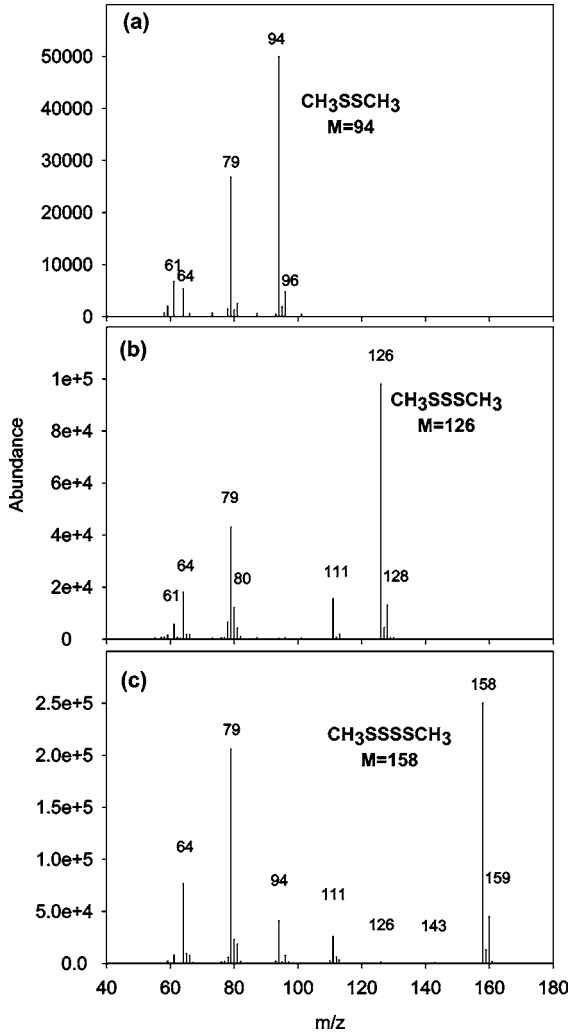

Figure 2. Mass spectra and proposed structures for initial reaction products between MeI and polysulfides following methylation.

Reaction Pathways. Reaction products of the selected fumigants with polysulfide dianions were qualitatively analyzed by GC-MSD following methylation. Three major MeI sulfur-substituted products were detected with significant molecular ions M^+ at *m*/*z* 94, 126, and 158, respectively (**Figure 2**). These mass spectra were consistent with the following dimethyl sulfur compounds: $CH_3-S-S-CH_3$, $CH_3-S-S-S-CH_3$, and $CH_3-S-S-S-S-CH_3$. Because a methyl group (CH_3) was expected to methylate a $-S^-$ group during methylation, the initial reaction products were tentatively identified as CH_3-S-S^-, $CH_3-S-S-S^-$, and $CH_3-S-S-S-S^-$. On the basis of the identified reaction products and a proposed S_N2 reaction, tentative transformation pathways of MeI by polysulfides are depicted in **Figure 3a**. Overall, a polysulfide dianion attacks CH_3I and directly replaces the iodine atom. However, it is likely that the number of sulfur atoms measured in this study may not reflect the identity of those products initially formed during the reaction, as the alkylated polysulfide products may undergo desulfurization by nucleophiles in the reaction solution to form a shorter sulfur chain (*9*, *10*).

The reaction products of 1,3-D and polysulfides were also identified after methylation (**Figure 4**). Reaction of 1,3-D with polysulfides yielded a number of products. Some major products were identified as $S(CH_2-CH)-CH_2-S^-$, $^-SCH{=}CH-CH_2S^-$, $Cl-CH{=}CH-CH_2SSS^-$, and $^-SSCH{=}CH-CH_2SS^-$. The partial reaction pathways for 1,3-D and polysulfides are proposed in **Figure 3b**. Polysulfides attack the sp^3-hybridized carbon (C3)

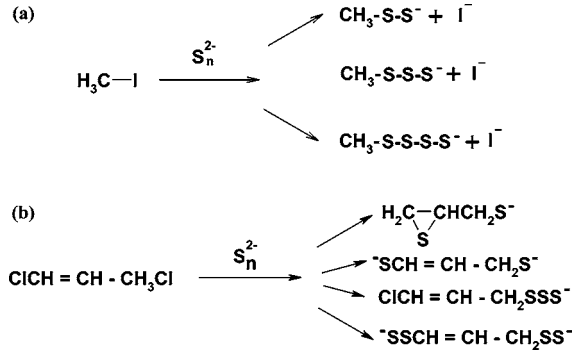

Figure 3. Proposed pathways of fumigant transformation by polysulfides: (**a**) MeI and (**b**) 1,3-D.

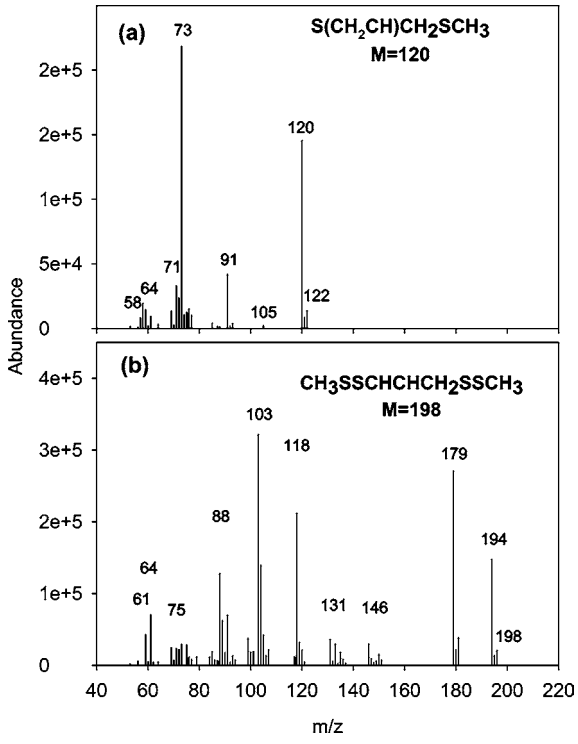

Figure 4. Mass spectra and proposed structures for initial reaction products between 1,3-D and polysulfides after methylation.

and replace the chlorine at C3 via S_N2 nucleophilic substitution. In addition, substitution may also occur at the sp^2-hybridized carbon (C1) due to the strong nucleophilicity of the polysulfide anions (*7*).

Analysis of the reaction mixture of CP and polysulfides by GC-MSD did not yield any useful information since the reaction was too rapid. However, it was observed that once CP was added into polysulfide solution, the colorless solution immediately changed into a reddish violet hue and a sweet odor was formed. From an early publication (*26*), alkali polysulfide solutions were found to destroy CP via a reductive dechlorination pathway. The transformation products were methylamine, carbon monoxide, and nitric oxide. As such, a redox reaction mechanism was suggested for the reaction of CP with hydrogen sulfide species (*27*). Therefore, transformation of CP by polysulfides as observed in this study may also be assumed to be a reductive dechlorination reaction.

In conclusion, this study showed that halogenated fumigants were readily dehalogenated in sodium tetrasulfide solutions. The reaction mechanism was likely S_N2 nucleophilic substitution for MeI and 1,3-D and reductive dehalogenation for CP caused by polysulfide dianions. As compared to previous studies, the results of this study suggest that the halogenated fumigants are much more reactive toward polysulfides than thiosulfate or thiourea (*11*−*14*). Because the wide availability of polysulfide salts and the high reactivity toward HOCs, polysulfide species have a great potential to be used for decontaminating fumigant residues. After the dehalogenation of the halogenated fumigants, these compounds are likely detoxified since previous studies have shown that the biological activity of alkyl halides originates from the halogen substitution (*28*, *29*). The potential applications of this reaction may include disposal of unused fumigant wastes, fumigant-containing wastewater, and flue gases. However, many other aspects must be studied before this reaction is used for remediation, e.g., toxicological characteristics of the transformation products.

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