Environ. Sci. Technol. **2000**, *34,* 3717−3721

Transformation and Detoxification of Halogenated Fumigants by Ammonium Thiosulfate

Q. WANG,† J. GAN,*
S. K. PAPIERNIK, AND S. R. YATES
U.S. Salinity Laboratory, Soil Physics & Pesticides Research Unit, 450 West Big Springs Road, Riverside, California 92507

Fumigants are commonly used at high rates (100−400 kg ha^{-1}) in warm regions to control soil-borne pests. Many fumigants, however, tend to move easily from the treated soil into the atmosphere or groundwater, resulting in air or groundwater pollution. We studied the transformation of the fumigants methyl bromide (MeBr), propargyl bromide (PBr), 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl iodide (MeI) by fertilizer ammonium thiosulfate (ATS). All fumigants were rapidly dehalogenated by thiosulfate via nucleophilic substitution, and the rate of transformation followed the order MeBr ≈ MeI > PBr > 1,3-D > CP. For all fumigants, the reaction followed second-order kinetics with activation energy of ∼73 kJ mol^{-1}, suggesting a similar rate-limiting step. In soil, amendment of ATS at 1.0 mmol kg^{-1} accelerated fumigant dissipation by 21−63 times for MeBr, MeI, and PBr and by 4.6−5.5 times for 1,3-D and CP. Preliminary toxicity assays using the luminescent bacterium *Vibrio fisheri* showed that ATS transformation largely eliminated the acute toxicity of fumigants to this organism. These results suggest that thiosulfate transformation of halogenated fumigants is likely a benign chemical approach that may be used for mitigating environmental and health risks in fumigation.

Introduction

Soil fumigants are heavily used in the production of many food crops for controlling nematodes and other soil-borne pests (*1, 2*). Most of the currently used fumigants are highly volatile halogenated compounds. After injection into soil, fumigants tend to diffuse rapidly in soil, and as a result, a significant fraction can enter the atmosphere or groundwater. Air and groundwater contamination by fumigants has toxicological significance due to their acute toxicity, probable carcinogenicity, or other adverse effects (*3*). For instance, discovery of residues in groundwater led to the ban of ethylene dibromide (EDB) and 1,2-dibromo-3-chloropropane (DBCP) in the early 1980s (*2*). Recently, atmospheric pollution by methyl bromide (MeBr) and 1,3-dichloropropene (1,3-D) during soil fumigation resulted in regulatory restrictions of their use (*4*−*6*).

We previously reported on the rapid transformation of MeBr and 1,3-D by thiosulfate salts in water and soil (*7, 8*). The reaction was defined as S_N2 nucleophilic substitution, in which MeBr and 1,3-D were dehalogenated by thiosulfate. Laboratory and field studies showed that application of thiosulfate fertilizers at the soil surface substantially decreased volatilization of these two fumigants due to rapid fumigant transformation (*7, 8*). Because ammonium thiosulfate (ATS) and potassium thiosulfate (KTS) are fertilizers that are relatively innocuous, there is a great promise to use this approach for field applications. Similar applications may also include treatment of fumigant wastes at manufacturing or dealership sites and disposal of formulation containers.

In this study, we extended our investigation to include all halogenated fumigants and compounds that are potential alternatives to MeBr. The test compounds consisted of MeBr, methyl iodide (MeI), propargyl bromide (PBr), chloropicrin (CP), and 1,3-D. Among these compounds, MeBr, CP, and 1,3-D are currently registered halogenated fumigants, while MeI and PBr are being developed as alternatives to MeBr (*9*−*12*). The specific objectives of this study were to (i) determine the transformation rate of these fumigants by ATS, (ii) to describe transformation mechanisms by evaluating reaction kinetics and activation energies, and (iii) to demonstrate that the transformation products are less toxic than the parent fumigants.

Experimental Section

Chemicals. Methyl bromide (>99%) was provided by TriCal (Hollister, CA). Propargyl bromide (97%) and ATS (>99%) were purchased from Fluka (Buchs, Switzerland). 1,3-Dichloropropene (47% cis and 51% trans), CP (99%), and MeI (99.5%) were purchased from Chem Service (West Chester, PA). Selected properties of the five fumigants are given in Table 1.

Soil and Bacterial Tester. The soil used in the incubation study was an Arlington sandy loam soil (coarse-loamy, mixed, thermic Haplic Durixeralf) that was sampled from the University of California, Riverside Agricultural Experiment Station in Riverside, CA. Soil organic matter content was 0.92% at pH 7.2. The test organism used in the acute toxicity assay was a luminescent bacterium (*Vibrio fisheri*) purchased from AZUR Environmental (Carlsbad, CA).

Aqueous-Phase Experiments. Transformation of fumigants by ATS was first studied in the aqueous phase with different initial ATS concentrations. Reaction was initiated by adding fumigants (1.0 mM) to 100-mL ATS solutions of known concentrations (0, 1.0, 2.0, 4.0 or 8.0 mM) in 125-mL serum bottles. The initial ATS:fumigant molar ratio was therefore 0:1, 1:1, 2:1, 4:1, or 8:1. The serum bottles were sealed with Teflon-faced septa and aluminum caps and then equilibrated at 20 ± 0.3 °C in the dark. After 2, 4, 8, 24, 48, and 96 h, 0.5-mL aliquots (triplicate) were withdrawn from each container using a gas-tight syringe and transferred into sealed glass vials containing 5.0 mL of ethyl acetate and 3.0 g of anhydrous sodium sulfate. The sample vials were vigorously vortexed for 2 min, and the ethyl acetate phase was analyzed on a Hewlett-Packard HP 6890 gas chromatograph (GC) equipped with an electron capture detector. The conditions used for GC analysis were a Rtx-624 column (30 m × 250 μm × 1.4 μm), 1.1 mL min^{-1} column flow rate, 220 °C inlet temperature, and 300 °C detector temperature. The oven was held at 40 °C for 3 min and then increased at 15 °C min^{-1} to 140 °C and kept at 140 °C for 2.0 min.

Measured fumigant concentrations were fitted to the following first-order decay kinetics to obtain the first-order decomposition rate constant k_f for the fumigant:

$$\text{fumigant disappearance} = k_f[\text{F}] \qquad (1)$$

* Corresponding author telephone: (909)369-4804; fax: (909)342-4964; e-mail: jgan@ussl.ars.usda.gov.
† Present address: Chemistry Department, Zhejiang University, Hangzhou, China.

10.1021/es000973z CCC: $19.00
Published on Web 07/22/2000

TABLE 1. Selected Physical–Chemical Properties of Halogenated Fumigants Used in This Study

compound	formula	boiling point (°C)	solubility (%)	vp (mmHg)	Henry's law constant	ref
methyl bromide	CH_3Br	4	1.4	1800	0.24	*13*, *14*
methyl iodide	CH_3I	42	1.4	398	0.21	*13*, *15*
propargyl bromide	C_3H_3Br	89	1.5	180	0.05	*11*, *13*
chloropicrin	CCl_3NO_2	112	0.23	24	0.01	*13*, *16*
1,3-dichloropropene	$C_3H_4Cl_2$	104–113	0.22	23–34	0.05	*14*, *17*

where [F] is the remaining fumigant concentration measured at time t. Under the assumption of S_N2 reaction, the overall reaction rate should obey a second-order kinetics (*21*):

$$\text{reaction rate} = k[\text{F}][S_2O_3^{2-}] \quad (2)$$

where $[S_2O_3^{2-}]$ is thiosulfate concentration, and k is the second-order reaction rate constant ($M^{-1}\ s^{-1}$). The k_f values derived from measured data were further correlated with the initial $[S_2O_3^{2-}]$ using eq 2 to estimate k. A linear relationship between k_f and $[S_2O_3^{2-}]$ would suggest second-order reaction kinetics that is characteristic of S_N2 reactions.

At each sampling time, 0.25-mL aliquots (triplicate) were additionally removed from the 2:1 treatment for analysis of ions. The samples were diluted with deionized water and analyzed on a Dionex DX-100 ion chromatograph (IC) for Cl^-, Br^-, and $S_2O_3^{2-}$ ions. An AS40 automated sampler was used for sample delivery, and an AS14 column (Dionex, Sunnyvale, CA) was used for separation. The mobile phase was made of 3.5 mM Na_2CO_3 and 1.0 mM $NaHCO_3$, and the flow rate was 1.0 mL min^{-1}.

In a second experiment, fumigant transformation by ATS was determined at different temperatures to obtain the activation energy of reaction (E_a). Similar procedures as given above were used to prepare reaction media, and the initial ATS and fumigant concentrations were 2.0 and 1.0 mM, respectively. The substrates were equilibrated at four temperatures, and the actual temperatures were recorded as 6.1, 19.7, 30.3, and 39.6 °C, with variation of <0.5 °C. After initiation of the reaction, 0.5-mL aliquots (triplicate) were withdrawn from each sample container and extracted with ethyl acetate using the same procedure as given above. Fumigant concentration in the ethyl acetate extract was determined on GC.

Soil Incubation Experiment. Fumigant transformation by ATS was further determined in soil. Soil was premixed with ATS at 0 or 1.0 mmol kg^{-1}, and soil water content was adjusted to 11.0% (w/w). Ten grams (dry weight equivalent) of the blank or ATS-amended soil in 20-mL glass vials was spiked with 5 μL of 1000 mM fumigant solution in acetone. The initial fumigant concentration in soil was 0.5 mmol kg^{-1}, and the initial ATS:fumigant molar ratio was 0:1 (control) or 2:1. The treated vials were immediately sealed with Teflon-faced rubber septa and aluminum caps and incubated at 20 ± 0.3 °C in the dark. At 0, 2, 4, 8, 24, 48, and 96 h after treatment, triplicate vials were removed and transferred immediately to a freezer (−21 °C) to stop the reaction. To analyze fumigant residues in soil, sample vials were opened when the soil was still frozen, and 10.0 g of anhydrous sodium sulfate and 10.0 mL of ethyl acetate were added. After the soil was thawed at room temperature, the vials were vigorously shaken for 2 min on a vortexer. A fraction of the ethyl acetate extract was transferred to a GC vial for analysis. Preliminary experiments showed >85% recovery for all fumigants using the above extraction procedures.

Toxicity Assay. The toxicity of fumigants before and after transformation by ATS was determined using a luminescent bacterium (*V. fisheri*). This bacterium has been frequently used for testing acute toxicity of both organic and inorganic toxicants in environmental samples (*18*–*20*). The test is based on the toxicant-induced suppression of bacterial luminescence in 2% NaCl solution. Standard procedures suggested by the manufacturer were followed in this study. Prior to the test, fumigant solutions (2.0 mM) were spiked with ATS (20 mM), and the mixtures were allowed to equilibrate at room temperature for >2 d. Analysis on GC showed that all fumigants were completely transformed by thiosulfate after the equilibration. These solutions, along with fumigant solutions (2.0 mM) with no ATS additions, were sequentially diluted with 2% NaCl and then exposed to test bacteria for 5 min in cuvettes. The light intensity was recorded at 490 nm using a SLM 8000 spectrofluorometer (SLM Instruments, Urbana, IL). Activity of 2% NaCl was measured simultaneously and used as the background to derive the relative light intensity. As the unreacted ATS could contribute to the activity in the ATS–fumigant mixtures, selected samples were also measured using ATS solution as the reference. Bacterial EC_{50} was determined by plotting the relative light intensity against fumigant concentration after logarithmic conversion and solving for the concentration at which 50% reduction in luminescence occurred.

TABLE 2. First-Order Dissipation Rate Constant k_f (h^{-1}) of Fumigants (1.0 mM) in Water and Ammonium Thiosulfate (ATS) Solutions

fumigant	initial ATS concn (mM)	rate constant k_f (h^{-1})	half-life $t_{1/2}$ (h)	r
methyl bromide (MeBr)	0	9.19×10^{-4}	754	0.55
	1.0	0.021	32.4	0.96
	2.0	0.103	6.7	1.00
	4.0	0.264	2.6	1.00
	8.0	0.554	1.2	1.00
methyl iodide (MeI)	0	9.56×10^{-5}	7250	0.43
	1.0	0.018	37.7	0.95
	2.0	0.082	8.5	0.99
	4.0	0.225	3.1	0.99
	8.0	0.487	1.4	1.00
propargyl bromide (PBr)	0	2.23×10^{-4}	3108	0.46
	1.0	0.021	33.6	0.96
	2.0	0.071	9.8	0.99
	4.0	0.149	4.6	0.98
	8.0	0.421	1.6	0.99
chloropicrin (CP)	0	3.45×10^{-4}	2009	0.31
	1.0	6.09×10^{-3}	114	0.92
	2.0	0.019	37.3	0.93
	4.0	0.023	30.1	0.86
	8.0	0.019	35.7	0.78
1,3-dichloropropene (1,3-D)	0	2.37×10^{-3}	292	0.99
	1.0	0.016	43.9	0.98
	2.0	0.027	26.2	0.97
	4.0	0.035	19.7	0.94
	8.0	0.067	10.4	0.94

Results and Discussion

Transformation Kinetics. Fitting of fumigant dissipation with time using a first-order model showed that except for CP, as the initial ATS:fumigant ratio increased, the quality of regression as indicated by the correlation coefficient (r) quickly improved (Table 2). Fumigant dissipation in water was negligible during the 96-h experiment. In ATS solutions, the rate of fumigant dissipation consistently increased with

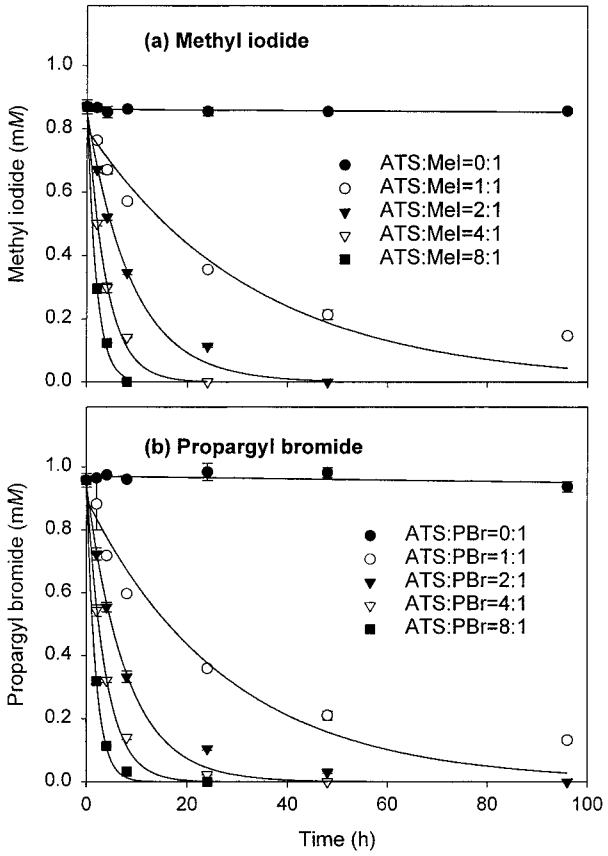

FIGURE 1. Dissipation of fumigants (1 mM) in aqueous solution with different initial concentrations of ammonium thiosulfate (ATS): (a) methyl iodide and (b) propargyl bromide.

TABLE 3. Reaction Rate Constant *k* (M^{-1} s^{-1}) and Regression Coefficient *r* of Fumigants and Ammonium Thiosulfate in Aqueous Phase at 20 °C

fumigant	*k*	*r*
methyl bromide	2.11×10^{-2}	1.00
methyl iodide	1.87×10^{-2}	1.00
propargyl bromide	1.59×10^{-2}	0.99
chloropicrin	3.5×10^{-4}	0.70
1,3-dichloropropene	1.95×10^{-3}	0.99

increasing ATS concentration (Table 2 and Figure 1). For instance, in solutions containing 2.0 mM ATS, the half-life ($t_{1/2}$) of MeI decreased from 754 to 8.5 h and that of PBr decreased from 3108 to 9.8 h (Figure 1 and Table 2). When the ATS concentration was further increased to 8.0 mM, the $t_{1/2}$ of MeI and PBr was only 1.4 and 1.6 h, respectively.

The second-order reaction constant *k* was calculated for each fumigant by plotting k_f vs the initial concentration of ATS using eq 2. Good correlation was found for all fumigants except CP, with correlation coefficients $r \geq 0.99$ (Table 3). These observations suggest that reaction between fumigants and ATS in aqueous solution follow second-order kinetics typically exhibited by S_N2 reactions (*22*). For different fumigants, the rate of transformation followed the order MeBr ≈ MeI > PBr > 1,3-D > CP, and the difference was tested significant at $P = 0.01$ (Table 3). The relative reactivity of these fumigants with $S_2O_3^{2-}$ may be explained from steric hindrance of substitution groups and the tendency for the leaving group (Br, I, or Cl) to leave during nucleophilic substitution. As the nucleophile ($S_2O_3^{2-}$) would attack a fumigant molecule from the direction opposite to the leaving group (Br, I, or Cl), a bulky substitution on the primary

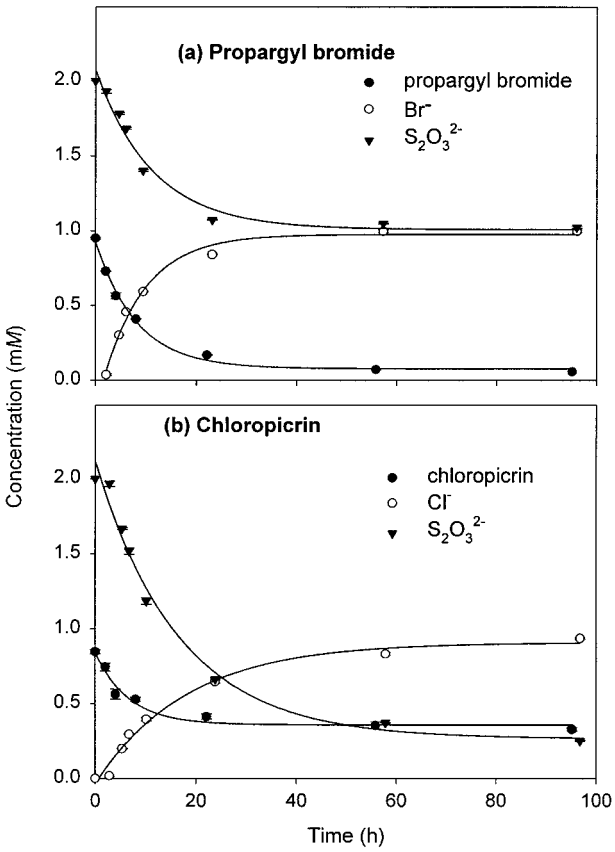

FIGURE 2. Consumption of fumigant (1 mM) and thiosulfate (2 mM) and accumulation of halogen ions in aqueous phase during fumigant transformation by ammonium thiosulfate: (a) propargyl bromide and (b) chloropicrin.

carbon would prevent easy approaching of the incoming nucleophile, rendering the reaction slower (*21*). With only substitutions of hydrogen, MeBr and MeI are thus more susceptible to nucleophilic attack than CP, 1,3-D, and PBr. On the other hand, Br and I are better leaving groups than Cl in S_N2 reactions (*21*), which may have separated PBr (with Br) from CP and 1,3-D (with Cl). The triple bond on the second and third carbons in PBr may have further enhanced the tendency for Br to leave in a nucleophilic substitution reaction (*23*, *24*).

The poor fit of CP dissipation to second-order kinetics (Tables 2 and 3) suggests a different mechanism for CP−thiosulfate interaction. Analysis for fumigant, $S_2O_3^{2-}$, and halogen ions showed that during the transformation of MeBr, MeI, PBr, and 1,3-D, $S_2O_3^{2-}$ and fumigant were consumed at the same rate, while substrate consumption coincided with the production of halogen ions, as shown for PBr in Figure 2a. However, in the transformation of CP, consumption of $S_2O_3^{2-}$ was nearly four times greater than that of CP, while accumulation of Cl^- was about two times faster than the dissipation of CP (Figure 2b). It is likely that more than one of the three Cl atoms were replaced by $S_2O_3^{2-}$ in the transformation or that other reactions occurred that consumed additional $S_2O_3^{2-}$.

Temperature Dependence of Fumigant Transformation by ATS. As temperature increased, fumigant transformation by ATS in the aqueous phase increased proportionally (Figure 3). Similar temperature dependence was observed for all the test fumigants, suggesting that thiosulfate-induced fumigant transformation was an endothermic reaction. Fumigant transformation rate constants at different temperatures were used to derive the reaction activation energy (E_a) using the Arrhenius equation. The activation energy (E_a) was

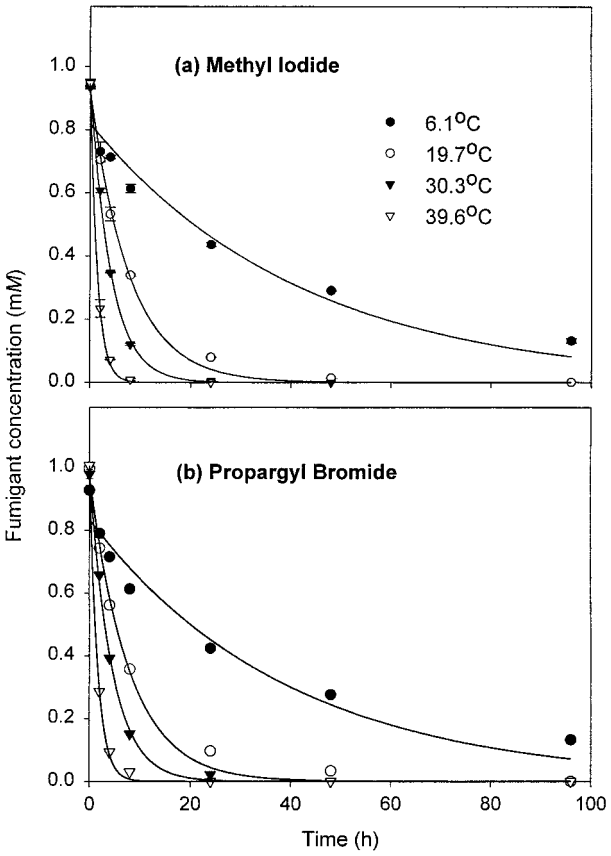

FIGURE 3. Transformation of fumigants (1 mM) by ammonium thiosulfate (2 mM) in aqueous phase at different temperatures: (a) methyl iodide and (b) propargyl bromide.

TABLE 4. First-Order Dissipation Rate Constant k_f (h^{-1}) of Fumigants (1.0 mM) in Ammonium Thiosulfate (ATS) Solution (2.0 mM) at Different Temperatures

temp (°C)	first-order rate constant, k_f (h^{-1})				
	MeBr	MeI	PBr	CP	1,3-D
6.1	0.025	0.019	0.019	0.010	0.011
19.7	0.126	0.087	0.094	0.040	0.046
30.3	0.286	0.219	0.236	0.113	0.094
39.6	0.760	0.578	0.592	0.305	0.277
E_a (kJ mol^{-1})	73.3	73.4	73.7	73.5	72.4

72.4−73.7 kJ mol^{-1} for the five fumigants tested (Table 4). With an E_a of this magnitude, fumigant transformation would increase by ~2.8 times with every 10 °C increase in temperature (*25*). The fact that temperature had essentially the same effect for all fumigants suggests that they may share a similar rate-limiting step in their reaction with $S_2O_3^{2-}$.

Positive correlation of fumigant transformation with temperature may have implications for practical application. Fumigation is typically conducted when soil is relatively warm. It is common that the field is immediately covered with polyethylene films after fumigation, which has been found to result in substantial temperature increases near the soil surface (*26*, *27*). Therefore, the effectiveness of using thiosulfate products to transform fumigants is likely to be influenced by soil and environmental conditions and may be optimized via fumigation timing or procedures.

Transformation of Fumigants in ATS-Amended Soil. Thiosulfate-facilitated fumigant transformation was further determined using soil as the reaction medium. Fumigant dissipation in ATS-amended Arlington soil was well described by first-order kinetics (Table 5). Compared to the unamended

TABLE 5. Half-Lives (h) of Fumigants (0.5 mmol kg^{-1}) in Arlington Sandy Loam with and without Amendment of Ammonium Thiosulfate (ATS) at 1.0 mmol kg^{-1}

fumigant	half-life (h)	
	ATS-amended	blank control
methyl bromide	20.5 (0.99)[a]	1300 (0.53)
methyl iodide	23.5 (0.98)	495 (0.91)
propargyl bromide	12.9 (0.97)	290 (0.93)
chloropicrin	30.1 (0.97)	139 (0.95)
1,3-dichloropropene	29.7 (0.98)	162 (0.99)

[a] Values in parentheses are regression coefficient *r*.

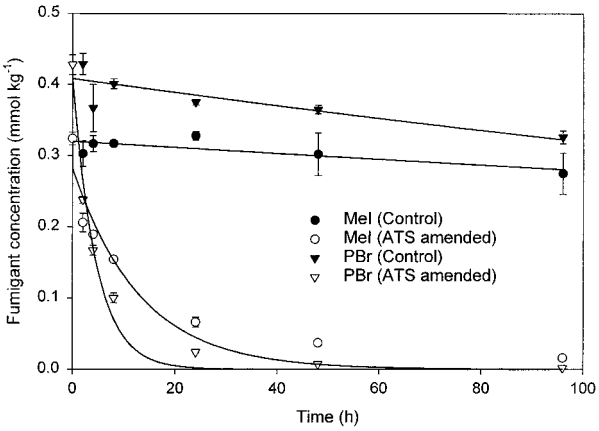

FIGURE 4. Dissipation of methyl iodide (MeI) (0.5 mmol kg^{-1}) and propargyl bromide (PBr) (0.5 mmol kg^{-1}) in blank soil and soil amended with ammonium thiosulfate (ATS) at 1.0 mmol kg^{-1}.

soil, the persistence of each fumigant greatly decreased after amending ATS at 1.0 mmol kg^{-1} (Figure 4). For MeBr, MeI, and PBr, $t_{1/2}$ of fumigant in soil was shortened by 21−63 times after ATS addition, while that of 1,3-D and CP was reduced by 4.6−5.5 times. The different enhancement may be caused by the fact that some fumigants (i.e., 1,3-D and CP) were more degradable in the unamended soil than the others (i.e., MeBr, MeI, and PBr), and the relative contribution of ATS-facilitated transformation was thus different. In ATS-amended soil, fumigant transformation rate varied much less among different fumigants than in the aqueous phase, and the overall order was PBr > MeBr ≈ MeI > 1,3-D ≈ CP (Table 5). This order may be attributable to the different transformation rates as observed in the aqueous phase and to different partition behavior among phases. In a vial filled with soil, a fumigant is distributed in the air, water, and solid (soil) phases, while ATS−fumigant reaction may only take place in the aqueous phase. Therefore, although MeBr and MeI reacted with ATS the most rapidly, they tend to distribute predominantly in the headspace, as suggested by their Henry's law constant (Table 1), which would slow their transformation by ATS in the solution phase. In contrast, PBr, 1,3-D, and CP should be present mainly in soil water, favoring aqueous-phase reaction with ATS. The relatively rapid reaction of PBr with ATS in aqueous phase, along with its affinity for the solution phase, may have determined that PBr degraded faster than all the other fumigants in ATS-treated soils.

Alteration of Fumigant Toxicity by Transformation. Bacterial EC_{50} increased significantly after fumigants were transformed by ATS (Table 6), suggesting that the transformed products were substantially less toxic than the parent fumigants. The greatest reduction was observed with CP, for which the bacterial toxicity was reduced by nearly 200 times after ATS transformation. It was clear that ATS was only slightly active to the test organism when compared with the

TABLE 6. Changes in Bacterial EC_{50} Values of Fumigants before and after Reaction with Ammonium Thiosulfate in Aqueous Phase

fumigant	EC_{50} (mM) fumigant solution	EC_{50} (mM) detoxified fumigant solution	difference (times)[a]
methyl bromide	1.22	4.38	3.6
methyl iodide	2.95	8.11 (>1000)[b]	2.7 (>300)
propargyl bromide	0.38	1.11 (2.58)	2.9 (6.7)
1,3-dichloropropene	0.13	0.99 (>100)	7.4 (>700)
chloropicrin	9.4×10^{-4}	0.18	191
ammonium thiosulfate	248		

[a] Difference was calculated by dividing EC_{50} after transformation over EC_{50} before transformation. [b] Values in parentheses were obtained by subtracting activity of unreacted ammonium thiosulfate through measurement.

unreacted fumigants. When the activity of the unreacted ATS was subtracted through measurement, EC*50* values for fumigant transformation products were even greater, as shown in Table 6 for MeI, PBr, and 1,3-D. Compared with the parent compound, transformation by ATS decreased the acute bacterial toxicity by 6.7 times for PBr and essentially eliminated the activity of MeI and 1,3-D (Table 6).

The biological activity of halogenated fumigants correlates with their alkylating ability (*28*). The activity arises from direct alkylation of critical biological molecules by fumigants via S_N2 reaction with functional groups such as sulfhydryl and amino groups (*28*, *29*). For instance, it has been shown that methyl halides conjugate with *S*-glutathione, forming methanethiol (*30*, *31*). It is likely that transformation by ATS removes the nucleophilic center (i.e., Cl, Br, or I) from the halogenated fumigants, thus deactivating them and inhibiting further reaction with biological systems. This suggests that fumigant transformation by ATS is a detoxification process. Given that ATS is a commercial fertilizer, the use of ATS is potentially feasible for alleviating environmental risks of fumigation and should be further investigated.

Acknowledgments

The authors thank Q. Zhang for help in obtaining some of the experimental data. This study is partially supported by USDA-CSREES-NIRCGP Grant 97-35107-4378.

Literature Cited

(1) Noling, J. W.; Becker, J. O. *J. Nematol.* **1994**, *26*, 573−586.
(2) Noling, J. W. In *Fumigants: Environmental Fate, Exposure and Analysis*; Seiber, J. N., et al., Eds.; ACS Symposium Series 652; American Chemical Society: Washington, DC, 1997; pp 14−24.
(3) Baker, L. W.; Fitzell, D. L.; Seiber, J. N.; Parker, T. R.; Shibamoto, T.; Poor, M. W.; Longley, K. E.; Tomlin, R. P.; Propeper, R.; Duncan, D. W. *Environ. Sci. Technol.* **1996**, *30*, 1365−1368.
(4) U.S. Environmental Protection Agency. *Fed. Regist.* **1993**, *58*, 15014−15049.
(5) California Department of Food and Agriculture (CDPA). *News Release* **1990**, *90*, 45.
(6) California Department of Pesticides Regulation (CDPR). *News Release* **1995**, *94*, 42.
(7) Gan, J.; Yates, S. R.; Becker, J. O.; Wang, D. *Environ. Sci. Technol.* **1998**, *32*, 2438−2441.
(8) Gan, J.; Becker, J. O.; Ernst, F. F.; Hutchinson, C. M.; Knuteson, J. A.; Yates, S. R. *Pestic. Man. Sci.* **2000**, *56*, 264−270.
(9) Zhang, W. M.; McGiffen, M. E.; Becker, J. O.; Ohr, H. D.; Sims, J. J.; Kallenbach, R. L. *Weed Res.* **1997**, *37*, 181−189.
(10) Becker, J. O.; Orh, H. D.; Grech, N. M.; McGiffen, M. E.; Sims, J. J. *Pestic. Sci.* **1998**, *52*, 58−62.
(11) Yates, S. R.; Gan, J. *J. Agric. Food Chem.* **1998**, *46*, 755−761.
(12) Hutchinson, C. M.; McGiffen, M. E.; Ohr, H. D.; Sims, J. J.; Becker, J. O. *Plant Dis.* **1999**, *83*, 33−36.
(13) *The Merck Index*; Budavari, S., et al., Eds.; Merck & Co: Whitehouse Station, NJ, 1996.
(14) *The Pesticide Manual*; Worthing, C. E., Ed.; The British Crop Protection Council: Surrey, U.K., 1991.
(15) Gan, J.; Yates, S. R. J. *Agric. Food Chem.* **1996**, *44*, 4001−4008.
(16) Schwazenbach, R. P.; Gschwend, P. M.; Imboden, D. M. In *Environmental Organic Chemistry*; Schwarzenbach, R. P., et al., Eds.; John Wiley & Sons: New York, 1993; pp 116−122.
(17) Leistra, M. *J. Agric. Food Chem.* **1970**, *18*, 1124−1126.
(18) Somasundaram, L.; Coats, J. R.; Racke, K. D.; Stahr, H. M. *Bull. Environ. Contam. Toxicol.* **1990**, *44*, 254−259.
(19) Galli, R.; Munz, C. D.; Scholtz, R. *Hydrobiologia* **1994**, *273*, 179−189.
(20) Kahru, A.; Tomson, K.; Pall, T.; Kulm, I. *Water Sci. Technol.* **1996**, *33*, 147−154.
(21) McMurry, J. In *Organic Chemistry*; McMurry, J. Ed.; Brook/Cole Publishing Co.: Pacific Grove, CA, 1992; pp 366−369.
(22) Atkins, P. W. In *Physical Chemistry*; Atkins, P. W., Ed.; Freeman & Co.: New York, 1987; pp 694−698.
(23) Moje, W.; Martin, J. P.; Baines, R. C. *J. Agric. Food Chem.* **1957**, *5*, 32−36.
(24) Moje, W. *J. Agric. Food Chem.* **1959**, *7*, 702−707.
(25) Schwazenbach, R. P.; Gschwend, P. M.; Imboden, D. M. In *Environmental Organic Chemistry*; Schwarzenbach, R. P., et al., Eds.; John Wiley & Sons: New York, 1993; pp 348−352.
(26) Katan, J.; DeVay, J. E. In *Soil Solarization*; Katan, J., et al., Eds.; CRC Press: Boca Raton, FL, 1991.
(27) Yates, S. R.; Gan, J.; Ernst, F. F.; Mutziger, A.; Yates, M. V. *J. Environ. Qual.* **1996**, *25*, 184−192.
(28) Yang, R. S. H.; Witt, K. L.; Alden, C. J.; Cockerham, L. G. *Rev. Environ. Contam. Toxicol.* **1995**, *142*, 65−85.
(29) Alexeeff, G. V.; Kilgore, W. W. *Residue Rev.* **1983**, *88*, 101−153.
(30) Barnsley, E. A.; Young, L. *Biochem. J.* **1965**, *95*, 77−81.
(31) Kornbrust, K. J.; Bus, J. S. *Toxicol. Appl. Pharmacol.* **1983**, *67*, 246−256.

Received for review February 7, 2000. Revised manuscript received June 12, 2000. Accepted June 13, 2000.

ES000973Z