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Transformation of Chloropicrin and 1,3-Dichloropropene by Metam Sodium in a Combined Application of Fumigants

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Combined application of fumigants is a potential strategy to replace methyl bromide in the control of soil-borne pests. Unfortunately, abiotic and biotic interactions among fumigants restrict some combined application approaches. In this study, the kinetics and mechanisms of reaction between metam sodium (sodium methyldithiocarbamate) and the halogenated fumigants chloropicrin (trichloronitromethane) and 1,3-dichloropropene (1,3-D) were investigated in aqueous solution. For chloropicrin, an extremely rapid oxidation−reduction process occurred in the presence of metam sodium. The second-order rate constant for the reaction between chloropicrin and metam sodium was approximately 2 orders of magnitude greater than that for the reaction between 1,3-D isomers and metam sodium. Transformation of 1,3-D by metam sodium was associated with an aliphatic S_N2 nucleophilic substitution process. The nucleophilic reaction of *cis*-1,3-D with metam sodium was significantly faster than that of the trans isomer and was correlated with a lower reaction activation energy for the cis isomer in the transition state. Combining Telone C-35 (65% 1,3-D and 35% chloropicrin) and metam sodium in solution might yield some nucleophilic sulfur species, which played an important role in the dissipation of 1,3-D. The incompatibility of chloropicrin and 1,3-D with metam sodium was also examined in soil under different application scenarios. Simultaneous application of metam sodium with chloropicrin or 1,3-D accelerated the transformation of the two halogenated fumigants, reducing their availability in soil. A sequential strategy for multiple fumigants was developed, which could be applied without the loss of active ingredient that occurs due to the reaction between fumigants. The proposed methodology may enhance pest control while maintaining environmental protection.

KEYWORDS: Fumigant; metam sodium; chloropicrin; 1,3-dichloropropene; transformation; simultaneous and sequential application

INTRODUCTION

Methyl bromide (MeBr) has been used extensively in agriculture as an indispensable pre-plant fumigant for decades. However, MeBr has been scheduled for phase-out in the United States and other industrialized countries because of its potential to deplete stratospheric ozone (*1*). The enormous economic impacts of the methyl bromide ban have triggered a feverish search for alternatives to MeBr. Although numerous nonchemical approaches have been proposed and developed as replacements for MeBr, unfortunately, most of these alternatives are less efficient or economical to meet current needs in soil-borne pest control. Therefore, chemical fumigation will likely continue to serve as a primary pest control practice in many economically important crops in the foreseeable future.

After the withdrawal of MeBr, a few registered soil fumigants will remain: chloropicrin, 1,3-dichloropropene (1,3-D), metam sodium and dazomet. None of these fumigants, however, can be considered an equivalent replacement for MeBr in most field applications because they lack the broad-spectrum activity of MeBr. For example, chloropicrin has strong funigicidal activity to control *Verticillium wilt* and beneficial nematicidal activity (*2*, *3*), but somewhat lacks activity against dormant weeds and seeds in soil (*4*). 1,3-D is an effective nematicide, but is not as effective as MeBr for weed and fungi control. To achieve the same pest control efficacy and crop yield obtained with MeBr, a stand-alone herbicide application would be required for adequate weed control after soil fumigation. Previous field research trials showed that Telone C-17 (83% 1,3-D + 17% chloropicrin) at 35 gal/ac may be a viable replacement for MeBr when combined with metolachlor or oryzalin at planting followed by a midsummer application of oryzalin (*5*). Metam sodium may be another option for weed control (*6*). According to a 1997 U. S. EPA study, metam sodium and plastic mulch controlled most

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weeds tested in the southeastern United States. Koster and van der Meer (*7*) found that soil treatment with metam sodium led to 90% yellow nutsedge control in The Netherlands. Therefore, metam sodium applied in combination with chloropicrin or 1,3-D has been attempted in some field trials to evaluate its potential to serve as a MeBr replacement (*4, 8*).

Metam sodium is a precursor of methyl isothiocyanate (MITC), which has pesticidal activity against nematodes, weeds, and fungi. Since 1995, the use of metam sodium has exceeded MeBr and it consistently ranks 3rd among all pesticides used in the U. S. (*9*). Metam sodium is relatively stable in water (e.g., Vapam HL, 42% metam sodium aqueous solution). Once in contact with warm soil or sediment, however, metam sodium decomposes rapidly to MITC. The conversion process is usually completed within a few hours to a day (*10*−*12*). Due to its high solubility, metam sodium can be applied with irrigation water through drip irrigation systems. Application of metam sodium via subsurface drip irrigation is attracting substantial attention, because this strategy may reduce application costs and mitigate the environmental and human health risks associated with fumigant emissions. However, problems achieving a uniform distribution of metam sodium or MITC in soil have resulted in inconsistent pest control and a lower crop yield than with MeBr treatment.

The realization that combinations of fumigants may broaden the spectrum of pest control has provided much of the impetus in the use of multi-fumigant formulations, such as commercial mixtures of 1,3-D with 17 and 35% chloropicrin (Telone C-17 and Telone C-35, respectively). However, the environmental impacts of a multi-fumigant formulation need to be determined and assessed prior to widespread adoption and use. Previous studies have shown that the application of multiple fumigants may have different effects on the soil environment compared to the individual fumigants, particularly on soil microorganisms (*13*, *14*). Furthermore, the different impacts of the fumigant mixtures on soil microbial communities may alter pesticide biotic transformation rates and affect their ultimate fate in the environment (*15*). Stiles et al. (*16*) reported that metam sodium would reduce soil microbial activity and thus protract the persistence of the herbicides EPTC and pebulate when applied in conjunction with metam sodium. Additionally, simultaneous application of multiple fumigants may lead to competitive degradation on the soil surface, which may alter the abiotic transformation rate in soil (*15*). Most noticeably, recent studies have shown that soil fumigation with metam sodium plus a mixture of 1,3-D and chloropicrin (Telone C35) did not increase strawberry yields compared to fumigation with metam sodium alone or Telone C35 alone, probably because of the reaction between the fumigants in aqueous solution (*4*). Therefore, extensive knowledge of the influence of fumigant mixture use on pest control efficiency and their transformation and persistence in the environment is necessary for successful application and operation of multiple fumigants in agriculture.

The objectives of this research were to (1) characterize the transformation of chloropicrin and 1,3-D by metam sodium in an aquatic environment and soil, (2) elucidate the incompatibility of simultaneous application for halogenated fumigants with metam sodium, and (3) propose a sequential strategy for multi-fumigant application. To comprehensively understand the reaction between metam sodium with chloropicrin and 1,3-D, the transformation processes were investigated systematically in the aqueous solution and soil, transformation products were identified and reaction mechanisms were proposed. The information obtained from these experiments is not only required in the instruction and regulation of multi-fumigant application in the field but is also necessary to accurately assess and predict the environmental fate of fumigants, to avoid or mitigate the risk to human and environmental health associated with fumigant application.

MATERIALS AND METHODS

Chemicals. Chloropicrin (99%) and metam sodium (dihydrate, 99%) were purchased from Chem Service (West Chester, PA). 1,3-Dichloropropene (Telone II, 50.5% cis and 46.9% trans isomer) was donated by Dow AgroSciences LLC (Indianapolis, IN). Methyl isothiocyanate (MITC) was obtained from Sigma Chemical Co. (St. Louis, MO). All chemicals were used as received.

Soil. The soil used in the incubation study was an Arlington sandy loam (coarse-loamy, mixed, thermic Haplic Durixeralf) that was collected from the University of California, Riverside Agricultural Experiment Station. Fresh soils were sampled from the top 15-cm (A horizon) of a field that has no history of fumigant application. Moist soils were passed through a 2.0-mm sieve without complete air-drying and stored at low temperature before use. Soil organic matter content was 0.92% and pH was 7.2.

Aqueous System Experiments. Transformation experiments between metam sodium and chloropicrin or 1,3-D were conducted to determine the reaction kinetics in pH 6.9 phosphate buffer solution at 21 ± 0.5 °C. Briefly, 1.0 mM solutions of chloropicrin, 1,3-D, or Telone C-35 (65% 1,3-D and 35% chloropicrin standard incorporated in lab) were prepared in aqueous solution, and aliquots were placed in 55-mL serum bottles. To initiate the reaction, all bottles were spiked with metam sodium stock solution using a gastight syringe. The initial molar ratio of metam sodium to chloropicrin or 1,3-D was 1:1 in the mixed aqueous solution. At regular intervals, aliquots (0.5 mL) were withdrawn from triplicate bottles and transferred into sealed glass vials containing ethyl acetate (3.0 mL) and anhydrous sodium sulfate (2.5 g). The vials were vigorously shaken for 10 min, and an aliquot of the ethyl acetate extract was immediately transferred to a GC vial for fumigant analysis. Preliminary experiments revealed that ethyl acetate efficiently extracted chloropicrin, 1,3-D and MITC from aqueous solution, while metam sodium remained in the aqueous phase. The reactions were quenched when solvent was added. Control experiments were concurrently performed in phosphate buffer solutions containing only chloropicrin, 1,3-D, or metam sodium to determine the hydrolysis of pesticides during the experimental period.

To identify transformation products, 10 mM metam sodium and 10 mM chloropicrin or 1,3-D were mixed in the aqueous solution and then incubated at room temperature. Aliquots of the solution were periodically extracted by ethyl acetate and analyzed by GC/MS.

Soil System Experiments. A series of experiments was conducted to elucidate the incompatibility between metam sodium and chloropicrin or 1,3-D when applied simultaneously to soil. In all cases, fumigant transformation was determined in fresh Arlington sandy loam at 21 ± 0.5 °C. Soil (10-g dry weight, initial moisture 4.6%) was weighed into 20-mL headspace vials. Soil vials were treated with chloropicrin, 1,3-D or Telone C-35 at 0.5 mmol/kg. The treated vials were sealed immediately with Teflon-faced butyl rubber septa and aluminum seals and then shaken to achieve uniform fumigant distribution in soil. Metam sodium solution (0.5 mL, 10 mM) was injected through the septum into the soil sample. Soil vials treated with only chloropicrin, 1,3-D or Telone C-35 were prepared and used as controls. All treated soils were shaken for 2.5 h at 21 ± 0.5 °C, and then chilled at −21 °C for 3h. To analyze the fumigant remaining in soil, samples were decapped when the soil was still frozen, anhydrous sodium sulfate (10 g) and ethyl acetate (10 mL) were added, and vials were resealed immediately. The samples were shaken for 1 h and vortexed for 2 min at room temperature. A portion of the ethyl acetate was transferred to a GC vial and analyzed using GC/ECD/NPD. The recovery of fumigants by this procedure ranged from 95 to 105% according to preliminary experiments.

A sequential treatment was also conducted to determine the fumigant transformation and demonstrate the application feasibility of metam sodium in conjunction with chloropicrin and 1,3-D in soil. Soil (10 g)

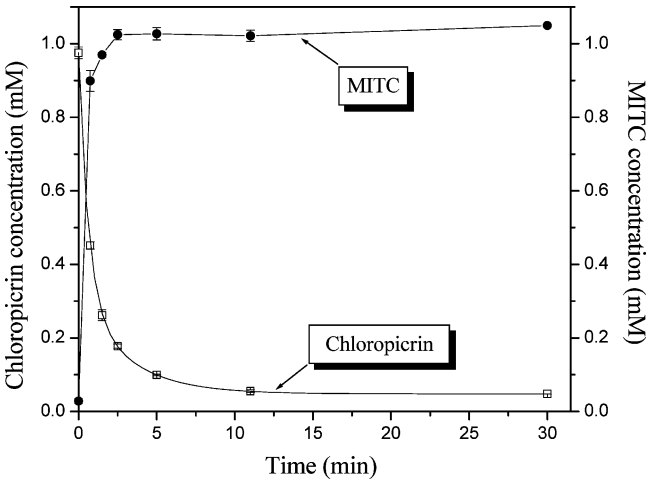


Figure 1. Transformation reaction of chloropicrin (1.0 mM) with metam sodium (1.0 mM) in pH 6.9 buffer solution at 21 °C. Error bars represent standard deviation of triplicate samples.

was treated with metam sodium at 0.5 mmol/kg and then incubated at 21 °C in the dark. After incubation for 2.5 h and 1 d, chloropicrin, 1,3-D or Telone C-35 solution (0.5 mL) was injected into sample vials using a gastight syringe, resulting in a concentration of 0.5 mmol/kg. The procedures described above were used for sampling, extraction, and analysis of residual fumigants in soils.

GC and GC/MS Analysis. Ethyl acetate extracts were analyzed for chloropicrin, 1,3-D and MITC using a Hewlett-Packard HP 6890 GC equipped with an on-column injector, a micro-electron capture detector (ECD) and a flameless nitrogen−phosphorus detector (NPD), 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 for both detectors. 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, monochloronitromethane, and dichloronitromethane were 10.97, 12.22, 13.56, 10.09, and 11.26 min on the ECD detector, respectively. MITC was analyzed simultaneously by the NPD detector, and its retention time was 11.10 min. Data were subjected to analysis of variance, and means were compared by least significant difference.

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 DISCUSSION

Reaction of Chloropicrin with Metam Sodium in Aqueous Solution. Initial experiments focused on the kinetics of chloropicrin reaction with metam sodium. In the control solutions containing only chloropicrin or metam sodium, no discernible pesticide degradation occurred during the experimental period. This observation is consistent with other reports that chloropicrin does undergo extremely slow hydrolysis without light and microorganisms (*17*, *18*). In buffer solution containing metam sodium, a substantially rapid disappearance of chloropicrin was observed (**Figure 1**), so that chloropicrin was almost completely dissipated within 10 min in the presence of metam sodium. In aqueous solution containing equimolar concentrations of chloropicrin and metam sodium, the second-order reaction rate coefficient (μ) and the 50% disappearance time (DT_{50}) for chloropicrin were obtained according to the equations described by Zheng et al. (*19*, *20*) (**Table 1**). The results indicated that the rapid reaction between chloropicrin and metam sodium resulted in a significant reduction of the aqueous persistence of both chemicals.

Table 1. Second-Order Transformation Rate Constant (μ) and 50% Dissipation Time (DT_{50}) for Chloropicrin and 1,3-D (1.0 mM) in Aqueous Solution Containing an Equal Initial Concentration Metam Sodium (1.0 mM) at 21 °C

fumigant	μ ($mM^{-1}\,min^{-1}$)	DT_{50} (min)	r^2
chloropicrin	1.73 (± 0.05)	0.58	0.996
cis-1,3-D	1.30 (± 0.03) × 10^{-2}	153.8	0.996
trans-1,3-D	3.90 (± 0.14) × 10^{-3}	532.0	0.984

As the reaction of chloropicrin with metam sodium proceeded, ethyl acetate extracts of the reaction mixture were analyzed by GC-MS. Three major metabolites were identified in the reaction process of chloropicrin and metam sodium; their mass spectra are exhibited in **Figure 2**. The EI spectrum indicates a significant molecular ion $M^{+\bullet}$ at *m*/*z* 73 (**Figure 2A**) and is consistent with an authentic standard of MITC. The identification of this product was further confirmed by its retention time on GC compared to that of authentic MITC. The MITC peak was invariably detected throughout the reaction process, and yields of MITC ranged between 97 and 103% in the final reaction solution. The dissipation of chloropicrin was accompanied by an increase in MITC (**Figure 1**), and the rate of MITC formation always equaled the rate of chloropicrin consumption.

Although not confirmed by an authentic standard, the other two major metabolites were identified as dichloronitromethane (Cl_2CHNO_2, **Figure 2B**) and monochloronitromethane ($ClCH_2NO_2$, **Figure 2C**) according to their mass spectra, which were consistent with those provided by Zheng et al. (*15*) and Castro et al. (*21*). The EI spectra of these two products do not demonstrate the formation of molecular ion $M^{+\bullet}$, but yield an intense fragment (parent − NO_2). This type of fragmentation is a typical characteristic of EI spectra of the family of chloronitromethanes, in which the parent ion is rarely observed (*21*).

Previous studies demonstrated that metam sodium could decompose to its breakdown product (MITC) via an oxidation process (*12*, *22*) and undergo an oxidation reaction in the presence of an oxidant (e.g., I_2, $FeCl_3$, or Br_2) (*23*). The oxidation potential of chloropicrin makes it susceptible to degradation via successive reductive dechlorination from chloropicrin to nitromethane under the reduction system. In the experiment, a rapid oxidation−reduction (redox) reaction occurred immediately once chloropicrin and metam sodium were combined in aqueous solution. Proposed reaction pathways of chloropicrin and metam sodium are depicted in **Scheme 1**: chloropicrin is rapidly decomposed to dichloronitromethane (**Scheme 1a**) and monochloronitromethane (**Scheme 1b**) within a few minutes via a reduction process ($Cl_3CNO_2 + H^+ + e^- \rightarrow Cl_2CHNO_2$ and $Cl_2CHNO_2 + H^+ + e^- \rightarrow ClCH_2NO_2$). Because the oxidation potential of chloronitromethane compounds decreases with an increasing number of hydrogen atoms in the molecule, a reactivity trend of $Cl_3CNO_2 > Cl_2CHNO_2 \gg ClCH_2NO_2$ is deduced for metam sodium. In the redox reaction system, metam sodium can completely convert to its expected product (MITC) via an oxidation process ($CH_3NHCSS^- \rightarrow CH_3NCS + H^+ + S + 2e^-$). Overall, the pest control efficacy and persistence of chloropicrin in the environment may be

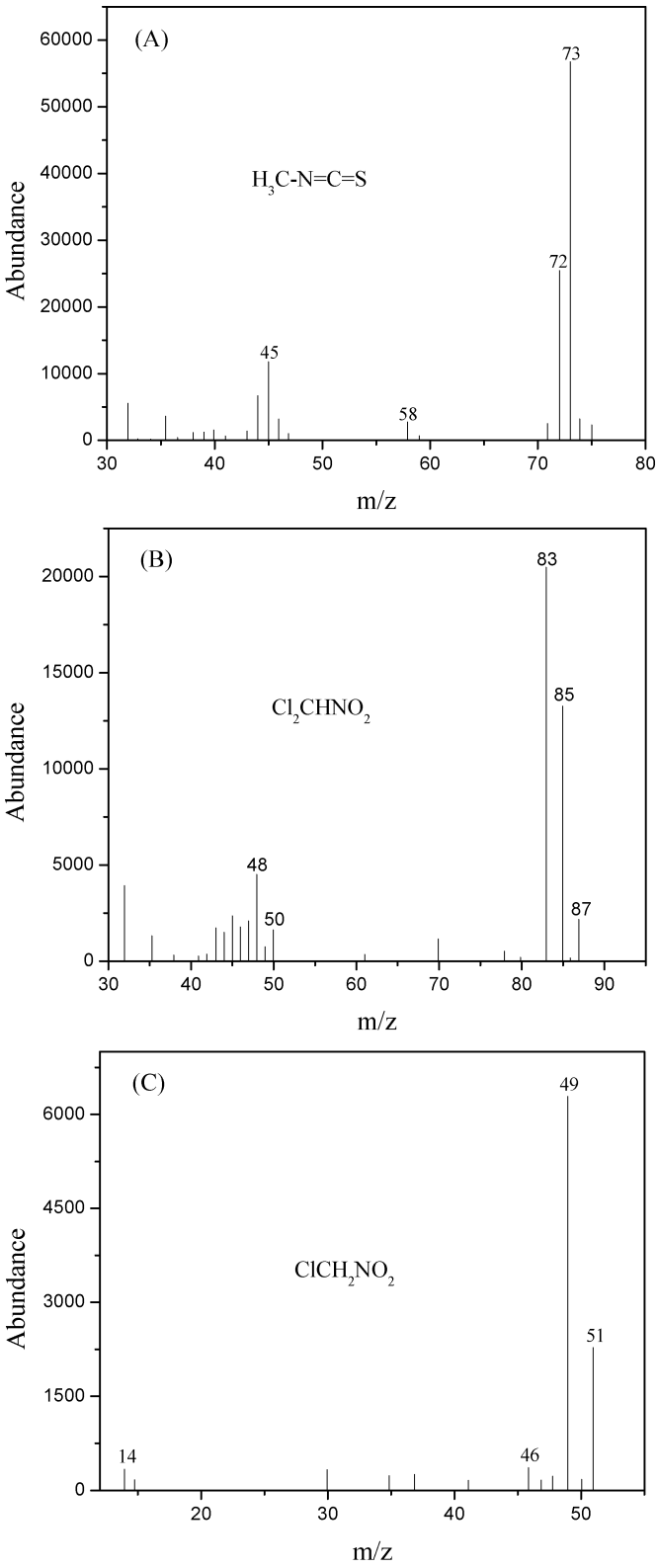


Figure 2. Mass spectra of products obtained from the reaction of chloropicrin with metam sodium.

Scheme 1

$$CH_3HNCSS^- + Cl_3CNO_2 \longrightarrow CH_3NCS + Cl_2CHNO_2 + Cl^- + S \quad (a)$$

$$CH_3HNCSS^- + Cl_2CHNO_2 \longrightarrow CH_3NCS + ClCH_2NO_2 + Cl^- + S \quad (b)$$

$$CH_3HNCSS^- + ClCH_2NO_2 \longrightarrow CH_3NCS + CH_3NO_2 + Cl^- + S \quad (c)$$

significantly altered because of the rapid transformation in the mixed fumigation system. The two principal reaction products (Cl_2CHNO_2 and $ClCH_2NO_2$) must be considered in evaluating the environmental behavior and health effects of chloropicrin when it is applied in conjunction with metam sodium.

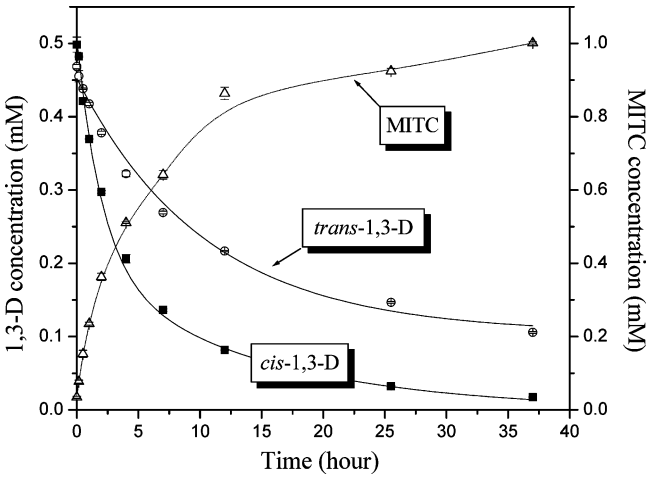


Figure 3. Transformation reaction of 1,3-D (1.0 mM, 50.5% *cis*- and 46.9% *trans*-1,3-D) with metam sodium (1.0 mM) in pH 6.9 buffer solution at 21 °C. Error bars represent standard deviation of triplicate samples.

Reaction of 1,3-D and Metam Sodium in Aqueous Solution. An example timecourse for 1,3-D reaction with metam sodium in aqueous solution is depicted in **Figure 3**. The transformation of 1,3-D by metam sodium was slow compared to that of chloropicrin, but dissipation of 1,3-D in metam sodium solution was more rapid than the hydrolysis rate of 1,3-D isomers (hydrolysis half-life >11 d) (*24*, *25*). At an initial concentration of 1.0 mM for both 1,3-D and metam sodium solution, the times of 50% *cis*- and *trans*-1,3-D dissipation were approximately 2.6 and 8.9 h, respectively (**Table 1**).

To investigate the reaction mechanism, transformation products were analyzed by periodically extracting the reaction solution. Four transformation products were characterized by GC/MS analysis. The mass spectrum and retention time of one transformation product was consistent with authentic MITC, which indicated that the major breakdown product of metam sodium was MITC. Two products have different retention times on the total ion chromatograms (TICs), but present consistent EI mass spectra (**Figure 4A**). These two transformation products gradually disappeared with the proceeding reaction between 1,3-D and metam sodium, and simultaneously, an additional product (**Figure 4B**) was formed.

On the basis of the identification of reaction intermediate products, a transformation mechanism is proposed for 1,3-D by metam sodium, which is different from chloropicrin. Similar to thiolate, a metam sodium anion (CH_3HNCSS^-) contains a strong nucleophilic center and is susceptible to S_N2 nucleophilic substitution reaction with halogenated hydrocarbons. It is proposed that metam sodium reacts with 1,3-D via the displacement of the chlorine at C3 to yield a dithiocarbamate substituted 1,3-D product (**Scheme 2**). Because 1,3-D is a mixture of cis and trans isomers, two corresponding transformation products (product 1 and 2 in Scheme 2) were observed to have different retention times but the same EI mass spectra (**Figure 4A**). The two sulfide products decompose to MITC and thiol, which may further convert to a symmetrical disulfide compound (product 3 in **Scheme 2**). The disulfide product peak increased in area with reaction time, and the disulfide compound and MITC were detected as major transformation products in the mixed solution of metam sodium and 1,3-D.

It was apparent that the transformation of *cis*-1,3-D by metam sodium was significantly faster than that of *trans*-1,3-D (**Figure**

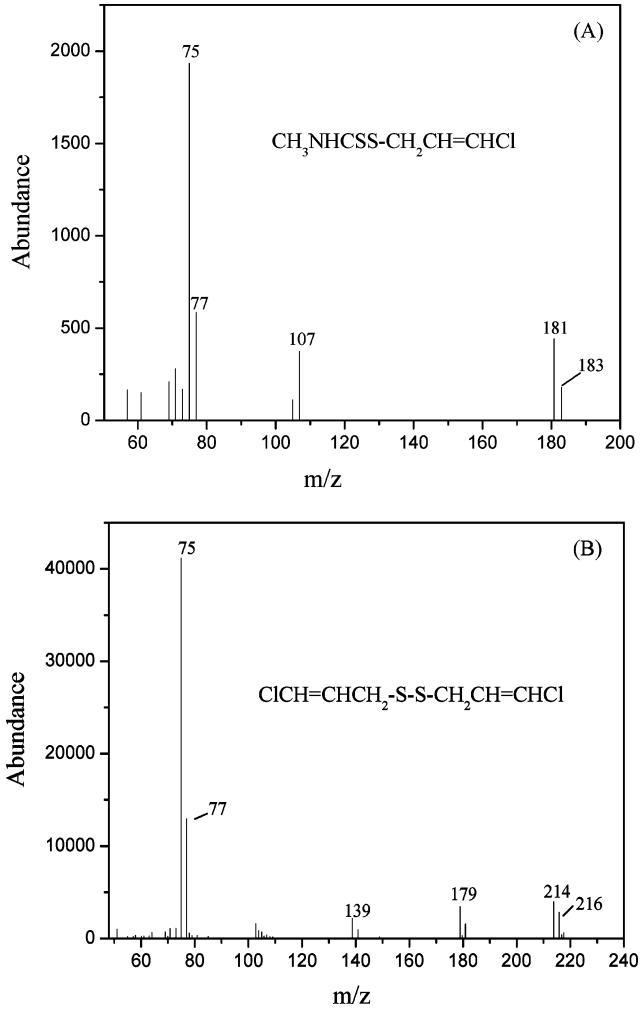


Figure 4. Mass spectra of products obtained from the reaction of 1,3-D with metam sodium.

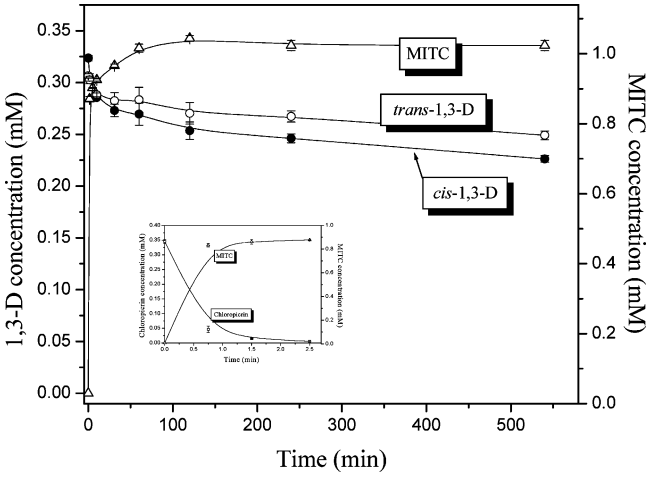


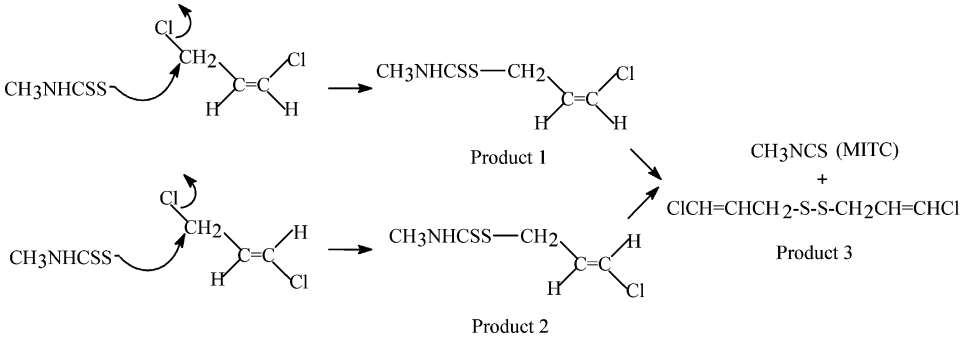
Figure 5. Transformation reaction of Telone C-35 (1.0 mM, 65% 1,3-D and 35% chloropicrin) with metam sodium (1.0 mM) in pH 6.9 buffer solution at 21 °C. Error bars represent standard deviation of triplicate samples.

3 and **Table 1**). According to the stereochemistry, the C═C bond and the four connected single bonds of 1,3-D are all in the same plane, suggesting that the spatial hindrance for approach of the nucleophile should be similar for both isomers (*26*). When the monomethyl dithiocarbamate anion (CH_3HNCSS^-) attacks 1,3-D (**Scheme 2**), a crowded transition state will be formed. In the transition state, the steric hindrance of cis form is greater than that of trans form. The greater static hindrance may facilitate further transformation of the cis transition state, yielding *cis*-1-chloro-3-dithiocarbamate-propene (product 1 in **Scheme 2**). The transition state of *trans*-1,3-D has higher stability in comparison with cis isomer, and the reaction with metam sodium shows a higher activation energy. This reaction mechanism is consistent with other similar nucleophilic reactions, for example, the reaction between 1,3-D and ATS (*25*, *26*) or Na-DEDTC (*15*). Also, GC/MS analysis showed that *cis*-1-chloro-3-dithiocarbamate-propene disappeared faster than the trans transformation product (product 2 in **Scheme 2**). The rapid dissipation of the cis intermediate product also facilitated the acceleration of the reaction of *cis*-1,3-D with metam sodium.

Reaction of Telone C-35 with Metam Sodium in Aqueous Solution. Telone C-35 solution in the experiment consists of 1,3-D (65%) and chloropicrin (35%). At an initial Telone C-35 concentration of 1.0 mM (sum of *cis*-1,3-D, *trans*-1,3-D, and chloropicrin), 1,3-D and chloropicrin exhibited different reactivity toward metam sodium (1.0 mM) in aqueous solution (**Figure 5**). The reactivity of the fumigants decreased in the following order: chloropicrin ≫ *cis*-1,3-D > *trans*-1,3-D. This reactivity is attributed to the different reaction mechanism between metam sodium and chloropicrin versus 1,3-D. The rapid oxidation−reduction reaction between chloropicrin and metam sodium preferentially occurred in the reaction system containing chloropicrin, 1,3-D, and metam sodium, so that chloropicrin was almost completely dissipated within a few minutes (**Figure 5**). The nucleophilic transformation of 1,3-D by metam sodium was much slower than the reduction of chloropicrin. These observations are consistent with the reaction rate constants shown in **Table 1**, in which the second-order transformation constant of chloropicrin is approximately 2 orders of magnitude higher than that of both 1,3-D isomers.

On the basis of the reaction process of chloropicrin and metam sodium (**Scheme 1**), one mole of chloropicrin may consume, theoretically, three moles of metam sodium. A stoichiometric

Scheme 2



analysis in this system indicated that a major proportion of the metam sodium reacted with chloropicrin in this experiment. Therefore, the release of MITC rapidly reached a maximum (1.0 mM) with the complete dissipation of chloropicrin, indicating metam sodium was completely consumed within a short reaction period (**Figure 5**). Note that even though the metam sodium was exhausted, dissipation of 1,3-D continued (**Figure 5**). **Scheme 1** showed that sulfur (S) was liberated as an inorganic product of metam sodium transformation by chloropicrin. In the redox reaction system, partial sulfurs can be further oxidized to yield a series of aqueous sulfur species, for example, sulfite (SO_3^{2-}), bisulfite (HSO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), tetrathionate ($S_4O_6^{2-}$), and sulfate (SO_4^{2-}). Evidence suggests several of these oxidized sulfur species (such as SO_3^{2-}, HSO_3^{2-}, and $S_2O_3^{2-}$) are powerful nucleophiles, and nucleophilic substitution reactions with halogenated aliphatic compounds may readily occur (*25*, *27*, *28*). The dissipation of 1,3-D observed in the absence of metam sodium in these experiments may have been due to S_N2 nucleophilic reaction between 1,3-D and certain nucleophilic sulfur species. The dissipation of *cis*-1,3-D was faster than that of the trans isomer, further suggesting the occurrence of a nucleophilic reaction in this system.

Simultaneous and sequential application of metam sodium with chloropicrin and 1,3-D in Soil. Metam sodium is highly unstable in the soil environment, undergoing rapid transformation to MITC. The decomposition of metam sodium and reaction with chloropicrin or 1,3-D will occur simultaneously when fumigant mixtures are applied to soil. The influence of combined application on the concentration of chloropicrin and 1,3-D in soil is depicted in **Figure 6**. Compared to control samples (no metam sodium, **Figure 6A**-a), approximately 40 to 50% of the applied chloropicrin was dissipated when applied simultaneously with metam sodium (**Figure 6A**-b), suggesting that a reaction occurred between metam sodium and chloropicrin in addition to the decomposition of metam sodium in soil. A sequential application of metam sodium and chloropicrin, however, may be effective in reducing the loss of chloropicrin to preserve pest control efficacy. The concentration of chloropicrin was substantially higher where metam sodium was applied to soil 2.5 h before addition of chloropicrin (**Figure 6A**-c). When metam sodium was added 24 h before chloropicrin, chloropicrin concentration (**Figure 6A**-d) was not significantly different from that in the control soil without metam sodium. These results suggest that metam sodium was completely dissipated within 24 h in soil, so that the reaction with chloropicrin did not occur. The yield of MITC was higher in the simultaneous application than in the sequential application (**Figure 6A**-b). Generally, the conversion of metam sodium to MITC ranges from approximately 70 to 90% in different soils (*22*, *29*). The reaction of metam sodium and chloropicrin could increase the conversion of metam sodium to MITC because its direct reaction product was MITC.

A similar influence of simultaneous application on the concentration of 1,3-D was observed (**Figure 6B**), although the decrease in 1,3-D concentration was not as significant as that of chloropicrin. These results suggest that the reaction mechanisms in soil were consistent with those in aqueous solution described above. The influence of metam sodium in sequential treatment with 1,3-D was different from that observed for chloropicrin. The maximum reduction of 1,3-D concentration in soil occurred when metam sodium was applied 2.5 h before the addition of 1,3-D (**Figure 6B**-c). The primary breakdown products of metam sodium in soil were HS^- and MITC ($CH_3NHCSS^- \rightarrow CH_3NCS + HS^-$). A wealth of literature has

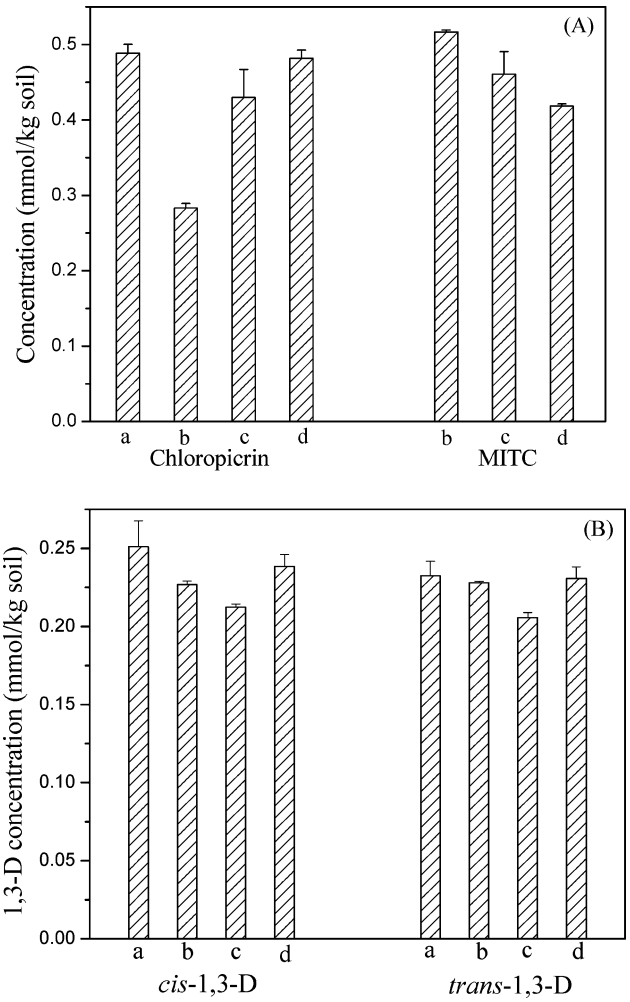


Figure 6. Influence of fumigant combined application on chloropicrin dissipation and MITC yield (**A**) and 1,3-D dissipation (**B**) in the Arlington sandy loam: (a) control (only chloropicrin or 1,3-D), (b) simultaneous application by metam sodium (0.5 mmol/kg), (c) sequential application by metam sodium 2.5 h early, (d) sequential application by metam sodium (0.5 mmol/kg) 24 h early.

reported the reactivity of HS^- associated with nucleophilic substitution with halogenated aliphatic compounds (*28*, *30*−*32*), and even with nucleophilic aromatic substitution with chlorozaines (*33*). The reduction of 1,3-D may be a result of HS^- nucleophilic reaction with 1,3-D. However, bisulfate is not stable in soil and gradually oxidized to SO_4^{2-}, so that when the time delay between metam sodium and 1,3-D application was increased to 24 h, no effect of metam sodium application on 1,3-D concentrations was observed (**Figure 6B**-d).

The influence of simultaneous and sequential application of Telone C-35 and metam sodium to soil was also investigated. The impact of metam sodium on the concentration of chloropicrin and 1,3-D in Telone C-35 was similar to that observed for chloropicrin and 1,3-D in isolation (**Figures 6** and **7**). Concentrations of chloropicrin and 1,3-D were decreased when metam sodium and Telone C-35 were applied simultaneously (**Figure 7**-b) as well as sequentially with a 2.5-h delay (**Figure 7**-c). The influence on chloropicrin concentration was more significant because of its high reactivity with metam sodium. The reaction between metam sodium and chloropicrin or 1,3-D was negligible if metam sodium was applied to soil 24 h before addition of Telone C-35 (**Figure 7**-d). It implies that sequential application

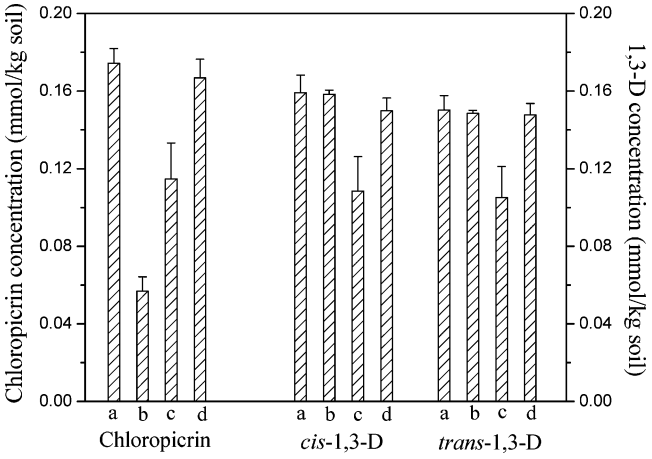


Figure 7. Influence of fumigant combined application on Telone C-35 (0.5 mmol/kg) in the Arlington sandy loam: (a) control, (b) simultaneous application by metam sodium (0.5 mmol/kg), (c) sequential application by metam sodium 2.5 h early, (d) sequential application by metam sodium (0.5 mmol/kg) 24 h early.

of chloropicrin and 1,3-D with metam sodium is likely a more effective strategy for multi-fumigant applications in the field.

Environmental Significance. Our results suggest that metam sodium is sufficiently reactive to alter the environmental fate of chloropicrin and 1,3-D, if they are simultaneously applied to soil or water. Metam sodium can accelerate the degradation of chloropicrin in the soil and aquatic environment by an oxidation−reduction reaction. The rapid transformation will have a profound effect on the suitability of multi-fumigant formulations in agronomic systems and could be a severe impediment to development of an adequate replacement for MeBr. However, the problem can be solved by a sequential application strategy. Sequential application of metam sodium followed by chloropicrin with a delay of 1 day may provide time for the conversion of metam sodium to MITC, which reduces the unnecessary loss of chloropicrin. On the other hand, chloropicrin may be first applied, and then metam sodium is followed after reaching the pest control target of chloropicrin. The transformation pathway of chloropicrin in mixture with metam sodium is similar to the degradation of chloropicrin itself in the environment via reductive dehalogenation (*18*, *21*). The sequential application practice could not only improve the convention efficacy of metam sodium to MITC but also eliminate the chloropicrin residue in soil and mitigate the potential phytotoxicity and negative environmental risk of fumigant. Therefore, further research is needed to comprehensively assess the impact of the sequential strategy on environment pollution prevention and pest control efficacy.

Reaction of metam sodium and 1,3-D followed an entirely different transformation pathway compared to the transformation of 1,3-D itself in the environment. Some sulfur-substituted transformation products are formed, which may necessitate future eco-toxicological assessments if metam sodium and 1,3-D are combined in field application. In addition, the high nucleophilicity of metam sodium indicates that it may also react with halogenated aliphatic compounds or pesticides, such as chloroacetanilide and triazine herbicides, via nucleophilic substitution processes.

Overall, the results of our experiments demonstrated the simultaneous application of metam sodium with chloropicrin and 1,3-D failed in maintaining fumigant efficacy. No significant influence on fumigant transformation, however, is expected if metam sodium is sufficiently converted to MITC prior to the addition of chloropicrin or 1,3-D. Furthermore, the influence of MITC as a major breakdown product of metam sodium on the abiotic and biotic transformation of chloropicrin and 1,3-D should be evaluated.

ABBREVIATIONS USED

1,3-D, 1,3-dichloropropene; MITC, methyl isothiocyanate; ATS, ammonium thiosulfate; Na-DEDTC, sodium diethyldithiocarbamate.

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