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ISOMERIC EFFECTS ON THIOSULFATE TRANSFORMATION AND DETOXIFICATION OF 1,3-DICHLOROPROPENE

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Abstract—The fumigant 1,3-dichloropropene (1,3-D) is one of the most heavily used pesticides but also a suspected carcinogen. Previous research has shown that 1,3-D was rapidly transformed and detoxified by ammonium thiosulfate (ATS), a sulfur and nitrogen fertilizer. As common formulations contain *cis* and *trans* isomers at roughly equivalent ratios, this study was conducted to understand isomeric differences in thiosulfate transformation and detoxification of 1,3-D. Under the same conditions, reaction of *cis*-1,3-D with thiosulfate was more than three times faster than *trans*-1,3-D, which was correlated with a lower reaction activation energy for the *cis* isomer. The *trans* isomer was considerably more toxic to the luminescent bacteria *Vibrio fisheri* than the *cis* isomer, but the toxicity was reduced by 14 times after thiosulfate transformation. Mutagenic activity to strains of *Salmonella typhimurium* was observed for *trans*-1,3-D but was not detected after thiosulfate transformation. These results suggest that thiosulfate transformation detoxifies 1,3-D primarily by deactivating the *trans* isomer, and the reaction is toxicologically beneficial, as it negates the potential harmful effects of 1,3-D to the environment and human health.

Keywords—1,3-Dichloropropene Ammonium thiosulfate Soil fumigants *Vibrio fisheri* Ames test

INTRODUCTION

The fumigant 1,3-dichloropropene (1,3-D) is widely used to fumigate soil for controlling soilborne nematodes and other pests. The annual use of 1,3-D during 1987–1997 was 13 to 20 million kg, which ranked at fourth to sixth among all pesticides used in the United States [1]. This use may increase further as the other major soil fumigant, methyl bromide (MeBr), is scheduled for a complete phaseout by 2005 [2]. Formulations of 1,3-D are typically injected into soils at depths of 30 to 45 cm by tractor-pulled chisels. Because of its high vapor pressure, 1,3-D has been shown to rapidly volatilize from treated fields, losing 20 to 77% of the applied material to the atmosphere [3–7]. Because 1,3-D is a B2 carcinogen and a skin and eye sensitizer, atmospheric emission of 1,3-D is a source of air pollution [8,9]. The use of 1,3-D was suspended for four years in California during 1990–1994 after detection of high 1,3-D concentrations in the air near fumigation sites. Therefore, risk-mitigation practices are needed to prevent excessive 1,3-D emissions during its use.

In a previous study, 1,3-D was found to rapidly undergo a nucleophilic substitution reaction with thiosulfate in water and soil, producing nonvolatile ionic products [10]. It was further shown that when the soil surface was sprayed with ammonium thiosulfate (ATS) solution, 1,3-D volatilization was greatly minimized while its ability to control nematodes was not affected [11]. Thiosulfate salts such as ATS and potassium thiosulfate are fertilizers, which make this approach highly feasible for application. Because commonly used 1,3-D formulations (e.g., Telone II®, DowAgro Sciences, Indianapolis, IN, USA) are roughly 50/50 mixtures of the *cis* and *trans* isomers, it is important to understand whether isomeric effects occur during 1,3-D's transformation by thiosulfate. Isomers of 1,3-D were found to differ significantly in their degradation rates in adapted soils [12,13]. In this study, we measured individual reaction rates of 1,3-D isomers with thiosulfate in aqueous solutions and the changes in acute toxicity and mutagenicity caused by the transformation for each isomer. The observed differences were further correlated with the structural characteristics of the isomers, and the implication of the isomeric differences for application was discussed.

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Reference to a company name or product does not imply an approval or recommendation by the U.S. Department of Agriculture to the exclusion of the others that may be suitable.

MATERIALS AND METHODS

Chemicals and test organisms

The *cis* and *trans* isomers of 1,3-D were donated by Dow AgroSciences (Indianapolis, IN, USA) (purity >97.6%). Ammonium thiosulfate was purchased from Fluka (Buchs, Switzerland) (purity >99.5%). All other reagents used in this study were of analytical grade.

The test organism used in the acute toxicity assay was luminescent bacteria *Vibrio fisheri* purchased from AZUR Environmental (Carlsbad, CA, USA). The *Salmonella typhimurium* strains TA97a, TA98, TA100, and TA102 used in the mutagenicity test were obtained from the Division of Biochemistry and Cell Molecular Biology, University of California, Berkeley (Berkeley, CA, USA). Rat hepatic fractions (S9) were purchased from BioReliance-Tox Labs (Rockville, MD, USA).

Kinetic experiments in aqueous solution

In the first aqueous-phase experiment, disappearance of *cis*- and *trans*-1,3-D was determined in aqueous solutions of different thiosulfate concentrations and was used to calculate the reaction rate constant for each isomer. Solutions of ATS were prepared by dissolving the salt in deionized water at 0, 1.0, 2.0, and 4.0 mM, and 100 ml of each solution were then

transferred into 125-ml glass serum bottles. To initiate the reaction, 0.10 ml of *cis*- or *trans*-1,3-D stock solution (10^3 mM in acetone) were added to the ATS solutions, and the initial concentration of 1,3-D isomers was thus 1.0 mM. The spiked containers were crimp sealed with aluminum caps and Teflon®-lined butyl rubber septa and equilibrated at 20 ± 0.5°C in the dark.

At different times, 0.5 ml (×3) of aliquot were withdrawn from each reacted solution using a syringe, and the sample was transferred into a 10-ml glass vial containing 5.0 ml ethyl acetate and 3.0 g anhydrous sodium sulfate. The sample vials were immediately crimp sealed and mechanically mixed on a vortexer for 2 min. A portion of the ethyl acetate phase was then transferred into a gas chromatography (GC) vial and analyzed using GC. The GC system was a Hewlett Packard HP6890 GC (Hewlett Packard, Avondale, PA, USA) with an electron capture detector. Analytical conditions were as follows: Rtx-624 column (30 m × 250 μm × 1.4 μm, Restek, Bellefonte, PA, USA), 1.2 ml/min column flow rate, 220°C inlet temperature, and 300°C detector temperature. The oven was held at 70°C for 0.5 min and then increased at 20°C/min to 140°C and kept at 140°C for 2.5 min. The injection volume was 2.0 μl, and the split ratio was 10:1. External standards were used for calibration. The decline of fumigant concentration with time was fitted to first-order decay kinetics to obtain the degradation rate constant k_f (1/h) for each fumigant isomer. Values of k_f were further correlated with the initial thiosulfate concentration by linear regression to estimate the second-order rate constant k (1/Ms) for the S_N2 reaction of each isomer with thiosulfate.

Temperature dependence was studied in a separate aqueous-phase experiment to understand the energy dynamics of the transformation of 1,3-D isomers by thiosulfate. The reaction solutions initially contained 1.0 mM *cis*- or *trans*-1,3-D, and 2.0 mM ATS. The reaction solutions were equilibrated at 6, 20, 30, and 40 ± 0.5°C in the dark, and the decline of fumigant concentration was measured over time by using the same procedures as given previously. The first-order degradation rate constants were correlated to the different temperatures using the Arrhenius equation to derive the activation energy E_a (kJ/mol) for the reaction of each isomer with thiosulfate.

Toxicological assessments

The change in acute toxicity of 1,3-D isomers caused by thiosulfate transformation was evaluated using luminescent bacteria *V. fisheri*. This method has been frequently used for testing acute toxicity of both organic and inorganic toxicants in environmental samples [14–16]. Briefly, prior to toxicity assay, 1,3-D isomers (2.0 mM) and ATS (20 mM) were mixed, and the reaction solutions were equilibrated at room temperature. Analysis by GC showed that 1,3-D isomers were completely transformed by ATS in 3 d. For toxicity assay, the reacted samples were serially diluted with 2% NaCl and transferred into cuvettes. An aliquot of the revived bacteria solution was added into the cuvettes, and after 5.0 min of contact at 20°C, the light intensity at 490 nm was measured on an SLM8000 Spectrofluorometer (SLM Instruments, Urbana, IL, USA). Solutions of 1,3-D isomers of the same concentrations were simultaneously measured under the same conditions. Light intensity of ATS solutions without 1,3-D was also measured and was used as the background for calculating the relative light intensity. The effective concentration at which 50% suppression occurred, or EC50, was obtained by plotting the relative light intensity against the logarithmic sample concentration and solving for the concentration at which 50% reduction in luminescence occurred.

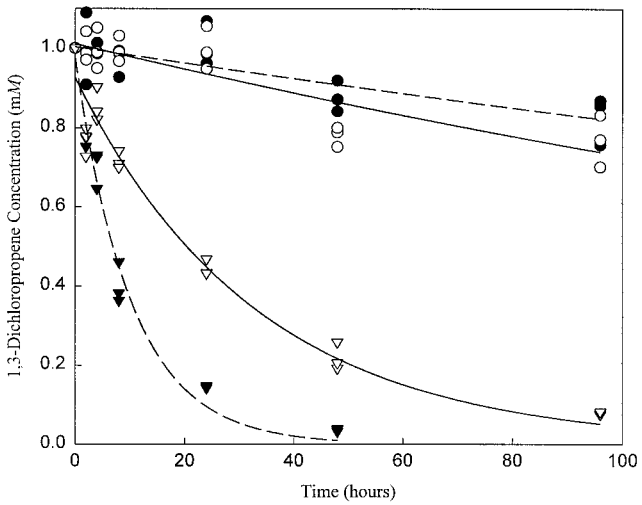

Fig. 1. Enhanced transformation of *cis*- and *trans*-1,3-dichloropropene (1,3-D) in the aqueous phase by ammonium thiosulfate at 20°C. Symbols are measured data, and lines are first-order regressions. ●, *cis*-1,3-D in water; ○, *trans*-1,3-D in water; ▼, *cis*-1,3-D in 2.0 mM ATS solution; and ∇, *trans*-1,3-D in 2.0 mM ATS solution.

The mutagenic activity of 1,3-D isomers before and after thiosulfate transformation was assessed using *S. typhimurium* strains TA97a, TA98, TA100, and TA102 following the Ames test method [17]. Prior to the test, 1,3-D isomers (100 mM) and ATS (500 mM) were allowed to react in water:acetone solution (4:1) at 20°C. Analysis by GC showed that complete transformation of 1,3-D was achieved in 4 d. The reacted solutions were then used to preincubate the test strains, with or without the addition of S9, for 20 min at 20°C in test tubes and then mixed with top agar. The rat hepatic fraction S9 was used as an exogenous metabolic activation system. The samples were poured into petri dishes containing minimal nutrition media and incubated at 37°C for 2 to 3 d [18]. The amounts of transformed products added to each plate were equivalent to 0.11 to 1,100 μg fumigant before transformation. Values of mutagenicity ratio (MR) were obtained by dividing number of revertant colonies of sample plates by that of the blank control. In principle, an MR ≥ 2 with a clear dose response suggests mutagenic activity, while an MR < 2 indicates a lack of activity [19]. Samples of 1,3-D isomers that did not undergo transformation by thiosulfate were also subject to the same test under similar conditions.

RESULTS AND DISCUSSION

Reaction kinetics in aqueous phase

Hydrolysis in deionized water was relatively slow for both isomers of 1,3-D, with only a limited loss occurring during the 96-h equilibration period (Fig. 1). Addition of ATS to the solution significantly accelerated the disappearance of 1,3-D isomers, and the rate of fumigant disappearance was proportional to the initial thiosulfate concentration (Fig. 1 and Table 1). Regression of fumigant concentration with time showed a first-order relationship, and the goodness of fit (R) improved as the initial thiosulfate concentration increased (Table 1), which is characteristic of a second-order reaction. Linear regression of the k_f values from Table 1 to initial thiosulfate

Table 1. First-order transformation rate constant k_f (l/h) and half-life $t_{1/2}$ (h) of *cis*- and *trans*-1,3-dichloropropene in blank and ammonium thiosulfate (ATS) solutions at 20°C

Thiosulfate concn. (mM)	*cis*-1,3-D			*trans*-1,3-D		
	k_f	$t_{1/2}$	R[a]	k_f	$t_{1/2}$	R
0 (no ATS)	0.0021	330	0.80	0.0032	216	0.86
1.0	0.0216	32.1	0.97	0.0137	50.6	0.99
2.0	0.0788	8.8	0.99	0.0262	26.5	0.99
4.0	0.2076	3.3	1.00	0.0664	10.4	1.00

[a] R = correlation coefficient.

concentrations validated that the overall reaction closely followed the second-order kinetics that is characteristic of S_N2 nucleophilic substitution reactions, with the correlation coefficient $R > 0.99$ for either isomer. In ATS solutions, pH (6.20) was not greatly different from that in the control solution, suggesting that pH did not play a role in thiosulfate-initiated transformation of 1,3-D isomers.

In solutions with the same initial thiosulfate concentration, transformation of *cis*-1,3-D was consistently faster than that of *trans*-1,3-D (Fig. 1 and Table 1). From the k_f values given in Table 1 for each isomer, the second-order reaction rate constant was calculated to be 1.73×10^{-2}/Ms for *cis*-1,3-D but only 5.0×10^{-3}/Ms for *trans*-1,3-D. This suggests that thiosulfate was about 3.5 times more efficient in reacting with *cis*-1,3-D than with *trans*-1,3-D. An examination of the stereochemistry of 1,3-D suggests that the C=C bond and the four connected single bonds (C_1–Cl, C_1–H, C_2–C_3, and C_2–H) are in the same plane (Fig. 2). Therefore, the space hindrance for thiosulfate ion to approach C_3 should be very similar for both isomers. On the other hand, it is likely that in the transition state, charge density distribution for *cis*-1,3-D is poorly balanced, with the charge center tilting to one side of the C=C bond (Fig. 2). The more polarized state may favor its interaction with the polar solvent (water), thus lowering the energy level of *cis*-1,3-D and facilitating its reaction with thiosulfate ion [20].

The transformation rate of 1,3-D isomers increased with increasing temperature (Table 2). Temperature dependence of fumigant transformation rate was found to fit well to the Arrhenius relationship, with $R \geq 0.99$. The activation energy E_a was subsequently calculated using the Arrhenius equation (Table 2). The E_a value (72.9 kJ/mol) for the reaction of *cis*-1,3-D with thiosulfate was smaller than that for *trans*-1,3-D (78.3 kJ/mol). The difference was tested to be significant at $P = 0.01$ using *t* test. This agrees with the observation that under the same conditions, reaction of *cis*-1,3-D with ATS was appreciably faster than that of *trans*-1,3-D. This also provides support to the previous postulation that during reaction with thiosulfate, the energy level of the transition state for the *cis* isomer should be lower than that for the *trans* isomer.

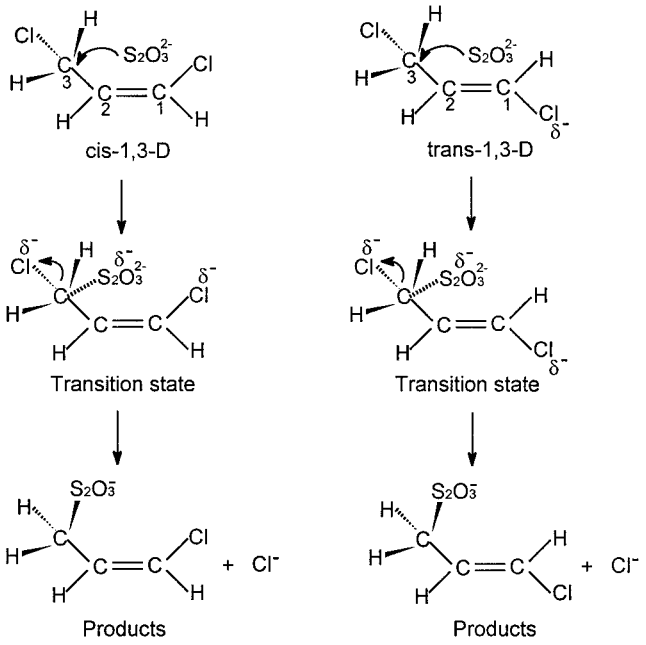

Fig. 2. Proposed steric structures and charge distribution patterns for *cis*- and *trans*-1,3-dichloropropene during their nucleophilic substitution reaction with thiosulfate in water.

Reduction in toxicity of 1,3-D isomers by thiosulfate transformation

Acute toxicity of 1,3-D isomers to the luminescent bacteria was determined before and after transformation by ATS. As indicated by the bacterial EC50 summarized in Table 3, the *trans* isomer was about seven times more toxic than the *cis* isomer to the test organism. Thiosulfate transformation did not significantly change the EC50 of *cis*-1,3-D, which may be attributed to the fact that the nontransformed *cis* isomer (EC50 >1 mM) was relatively innocuous to the test organism. However, the EC50 for *trans*-1,3-D increased 14-fold after transformation by ATS, indicating that thiosulfate transformation was indeed a detoxification process for the *trans* isomer. In our previous study, where a mixture of 1,3-D isomers (*cis*/*trans*: 47/51) was used, an overall increase in EC50 of 7.4 times was found after ATS transformation [21]. The present study showed that the bacterial toxicity of 1,3-D isomer mix-

Table 2. Effect of temperature on transformation kinetics of *cis*- and *trans*-1,3-dichloropropene (1,3-D) by ammonium thiosulfate (ATS) in aqueous solution[a]

Temperature (°C)	*cis*-1,3-D			*trans*-1,3-D		
	k_f	$t_{1/2}$	R	k_f	$t_{1/2}$	R
6.0	0.0154	4.50	0.99	0.0053	132	0.95
20.0	0.0788	8.8	0.99	0.0262	26.5	0.99
30.0	0.2025	3.4	1.00	0.0760	9.1	0.99
40.0	0.4643	1.5	1.00	0.2081	3.3	1.00
E_a (kJ/mol)[b]		72.9 ± 2.1			78.3 ± 0.3	

[a] k_f = first-order transformation rate constant in 1/h; $t_{1/2}$ = first-order transformation half-life in h; R = correlation coefficient.
[b] E_a is activation energy that was calculated from the Arrhenius equation: $k = A \cdot e^{-Ea/RT}$, where k is the reaction rate constant at a given temperature T (°K), R is the gas molar constant, and A is a fitted constant.

Table 3. Changes in bacterial EC50 against *Vibrio fisheri* for 1,3-dichloropropene isomers after transformation by ammonium thiosulfate (ATS) in aqueous solution

1,3-D isomer	ATS transformation	EC50 (mM)	Difference
cis	No	1.17	No difference
	Yes	1.09	
trans	No	0.15	14.2 times
	Yes	2.27	

ture in the previous study could be mainly attributed to the *trans* isomer and that the effect of thiosulfate detoxification was caused primarily by the deactivation of *trans*-1,3-D.

Reduction in mutagenicity of 1,3-D isomers by thiosulfate transformation

The Ames test method has been extensively used for screening genotoxicity of environmental samples because of its high sensitivity and simplicity [19,22,23]. In this study, mutagenicity of *cis*- and *trans*-1,3-D and their thiosulfate transformation products were evaluated using the revised Ames test method [17]. For the *cis* isomer and its transformation products, all MR values were <2.0 for the test concentration range of 0.01 to 100 mM, with or without activation by S9 mixture. This suggests that *cis*-1,3-D itself was not mutagenic to the test systems under the experimental conditions, and transformation by thiosulfate did not alter this status. On the other hand, the same test showed that at the highest concentration used (100 mM), *trans*-1,3-D was mutagenic to two (TA97a and TA100) of the four test strains without S9 activation and three (TA97a, TA98, and TA100) of the four strains with S9 activation (Table 4). The highest MR values were observed with the TA100 strain, which was >4.0 with or without S9 activation. A dose–response effect for TA100 was apparent, for both systems with and without the treatment of the S9 mixture. The S9 activation system appeared to enhance the expression of mutagenicity of *trans*-1,3-D. These observations together suggest that the *trans* isomer of 1,3-D possessed mutagenic activity to some strains of *S. typhimurium*. However, after transformation by thiosulfate, all MR values fell below 2.0 for the tested concentrations, and no clear dose response (shown in Table 5 for S9-activated samples) was seen. Therefore, it may be concluded that thiosulfate transformation reduced the mutagenicity of *trans*-1,3-D below the detection limit of the method used.

Table 4. Values of mutagenicity ratio of *trans*-1,3-dichloropropene (mean ± standard deviation)

Strains	1,110 μg/plate[a]	55.5 μg/plate	2.22 μg/plate	0.11 μg/plate
		Without S9 activation		
TA97a	2.10 ± 0.05[b]	1.02 ± 0.08	0.51 ± 0.08	1.14 ± 0.12
TA98	1.06 ± 0.10	1.14 ± 0.18	0.92 ± 0.01	1.10 ± 0.05
TA100	4.26 ± 0.28[b]	1.26 ± 0.00	1.04 ± 0.14	1.00 ± 0.04
TA102	1.38 ± 0.16	1.13 ± 0.03	1.10 ± 0.04	1.15 ± 0.10
		With S9 activation		
TA97a	2.36 ± 0.01[b]	1.16 ± 0.14	0.96 ± 0.09	0.96 ± 0.23
TA98	2.10 ± 0.06[b]	0.82 ± 0.07	0.92 ± 0.06	1.18 ± 0.02
TA100	5.73 ± 0.03[b]	1.60 ± 0.10	1.31 ± 0.17	1.16 ± 0.04
TA102	1.55 ± 0.14	1.12 ± 0.02	1.03 ± 0.09	1.03 ± 0.13

[a] 0.11 to 1,110 μg/plate was equivalent to 0.01 to 100 mM fumigant concentration range used for preincubation.
[b] Values are >2 and defined as positive.

Table 5. Values of mutagenicity ratio for *trans*-1,3-dichloropropene after transformation by ammonium thiosulfate (with S9 activation) (mean ± standard deviation)

Strains	1,110 μg/plate[a]	55.5 μg/plate	2.22 μg/plate	0.11 μg/plate
TA97a	0.94 ± 0.21	0.74 ± 0.09	0.63 ± 0.03	0.82 ± 0.12
TA98	1.08 ± 0.15	1.05 ± 0.14	1.41 ± 0.21	1.26 ± 0.03
TA100	1.25 ± 0.06	0.75 ± 0.02	0.77 ± 0.22	0.98 ± 0.09
TA102	0.98 ± 0.02	0.88 ± 0.11	1.00 ± 0.03	0.92 ± 0.05

[a] 0.11 to 1,110 μg/plate was equivalent to 0.01 to 100 mM fumigant concentration range used for preincubation.

Bacterial mutagenicity of 1,3-D isomers was previously demonstrated using other *S. typhimurium* strains [24,25]. The reactivity was attributed to the electrophilicity of the methylene carbon (C_3 in Fig. 2), which stimulates nucleophilic substitution reactions of 1,3-D with nucleophilic centers in DNA. In mammals, glutathione-initiated biotransformation was shown to deactivate 1,3-D by causing concomitant loss of its alkylating reactivity. The reaction with thiosulfate may have deactivated 1,3-D in a similar manner by eliminating its reactivity with essential cellular macromolecules.

CONCLUSIONS

Many of the currently used chlorinated pesticides, including the soil fumigant 1,3-D, have suspected carcinogenicity and other undesirable toxicological properties, making their potential to contaminate air and water resources a concern. Common formulations of 1,3-D are mixtures of its *cis* and *trans* isomers at roughly equivalent ratios. Our study showed that the *trans* isomer was much more active than the *cis* isomer against the indicator organism *V. fisheri*. At high concentrations, *trans*-1,3-D also caused positive mutagenic reaction to strains of *S. typhimurium*. These results suggest that the *trans* isomer of 1,3-D is toxicologically more active than the *cis* isomer, and formulations that have a greater ratio of *cis*-1,3-D may be less harmful to the environment or human health and therefore should be recommended. Such formulations should not compromise the effectiveness of 1,3-D, as early studies showed that *cis*-1,3-D was considerably more effective against soil nematodes [26,27]. In fact, formulations consisting mainly of the *cis* isomer were recently introduced in countries such as the Netherlands. Because of the higher potency of *cis*-1,3-D, the overall dosage has been reduced to only a half of what was used before [28].

Emission of 1,3-D into the atmosphere is of concern because of its toxicity and carcinogenicity. Previous studies showed that 1,3-D was rapidly transformed by thiosulfate salts, and surface spray of thiosulfate salt solution substantially reduced 1,3-D emission. As ammonium and potassium thiosulfates are fertilizers, this reaction may be used as a preventive or remedial measure to mitigate the risks involved in 1,3-D uses. This study showed that the *cis* and *trans* isomers of 1,3-D differed significantly in their reaction rate with thiosulfate, with the *cis* isomer being transformed about 3.5 times faster than the *trans* isomer. This difference correlates well with the differences in steric characteristics of these isomers. Reaction with thiosulfate decreased *trans*-1,3-D's activity against *V. fisheri* by 14 times and also eliminated its mutagenicity to strains of *S. typhimurium*. These preliminary assays imply that thiosulfate transformation detoxifies 1,3-D and therefore is a toxicologically advantageous process. Further evaluation

should be conducted to develop this approach into practices for reducing 1,3-D emissions from fumigated fields or leaching into groundwater and for safer disposal of 1,3-D wastes.

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