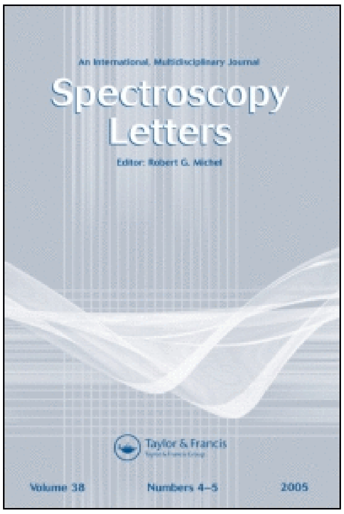

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Degradation of Sulfur Mustard on Moist Sand as Determined by ^{13}C Solid-State Magic Angle Spinning Nuclear Magnetic Resonance

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ABSTRACT The degradation of sulfur mustard, bis(2-chloroethyl) sulfide, on three types of moist sand at 22°C and 35°C was followed using ^{13}C solid state-magic angle spinning nuclear magnetic resonance (SSMAS NMR). The sulfur mustard degraded completely on moist sand within 8 weeks at 22°C and 1 week at 35°C, whereas degradation on dry sand at 22°C required more than 6 weeks. The major product, the toxic sulfonium ion H-2TG, and the minor product, nontoxic thiodiglycol, were detected on all sand samples. The intermediate chlorohydrin was detected on one sand at 22°C, and evidence for the intermediates CH-TG and H-TG was detected on this same sand at 35°C. The H-2TG that was initially formed degraded to thiodiglycol; completion of this degradation would require months. The lack of reaction on the ambient substrates, plus the formation of sulfonium ions, similar to the products that were previously seen in water and on moist soil, suggested that the sand functioned as a support on which the reaction between sulfur mustard and water occurred.

KEYWORDS chlorohydrin, CH-TG, H-TG, H-2TG, sulfonium ion, sulfur mustard, thiodiglycol

INTRODUCTION

The chemical warfare agent (CWA) sulfur mustard, bis(2-chloroethyl) sulfide, (H), was used during World War I and was used most recently in the Iran–Iraq wars of the 1980s.[1–4] Poor disposal methods of unused sulfur mustard stockpiles and ordnance, especially ocean dumping, have led to the resurfacing and continuance of sulfur mustard in the environment.[5–7] In addition, there is the possibility that various terrorist groups may manufacture or procure CWAs to harm civilian populations, as happened when the group Aum Shinrikyo released sarin (GB) in the Tokyo subway in March 1995.[8]

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In the event of contamination of a large area with sulfur mustard, decisions must be made whether to decontaminate an area or allow resumption of normal operations after an acceptable waiting period, during which natural weathering occurs. Knowledge of whether the CWA will degrade on a given surface, how quickly decomposition will occur, and the correct assessment of the identity, amount, and toxicity of products formed is crucial for making correct decisions about the need for additional decontamination.

Environmentally, sulfur mustard has been observed to persist for 4 years in soil.[9] Wagner and MacIver[10] used ^{13}C solid-state magic angle spinning nuclear magnetic resonance (SSMAS NMR) to show that sulfur mustard persisted for several weeks on dry soil but hydrolyzed and polymerized to form the toxic sulfonium ions CH-TG and H-2TG within 2 days when water was added. The addition of water to the sulfur mustard on soil resulted in narrower peaks, thus indicating that the water had absorbed onto the soil and thus displaced the sulfur mustard from the soil surface. The narrower peaks also indicated that the water had been distributed throughout the sample by the time the sample was spinning.

Wilson et al.[11] found that the solubility of sulfur mustard in water was 4.3 mM and that hydrolysis occurred via the chlorohydrin (CH: $ClCH_2CH_2SCH_2CH_2OH$) intermediate to eventually form thiodiglycol (TDG: $HOCH_2CH_2SCH_2CH_2OH$). Bales and Nickelson[12] studied the hydrolysis of sulfur mustard and claimed the formation and isolation of CH, which has milder vesicant properties than the sulfur mustard itself. Davies and Oxford[13] proposed a scheme for the oligomerization of H, CH, and TDG, forming a variety of sulfonium ions. Davies and Oxford recognized that the sulfonium ions would eventually decompose to form TDG but had the potential to re-form mustard in the presence of chloride ions. Stein et al.[14] isolated the CH-TG and H-2TG intermediates formed from the hydrolysis of sulfur mustard. Yang et al.[15–17] used ^{13}C NMR to identify the sulfonium ions and study the rate of sulfur mustard hydrolysis, thus confirming the reaction pathways proposed by Davies and Stein.

Tilley[18] measured the hydrolysis of 0.35 mM sulfur mustard in aqueous mixtures of ethanol, acetone, and dimethyl sulfoxide at 25°C and calculated a hydrolysis half-life for mustard in pure water of 4 min. Bartlett and Swain,[19] recognizing that the hydrolysis of mustard to thiodiglycol was a two-step process, first measured the hydrolysis of the intermediate, chlorohydrin, in 5% acetone at 25°C, and then measured the hydrolysis of distilled sulfur mustard (HD) under the same conditions. This yielded a sulfur mustard hydrolysis half-life of 4.3 min. The half-life of 2 mM sulfur mustard in D_2O at 22°C as measured by Logan and Sartori[20] was 7 min; thus showing a kinetic isotope effect of $\sim$2.

Brevett et al.[21] used ^{13}C SSMAS NMR to show that sulfur mustard on ambient concrete would remain intact as sulfur mustard for 12 weeks, despite the fact that after the passage of 2 weeks it was nonextractable. Tang et al.[22] showed that sulfur mustard vapor diffused into cement, and droplets of sulfur mustard migrated through a layer of cement at the rate of 1.3×10^{-4} cm/min. Loss of sulfur mustard and formation of products were detected by extraction with acetonitrile followed by Gas Chromatography/Mass Spectrometry (GC/MS). The rate for sulfur mustard loss was calculated to be $4.8 \times 10^{-5}\ min^{-1}$, which corresponded with a first-order half-life of 10 days. Products observed in the GC/MS in were 2-chloroethyl vinyl sulfide (CEVS), 1,4-oxathiane, Q (sesquimustard: $ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$), and sulfur mustard disulfide [$(ClCH_2CH_2S)_2$].

Wagner et al. showed that when sulfur mustard was placed on MgO[23] or CaO,[24] the products TDG, CEVS, and divinyl sulfide (DVS) were formed. Degradation of sulfur mustard on CaO also led to minor amounts of sulfonium ions. On the surface of ambient alumina, sulfur mustard reacted to give mostly TDG with minor amounts of CEVS and DVS. When excess water was added, the sulfonium ions H-2TG and CH-TG were formed, and $Al(H_2O)_6^{3+}$ was liberated from the surface.[25] On NaY zeolite, sulfur mustard formed the sulfonium ion H-2TG, whereas on AgY zeolite the sulfur mustard formed 1,4-oxathiane and DVS.[26] Vinyl products have also been observed in alkaline aqueous solutions. [1]

Gas masks contain carbon in their cartridges, and thus knowing if sulfur mustard degrades in the cartridge or is merely absorbed, and thus amenable to future liberation, is important. Karwacki et al.[27] showed that sulfur mustard degradation on dry coconut shell carbon (CSC) at 50°C produced the elimination product, CEVS, and the cyclic ether 1,4-oxathiane. Wagner et al.[28] demonstrated that on wet CSC at 30°C, the products CH and TDG were produced in addition to the products that were formed on the dry CSC. The first-order half-life was 25 days. Prasad et al.[29,30] impregnated high-surface-area carbon with a variety of oxidizing agents to form the products CH, TDG, 1,4-oxathiane, 1,4-thiazane, and divinyl sulfone, depending upon the oxidant used. Sharma et al. showed that carbon impregnated with a vanadium/ruthenium mixture would oxidize sulfur mustard to the sulfoxide.[31]

Wagner et al.[32] studied the thermal degradation of sulfur mustard with and without water, finding that the "dry degradation" products were 1,2-dichloroethane, polysulfides, Q ($ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$), and 1,4-dithiane, whereas the "moist degradation" products were 1,4-oxathiane, 2-chloroethanol, and numerous sulfonium ions. The product 1,4-dithiane from the thermal decomposition of mustard was observed by Williams,[33] and its presence was explained by Bell et al.[34] via a mechanism that involved sulfonium ion intermediates.

The formation of sulfonium ions from sulfur mustard is important as they have been determined to be a cause of the toxicity of sulfur mustard,[35] although the sulfonium ions are generally less toxic than sulfur mustard itself.[36] In addition, the analytical techniques needed for the detection of sulfonium ions differ from those needed for sulfur mustard and TDG. Extraction followed by GC/MS is suitable for detecting sulfur mustard and TDG,[2,37] whereas extraction with a polar solvent followed by Liquid Chromatography Electrospray Ionization Mass Spectrometry (LC/ESI MS) is needed for the sulfonium ions.[38]

In the current study, ^{13}C SSMAS NMR techniques were employed to quantitatively study the rate of and identify the products for sulfur mustard degradation on three environmentally and operationally relevant sand substrates.

MATERIALS AND METHODS

Sand

The sand used was obtained from three sources. Sand E, Foundry Sand Washed 0–17, was produced by Moravske Keramicke Zavody A. S. in Europe (Rajec–Jestribi, Czech Republic); Sand U, AFS-50 Fine Sand, was produced by Warmwell Quarry in the United Kingdom (Warmwell, Dorset); and Sand A, Filter Sand #2, was produced by Southern Products & Silica Co. (Hoffman, NC, USA) and obtained via the distributor Charles Reade Co. (Providence, RI, USA). The particle sizes and elemental compositions, based on the specifications sheets of the suppliers, are compared in Table 1. The surface areas were measured by Micromeritics Analytical Services (Norcross, GA, USA), using nitrogen gas absorption with a 5-point Brunaver–Emmett–Teller (BET) analysis.

Sands E and A were free-flowing and were used as-received (containing 0.2% moisture) and with added water, which were labeled "moistened". Sand U was visibly moist when supplied; allowing it to dry in a fume hood for 96 h showed that it contained 6.7% moisture. Three experiments were run with Sand U: HD* on hood-dried, as-received, and with added water on hood-dried sand (which will be referred to as "re-wet" Sand U).

Agent

The sulfur mustard used, ^{13}C-labeled (HD*), 99.5% pure by GC, was synthesized at the Edgewood Chemical Biological Center (Aberdeen Proving Ground, MD, USA). The HD* was 50% labeled at each carbon position, such that two ^{13}C would not be adjacent. This allowed for good detection of the ^{13}C signal but avoided the $^{13}C-^{13}C$ couplings that would be present if 100% labeling were used. (*Caution*: sulfur mustard, bis(2-chloroethyl) sulfide, is a potent vesicant, and care must be taken to prevent exposure to liquid or vapor. It should only be manipulated by trained personnel employing appropriate engineering controls and personal protective equipment.) The rotor was packed with 200 mg (~135 mm^3) as-received (or hood-dried) sand, and 5 μL agent was added to the sand using a microliter syringe. The sample was then capped and spun at ~1500 to 2000 Hz; after 1 of spinning, examination of the sample showed that all of the sand had been moistened and lined the sides of the rotor; no free

TABLE 1 **Physical Properties of the Sand**

Property	Sand E	Sand U	Sand A
Predominant particle size (mm)	0.14–0.2	0.25–0.50	0.8–1.2
Sand type	Fine	Medium	Coarse
Silica (SiO_2)%	97.0	98.6	99.8
Aluminum oxide%	—	0.39	0.04
Ferric oxide%	0.3	0.09	0.05
Surface area, m^2/g	0.14	0.32	0.11

liquid was observed. For the moistened samples, the rotor was packed with 200 mg (~135 mm^3) as-received (or hood-dried) sand; 5 μL agent was added, followed by distilled water at a ca. 20:1 molar ratio. The sample was then spun at ~1500 to 2000 Hz, and after 1 hour the sand was completely moistened.

NMR Instrumentation

^{13}C SSMAS (solid-state magic angle spinning) spectra were collected at 9.4 Tesla and 22°C using a narrow-bore Varian Inova NMR spectrometer (Varian, Palo Alto, CA, USA) equipped with a Doty Scientific 7-mm standard series VT-MAS (variable temperature magic angle spinning) probe (Doty Scientific, Columbia, SC, USA). The spectra were obtained using direct polarization at spinning rates of ~1500 to 2000 Hz. The spectra at 35°C were acquired at 9.4 Tesla using a wide bore Varian Inova NMR spectrometer equipped with a Doty Scientific 7-mm Supersonic VT-MAS probe with spinning at ~3500 Hz.

Delay times between pulses were at least 5 times the measured relaxation time, T_1, and spectra were referenced to external tetramethylsilane (TMS). A standard (^{13}C-labeled 2-chloroethyl phenyl sulfide, CEPS*, plus TMS on sand) was run daily as a reference and to ensure that the total integrated peak areas were unchanged and unaffected by the instrumentation. The spin-lattice relaxation times, T_1, were measured using a standard inversion recovery sequence.[39] Chemical shifts of H-TG and CH were calculated (Table 2) using ACD/CNMR Predictor v. 5.12 from Advanced Chemistry Development Inc. (Toronto, Ontario, Canada.)

RESULTS

Degradation at Ambient Temperatures

When placed on as-received Sand E, the sulfur mustard was unreactive over a period of 23 months. When HD* and water were placed on this sand, with a H_2O:HD* molar ratio of 17:1, a reaction was detected in 6 days, and the degradation was complete within 8 weeks. The chemical shifts and integrated peak areas were consistent with the production of the sulfonium ion H-2TG (87%) and TDG (13%) (Fig. 1 and Table 3).

When HD* and water were placed on as-received Sand A with a H_2O:HD* molar ratio of 17:1, a reaction was detected in 2 weeks, and the degradation was complete within 8 weeks. The chemical shifts and integrated peak areas were consistent with the production of the sulfonium ion H-2TG (90%) and TDG (10%) (Fig. 2 and Table 3). When placed on as-received Sand A, only 5% of the total integrated peak area was accounted for by the spinning side bands, and the sulfur mustard did not degrade over a period of 6 weeks.

Sand U was moist when supplied; allowing it to dry in a fume hood for 96 h showed that it contained 6.7% moisture. Three experiments were run with Sand U: HD* on hood-dried, as-received, and with added water on hood-dried Sand U (which will be referred to as "re-wet" Sand U). When placed on the hood-dried Sand U, the sulfur mustard did not degrade over a period of 6 weeks.

The H_2O:HD* molar ratios were 23:1 for the as-received Sand U and 17:1 for the re-wet Sand U. A reaction was seen in 6 days for both samples; the

TABLE 2 **Calculated Chemical Shifts for Sulfur Mustard and Its Degradation Products**

Abbreviation	Name	Formula	^{13}C chemical shift (ppm)	Toxicity comment Ref.
H, HD	Sulfur mustard; bis(2-chloroethyl) sulfide	$(ClCH_2CH_2)_2S$	43, 35	Blister agent, PGI[11]
CH	Chlorohydrin	$ClCH_2CH_2SCH_2CH_2OH$	43, 33, 35, 61	PGI[11]
TDG	Thiodiglycol	$(HOCH_2CH_2)_2S$	61, 35	Nontoxic[11]
CH-TG	—	$HOCH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$	62, 35, 27, 43, 45, 58	Toxic[7]
H-TG	—	$ClCH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$	43, 33, 29, 44, 46, 59	PGIII[11]; PGI[12]
H-2TG	—	$S[CH_2CH_2S^+(CH_2CH_2OH)_2]_2$	27, 44, 46, 59	PGII[11]

Toxicity ratings from 49CFR 173.133 (a)(1): Oral LD_{50}: Packing Group (PGI) < 5 mg/kg; PGII between 5 and 50 mg/kg; PGIII between 50 and 200 mg/kg for solids and 50 to 500 mg/kg for liquids.

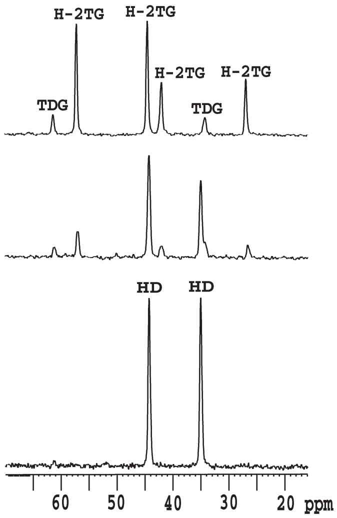

FIGURE 1 ^{13}C SSMAS Spectra of the Degradation of Sulfur Mustard on Moistened Sand E, Showing HD* (44.3 and 35.1 ppm), TDG (61.6 and 34.2 ppm), and H-2TG Sulfonium Ion (57.3, 44.6, 42.0, 26.9 ppm). Reaction Times from Bottom to Top: Initial, 6 Days, and 8 Weeks.

thiodiglycol peaks initially occurred at 61.4 and 34.5 ppm; the product chemical shifts moved downfield by ~3 ppm during the 8-week period of observation, by which point the degradation was complete.

The as-received Sand U gave T_1 relaxation times that were 3.1 s for the sulfur mustard and 0.014 s for the final products (Table 4). The chemical shifts and integrated peak areas were consistent with the formation of the sulfonium ion H-2TG (81%), TDG (11%), and CH (8%), although the broadness of the peaks does not preclude the presence of CH-TG (Fig. 3 and Table 3).

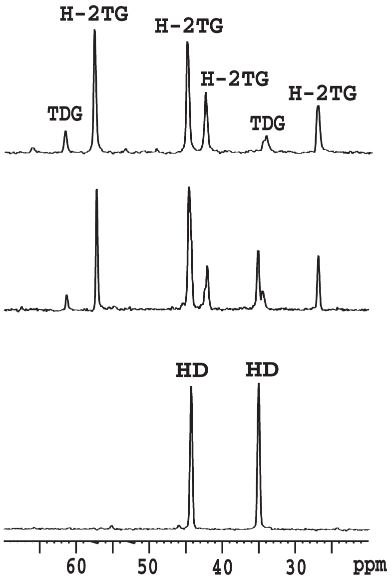

FIGURE 2 ^{13}C SSMAS Spectra of Sulfur Mustard and Water on Moistened Sand A showing HD* (44.3 and 35.1 ppm), TDG (61.7 and 34.7 ppm), and H-2TG Sulfonium Ion (57.8, 45.1, 42.6, and 27.4 ppm). Reaction Times from Bottom to Top: Initial, 2 Weeks, and 8 Weeks.

The re-wet Sand U exhibited T_1 relaxation times of 2.6 s for the sulfur mustard and 0.024 s for the final products (Table 4). The chemical shifts and integrated peak areas were consistent with the formation of the sulfonium ion H-2TG (80%), TDG (10%), and CH (10%), although the broadness of the peaks does not preclude the presence of CH-TG (Fig. 3 and Table 3).

Resonances observed in the 35 to 40 ppm range in as-received Sand U indicated the presence of another minor product, likely CH, whose calculated chemical

TABLE 3 ^{13}C Chemical Shifts and Product Distributions for Sulfur Mustard Degradation on Moist Sand at 22°C

Calculated	Sand E moistened	Sand A moistened	Sand U as-received	Sand U re-wet
H-2TG	H-2TG, 87%	H-2TG, 90%	H-2TG, 81%	H-2TG, 80%
26.8	26.9	26.9	31.8	29.8
59	57.3	57.2	61.3	59.9
46.4	44.6	44.6	49.4	47.7
43.8	42.0	41.9	47.0	45.3
TDG	TDG, 13%	TDG, 10%	TDG, 11%	TDG, 10%
61.3	61.6	61.7	63.8	63.2
35.4	34.2	34.4	37.6	36.8
CH			CH, 8%	CH, 10%
60.7			63.8	63.2
35			42.8	Hidden
43			Hidden	Hidden
33			36.5	34.2
Age of final sample	8 weeks	8 weeks	8 weeks	7 weeks

shifts were 60.7, 35, 43, and 33 ppm, which had shifted to 63.2, 42.6, hidden, and 34 ppm in the 8-week spectrum. The 63.2 ppm CH resonance was coincident with the TDG resonance at the same chemical shift, but the integrated peak area for the 63.2 ppm TDG peak was larger than that of the ~37 ppm TDG, which was consistent with the presence of a CH species. Thus, the third species in the as-received Sand U was assigned to CH, although the broad peaks do not preclude the possibility of the presence of CH-TG.

Degradation on Re-wet Sand U at 35°C

HD* and water were placed onto hood-dried Sand U with a H_2O:HD* molar ratio of 18:1 and monitored over a period of 4 weeks. Products were seen in 22 h, and all sulfur mustard had disappeared by 167 h (Fig. 4). Zero-order kinetics for the loss of sulfur mustard were evident by the plot of mg HD* versus. time (Fig. 5); the plot was a straight line of slope k, and each half-life was half as long as the previous. In addition, the first-order plot of ln (mg H) versus time was curved, which confirmed that the kinetics were not first order. The observed zero-order rate constant was 0.073 mg h^{-1}, with $r^2 = 0.992$.

At 22, 46, and 69 h the peaks seen were consistent with HD, a sulfonium ion, and CH with the 35 ppm peak hidden under the mustard. At 91 h, the second peak at ca. 43 ppm that had been originally assigned to the CH was not present, implying that the CH had reacted; HD and products were observed. At 167 h the peaks at 28 ppm, 36 ppm, and 46 ppm had split into two. In addition, the product chemical shifts gradually moved downfield by about 3 ppm during the 4 weeks over which the sample was monitored.

TABLE 4 T_1 Relaxation Times^a (in Seconds) for Sulfur Mustard and Its Degradation Products on Moist Sand at 22°C

	Sand E moistened	Sand A moistened	Sand U as-received	Sand U re-wet
Initial HD^a	2.7	2.8	3.1	2.6
6-day HD^a	2.5	2.0	2.7	2.3
6-day products	0.7	0.4	0.4	0.3
Final products	0.3	0.07	0.014	0.024

^{a}T_1's based on average of both HD and four sulfonium ion peaks.

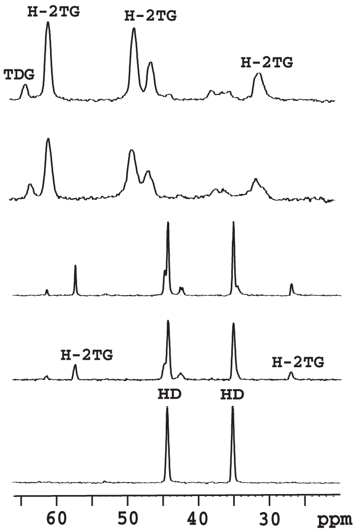

FIGURE 3 ^{13}C SSMAS Spectra of Sulfur Mustard on Sand U Showing HD* (44.3 and 35.1 ppm), TDG (63.2 and 36.8 ppm), and H-2TG Sulfonium Ion (59.9, 45.7.7, 45.3, and 29.9 ppm). Reaction Times from Bottom to Top: Initial; As-received at 6 days; Re-wet at 6 days; As-received at 8 Weeks; Re-wet at 7 Weeks.

The total integrated peak area for the sample was unchanged during the course of the degradation; thus the integrated peak areas for each resonance in every spectrum were normalized to a total of 100,000 units for ease of comparison (Figs. 6 and 7). Figures 6 and 7 show that the sulfonium ion concentration reached a plateau, whereas that of the hydroxyl species rose gradually.

The T_1 relaxation times of the products decreased during the 4-week period of study, whereas the sulfur mustard T_1 relaxation times remained invariant (Fig. 8).

DISCUSSION

Degradation at Ambient Temperatures

The products were identified on the basis of their chemical shifts, which were obtained from the literature[16] and calculations (H-TG and CH). In all cases, comparison of the total integrated peak areas for all of the spectra showed that mass balance was maintained throughout the period of study.

Because the mustard was fully distributed on the sand during the first hour of spinning, while the initial spectrum was being acquired, the sample was considered thoroughly mixed into the 200 mg of sand for all subsequent spectra. Hence, no effects due to

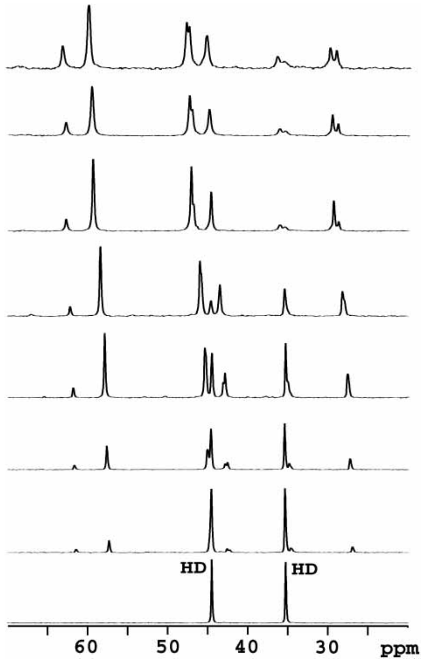

FIGURE 4 ^{13}C SSMAS Spectra of Sulfur Mustard on re-wet Sand U at 35°C Showing HD* (44.4 and 35.3 ppm), TDG (62 and 35 ppm), and H-2TG Sulfonium Ion (58, 47, 44, and 29 ppm). Reaction Times from Bottom to Top: Initial, 22, 46, 69, 91, 167, 360, and 570 h.

the material transfer of the sulfur mustard migrating from a liquid phase to surface-adsorbed phase during the course of the chemical reaction were present. Assuming a molecular surface area of 38 Å,[10] a 5-μL drop of sulfur mustard would require 7 m^2 for monolayer coverage of the sand. The available surface area from 200 mg of Sand U was 0.064 m^2, corresponding with 109 monolayers. Sands E and A were covered with 250 and 318 monolayers, respectively. Thus, only 0.3% to 0.9% of the mustard would be adsorbed on the surface of the sand.

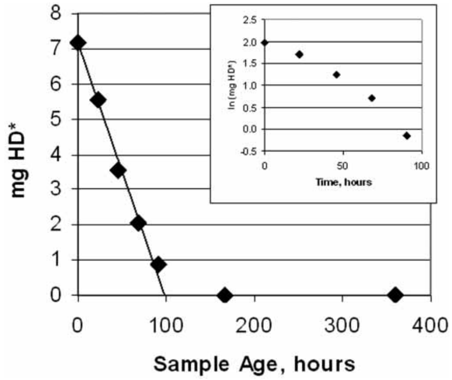

FIGURE 5 Zero-order Kinetic Plot for the Loss of HD* When it Reacts with Water on Sand U at 35°C; First-order Kinetic Plot Shown in Inset.

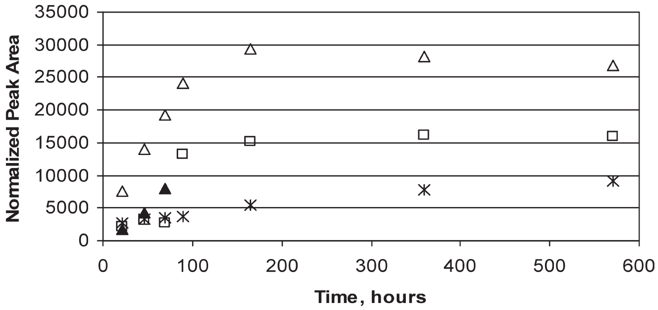

FIGURE 6 Normalized Peak Areas for 62.8 (☆), 59.6 (△), 42.3 (▲), and 44.9 (≤) ppm Resonances for the Degradation of Sulfur Mustard on Re-wet Sand U at 35°C.

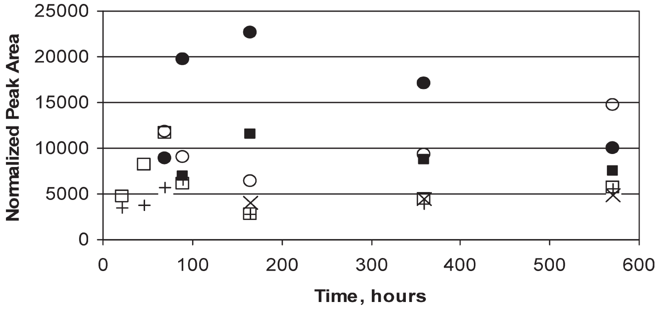

FIGURE 7 Normalized Peak Areas for the Resonances Associated with Sulfonium Ions for the Degradation of Sulfur Mustard on Re-wet Sand U at 35°C: 47.4 (●), 47.1 (○), 36.1 (×), 35.4 (+), 29.5 (■), and, 28.8 (□) ppm.

Spectra of moistened Sand E and Sand A indicated two products, TDG and H-2TG, by the end of the monitoring period (Table 3), whereas the chemical shifts detected in both samples of Sand U were consistent with the additional presence of small amounts of CH in addition to TDG and H-2TG. Reaction schemes for the formation of H-2TG, CH, and TDG

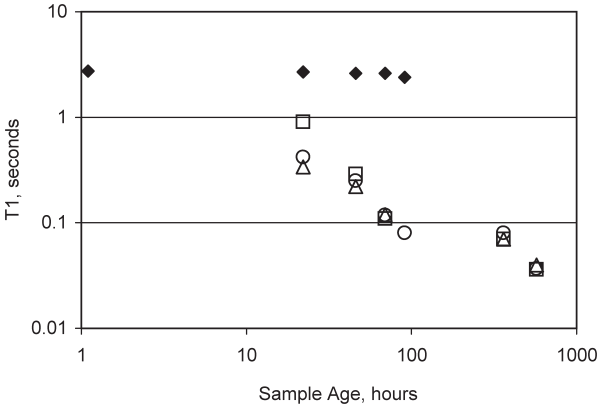

FIGURE 8 Average ^{13}C T$_1$ Relaxation Times as a Function of Time on Re-wet Sand U at 35°C: Sulfur Mustard (◆); TGD at 61.4 ppm (□); Sulfonium Ion at 27 ppm (△) and 57.4 ppm (○).

from HD have been previously elucidated and are shown in Fig. 9.[13,14,16]

Broad peaks were only observed on Sand U, which also had a very short product T_1 relaxation time of 0.024 s, compared with 2.6 s for the sulfur mustard (Table 4). The final T_1 relaxation times were 10 times shorter for Sand U than for Sand E, and 4 times shorter for Sand A than for Sand E (Table 4); the different magnitudes suggested an interaction that was specific to the sand used. The chemical shifts on Sand U moved downfield by ~3 ppm over 8 weeks; this downfield shift was ~0.8 ppm for Sand A and was not observed at all for Sand E. The changes in the T_1 relaxation times and chemical shifts with time may both be ascribed to the formation of ions in the fluid around the sand.[40] In particular, Sand U, which had the most alumina, showed the greatest effects, and Sand E, which had no alumina, exhibited the least effect. The hydrochloric acid produced during reactions of sulfur mustard and water on alumina has been observed to liberate aluminum ions, $Al(H_2O)_6^{3+}$;[25] the aluminum and chloride ions could produce the observed changes in the chemical shifts and T_1 relaxation times. Another possibility for the shorter T_1 relaxation times was an interaction between the products and the sand substrate. However, consideration of the percentage sulfur mustard on the surface, 0.3% to 0.9%, would relegate any interaction between the products and the sand substrate to a small fraction of the sulfur mustard, rather than the majority.

Degradation on Re-wet Sand U at 35°C

The 35°C studies had four notable aspects: zero-order kinetics for the loss of sulfur mustard, the gradual shifting of all product chemical shifts downfield, the gradual decrease in product T_1 relaxation time, and the splitting of three of the six product peaks.

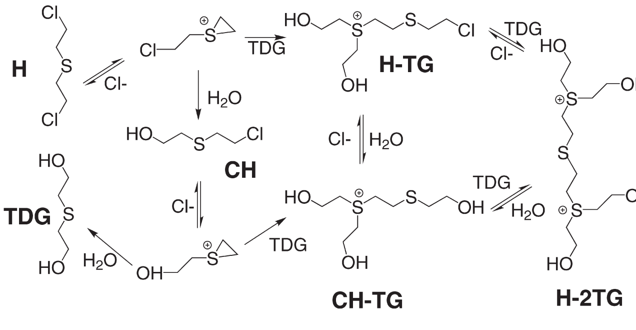

FIGURE 9 Degradation Scheme for Sulfur Mustard.[13,14,17]

Zero-order kinetics may occur when an enzyme or surface catalyst is present and manifest when the reactant saturates the catalyst surface.[41] In this case, the presence of zero-order kinetics suggested that the sand surface played a role in facilitating the degradation of the sulfur mustard. One possibility is an interaction of the sulfur mustard with the sand, and then formation of the $ClC_4H_8S^+Cl^-$ sulfonium ion, which would then react with the water to form CH, a process that has a half-life of minutes in aqueous solution.[18,19] The subsequent steps would be consistent with the previously published reaction scheme (Fig. 9).[13,14,16]

Another possible source of the zero-order kinetics is the dissolution of the sulfur mustard at the water–surface interface; that is, the sulfur mustard coated the sand and gradually dissolved into the water and then reacted. Because the dissolution of sulfur mustard is slow relative to its reaction rate in water,[17] the dissolution of sulfur mustard would be the rate-determining step of the reaction. This scenario is consistent with the observed T_1 relaxation time values of 2 s that persisted until all of the sulfur mustard was used and is also consistent with the observation of zero-order kinetics.[41]

Over the period of 1 month, all of the product chemical shifts gradually shifted downfield by 3 ppm, whereas the mustard chemical shifts were unchanged. This shift may be due to the increase in ionic character of the water surrounding the sand, as a result of both aluminum and chloride ion liberation during the reaction.[40] It was also noticed that the tuning of the probe, which was sensitive to the material in the sample, shifted as the sample aged.

The gradual decrease in product T_1 relaxation time, from 0.9 to 0.03 s (Fig. 8), may also be ascribed to the formation of ions in the fluid around the sand;[40] consideration of the percentage sulfur mustard on the surface would relegate any interaction between the products and the sand substrate to a small fraction of the sulfur mustard, rather than the bulk.

The peaks that split were those at ~28, ~35, and ~46 ppm. The ~28 and ~46 ppm split peaks likely signify the presence of a mixture of the sulfonium ion species H-TG, CH-TG, and/or H-2TG; the ~35 ppm split peak may be due to CH, CH-TG, H-TG, and/or TDG (Fig. 9 and Table 2). A small peak at 43 ppm in the 22-h and 46-h samples was also suggestive of the presence of CH; it was not present in the sample after 90 h (Figs. 4 and 6).

The normalized integrated peak areas showed that the peak at 47.4 ppm had the same growth and decay profile as the 29.5 ppm peak. In addition, the integrated peak areas shifted from the 47.4 ppm peak to the 47.1 ppm peak and from the 29.5 ppm peak to the 28.8 ppm peak with time (Fig. 7). Hence, the first sulfonium ion product, which had chemical shifts at 47.4 and 29.5 ppm, degraded to a second sulfonium ion product that had chemical shifts at 47.1 and 28.8 ppm; both sulfonium ion products had coincident resonances at 59.6 and 44.9 ppm.

The normalized integrated peak areas at 59.6 and 44.9 ppm, which represented total sulfonium ion present, reached a maximum at 167 h and gradually decreased; the hydroxyl resonance at 62.8 ppm steadily grew. This indicated that some of the intensity in the 62.8 ppm peak was not due to a sulfonium ion (i.e., CH-TG), but rather to another species, likely TDG. Given this information, an attempt was made to deconvolute the spectra acquired after 50 h based on combinations of CH-TG, H-TG, TDG, and/or H-2TG. An agreement for all peaks of 2% or less was considered an acceptable possibility for the identity of the species present. The calculated percentage of products is shown in Table 5; for the 167-h, 330-h, and 570-h samples, it was not possible to unequivocally distinguish between CH-TG and H-TG. Nonetheless, the %TDG increased, and the %H-2TG had a maximum at 167 h, as shown in Figs. 6 and 7, thus suggesting the formation of TDG from the degradation of H-2TG.

TABLE 5 **Calculated Percentages of Sulfur Mustard and Its Degradation Products in Sand U at 35°C**

Time (h)	%HD	%CH-TG	%H-TG	%TDG	%H-2TG	Sum
69	28	41	19	—	—	88
90	12	49	—	—	41	102
167[a]	0	22	—	8	67	97
167[b]	0	—	20	8	67	95
360[a]	0	36	—	9	53	98
360[b]	0	—	32	9	54	95
570[a]	0	45	—	10	44	99
570[b]	0	—	45	10	44	99

[a] Peaks at 62, 35, 27, 43, 45, and 58 ppm were attributed to CH-TG.
[b] Peaks at 43, 33, 29, 44, 46, and 59 ppm were attributed to H-TG.

Spectra acquired in the first 50 h had large amounts of mustard, which dwarfed the product peaks; it was possible to calculate multiple combinations for the product mixture, but all these were poor. Hence, peak assignments for these spectra were not reported.

CONCLUSIONS

The lack of degradation of mustard on the ambient substrates, plus the formation of the products similar to those seen in aqueous solution and moist soil, suggested that the sand functioned as a support on which the reaction between sulfur mustard and water occurred. The degradation of mustard at room temperature on moist silicate sand from three different locations indicated two products, ∼10% non toxic TDG and ∼90% toxic H-2TG on Sands E and A; on Sand U ∼10% CH, ∼10% TDG, and ∼80% H-2TG were observed. T_1 relaxation time data and final chemical shifts suggested that the interaction between the sand and products was stronger on Sands U and A than on Sand E.

The degradation of sulfur mustard on moist Sand U at 35°C exhibited zero-order kinetics in sulfur mustard, which suggested that the surface was involved in the first step of the reaction. The subsequent reaction and products were consistent with previously published reaction mechanisms. The first product observed was H-2TG, which then decomposed to TDG plus a second sulfonium ion. Trace quantities of CH were detected in the early stages of the reaction.

The formation of toxic sulfonium ion products during the degradation of sulfur mustard indicated that an area that has been contaminated with sulfur mustard must be assayed for not only mustard but also degradation products before the area can be declared safe for re-entry and re-use.

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