

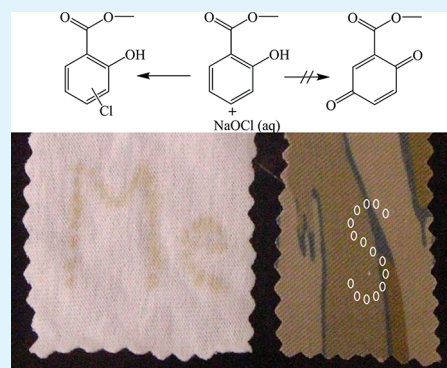
Methyl Salicylate: A Reactive Chemical Warfare Agent Surrogate to Detect Reaction with Hypochlorite

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ABSTRACT: Methyl salicylate (MeS) has a rich history as an inert physical simulant for the chemical warfare agents sulfur mustard and soman, where it is used extensively for liquid- and vapor-permeation testing. Here we demonstrate possible utility of MeS as a reactivity simulant for chlorine-based decontaminants. In these experiments MeS was reacted with sodium hypochlorite varying stoichiometry, temperature, reaction time, and pH. No colored oxidation products were observed; however, chlorination of the aromatic ring occurred ortho (methyl 3-chlorosalicylate) and para (methyl 5-chlorosalicylate) to the position bearing the $-OH$ group in both the mono- and disubstituted forms. The monosubstituted para product accumulated initially, and the ortho and 3,5-dichloro products formed over the next several hours. Yields from reactions conducted below pH 11 declined rapidly with decreasing pH. Reactions run at 40 °C produced predominantly para substitution, while those run at 0 °C produced lower yields of ortho- and para-substituted products. Reactions were also carried out on textile substrates of cotton, 50/50 nylon–cotton, and a meta aramid. The textile data broadly reproduced reaction times and stoichiometry observed in the liquid phase, but are complicated by physical and possibly chemical interactions with the fabric. These data indicate that, for hypochlorite-containing neutralizing agents operating at strongly alkaline pH, one can expect MeS to react stoichiometrically with the hypochlorite it encounters. This suggests utility of MeS in lieu of such highly hazardous surrogates as monochloroalkyl sulfides as a simulant for threat scenarios involving the stoichiometric decomposition of sulfur mustard. Specifically, the extent of coverage of the simulant on a fabric by the neutralizing agent can be directly measured. Similar reactivity toward other halogen oxidizing agents is likely but remains to be demonstrated.

KEYWORDS: electrophilic aromatic substitution, methyl salicylate, chemical warfare, simulant, decontamination, and textile



INTRODUCTION

Because they share similar physical properties—vapor pressure, viscosity, dipole moment, and enthalpy of vaporization—methyl salicylate (MeS) is the physical surrogate^{1,2} of choice for two chemical warfare agents (CWAs), *O*-pinacolyl methylphosphonofluoridate (soman, GD) and bis(2-chloroethyl) sulfide (sulfur mustard, HD), in tests such as liquid–liquid and liquid–vapor permeation. However, chemical properties of the same three compounds differ grossly and, consequently, different chemically reactive surrogates—e.g., 2-chloroethyl ethyl sulfide (2-CEES), whose oxidizable sulfide functional group better mimics the reactivity of HD—are employed in challenges designed^{1–3} to quantify the effectiveness of oxidative decontamination agents. The phenolic functionality of MeS implies susceptibility to oxidation, which suggests that MeS might serve as a less-hazardous surrogate having better-matched physical properties for examining the efficiency of coverage and distribution of a sprayed or wiped chlorine-based neutralizant for HD and for a family of similarly oxidizable CWAs, alkyl 2-*N*-, 2-*N*'-di(isopropylamino)ethylthio methylphosphonates (V-agents). If MeS could be fully oxidized to a quinone (an intensely colored, conjugated, cyclic dione) then surface coverage could be quickly evaluated by visual recognition of a colorimetric reaction.

Hypochlorite oxidants are used as decontaminants^{4–6} in applications ranging from household cleaning to the detoxification of CWAs. A typical mode of HD decontamination is oxidation of the electron-rich heteroatom, sometimes followed by rearrangement to form less-toxic chemical species. However, during the investigation described herein we were reminded that a second mode of reaction with an electrophile is available to MeS—electrophilic aromatic substitution (EAS) of chlorine onto the activated aromatic ring. Reactions involving EAS were studied extensively during the early midtwentieth century⁷ and are well understood. Nuclear chlorination is known^{8,9} to occur on phenols and other aromatic compounds exposed to hypochlorite or other chlorine-based oxidants.

EXPERIMENTAL SECTION

Materials. MeS (Fisher Scientific, Fair Lawn, NJ), 6% sodium hypochlorite (NaOCl) (Clorox Company, Oakland, CA), sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) (EMD Chemicals, Darmstadt, Germany), methanol (Acros, Geel, Belgium), 5-chlorosalicylic acid, 98% (Aldrich, Milwaukee, WI), 3-chlorosalicylic acid, 98% (Aldrich,

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Milwaukee, WI), sulfuric acid (Sigma, St. Louis, MO), potassium peroxydisulfate (Aldrich, Milwaukee, WI), and chloroform-*d* (Aldrich, Milwaukee, WI), were purchased and used without modification. Hydrochloric acid (Fisher Scientific, Fair Lawn, NJ) was diluted to 1.0 M in water purified by reverse osmosis.

Methods. Reactions were initially examined by liquid injection into a Thermo–Finnigan gas chromatograph (GC) interfaced to a Thermo–Fisher mass spectrometer (MS) fitted with a Thermo–Fisher TR5-MS 30 m × 0.25 mm × 0.25 μm fused silica capillary column coated with 5% polysilphenylene siloxane. The GC injection port was held at constant temperature ($T = 250\text{ }^{\circ}\text{C}$) in splitless mode with a helium flow rate of 1 mL/min. The initial column temperature of 40 °C was held for 4 min, then ramped at 20 °C/min to 270 °C and held for 2 min; the MS was scanned from m/z 45 to 250 at 1807.1 amu/s; the ion source and transfer line were also kept at 270 °C. ^1H nuclear magnetic resonance (NMR) spectra were measured using an Anasazi Eft-90, 90 MHz NMR spectrometer. Samples were placed in 5 mm tubes and dissolved in 1 mL of chloroform-*d* containing a trace of tetramethylsilane.

Chlorination of MeS. Initially, oxidation of MeS by hypochlorite was attempted in a 20 mL glass vial by adding 1.0 mL of MeS to 10.0 mL (1:1 mol ratio) of 6% NaClO at ambient temperature and vortexing; all further references to hypochlorite imply this concentration. No effort was made to control the mild exotherm during reaction. Subsequent reactions were carried out in 20 mL glass scintillation vials and magnetically stirred. Precipitation of solid products caused the stir bar to stall, so methanol (20% v/v) was added to the reaction mixture. The inclusion of the cosolvent kept the products in solution and lowered the viscosity, allowing adequate stirring.

The exotherms produced by the reaction were measured with a K-type thermocouple (Omega Engineering, Inc.) interfaced with a digital multimeter (Fluke 189). These reactions were carried out at a 1:2 mol ratio (MeS:hypochlorite)—one following the original procedure and one with methanol added—to drive conversion and were vortexed for 15 s before the thermocouple was inserted into the reaction vessel. Before GC-MS or NMR analysis, 100 mg of $\text{Na}_2\text{S}_2\text{O}_3$ was added to quench unreacted halogen, and the mixture was diluted in methanol or chloroform-*d*, respectively.

Authentic samples of the two monosubstituted products were prepared by dissolving 100 mg of the respective commercially acquired acids in 5 mL of methanol containing a drop of concentrated sulfuric acid and warming to 50 °C for an hour. Methyl 3,5-dichlorosalicylate was prepared by stirring a mixture of 0.50 mL of MeS and 10 mL of hypochlorite for 1 h, quenching with ~100 mg of $\text{Na}_2\text{S}_2\text{O}_3$, and extraction into 2 mL of methanol.

Reactions at lower pH were conducted as above after titration of the hypochlorite with hydrochloric acid (1.0 M) to the desired pH (8, 9, 10 and 11). For studies of time dependence (5, 15, 30, 60, 120, 240 min, and 24 h), we drew 400 μL aliquots, diluted them to 2 mL with methanol, and analyzed them as above by GC-MS. Because of the formation of insoluble products, 2 mL of methanol was added to the reaction mixture before MeS was added to maintain a single-phase solution. In separate experiments, 5 mL of hypochlorite was reacted with 0.5 mL of MeS (1:1 mol ratio) and maintained at ~0 °C for 10 min, followed by workup as above.

Procedure for Textile Surfaces. For textile experiments, two sets of tests were performed. For the first, droplets of MeS (1 μL) were applied to swatches of three fabrics: 100% cotton, 50/50 nylon–cotton (NyCo), and a meta-aramid (nomex). A white nomex scrim, style 4012 was provided by Warwick Mills, Inc. (New Ipswich, NH); the NyCo was a Realtree tree bark camouflage pattern, c. 1995, incorporating several shades of green and brown; the cotton was plain white Wamsutta bed sheeting. One molar equivalent of hypochlorite was applied directly at the site of each MeS droplet and allowed to stand at room temperature for 1, 5, 15, or 60 min. In the second test, one molar equivalent of

hypochlorite was applied to three regions of the MeS droplet—directly on top of, adjoining, or remote (1 cm) from the visible edge—on just the NyCo textile and allowed to react for 1 h. For both tests the droplets were then extracted into methanol and analyzed by GC-MS using the conditions listed above.

RESULTS AND DISCUSSION

Spectroscopic and Spectrometric Data. GC-MS analysis of the extracts revealed extensive conversion of MeS into several chlorinated products, presumably via EAS followed by steps of base-catalyzed ester hydrolysis and decarboxylation. Hypochlorite reactions can be complicated by the formation of multiple products and side reactions; however, the three major products identified from this reaction series were substitution products of the original ester, methyl 5-chlorosalicylate (5-ClMeS), methyl 3-chlorosalicylate (3-ClMeS), and methyl 3,5-dichlorosalicylate (3,5-DMeS). Phenol, mono-, di-, and trisubstituted chlorophenols, and methyl acetylsalicylate were also detected as minor products (<5% of the total yield). Chlorophenols likely resulted first from EAS followed by decarboxylation of the ester moiety after hydrolysis, while phenol synthesis likely occurred by ester hydrolysis and decarboxylation of the starting material.

The major product from these reactions was identified as 5-ClMeS⁹ (retention time (t_R) = 13.14 min) by its mass spectrum (m/z 186, 188, 190, M^+ ; 154, 156, 158; M^+ -MeOH; 126, 128, 130; M^+ -H and CO_2Me) and by the splitting patterns observed for the aromatic protons in the ^1H NMR spectrum (δ 6.891, 1Hd, $J = 8.9$ Hz, H-3; δ 7.453, 1Hdd, $J = 2.7, 8.9$ Hz, H-4; δ 7.785, 1Hd $J = 2.7$ Hz, H-6; δ 3.957, 3Hs, $-\text{OCH}_3$). In general, smaller amounts were observed of 3-ClMeS¹⁰ ($t_R = 13.70$ min), ^1H NMR spectrum δ 6.990, 1Hdd $J = 7.9, 7.9$ Hz, H-5; δ 7.687 1Hdd $J = 1.6, 7.9$ Hz, H-4; δ 7.862, 1Hdd, $J = 1.6, 7.9$ Hz, H-6; δ 4.026, 3Hs, $-\text{OCH}_3$, and of 3,5-DMeS^{11,12} ($t_R = 14.83$ min). The 3,5-DMeS crystallized spontaneously¹¹ as colorless needles, melting point 143–146 °C; ^1H NMR data: δ 7.785, 1Hd, $J = 2.6$ Hz, H-2; δ 7.715, 1Hd, $J = 2.6$ Hz, H-4; δ 4.017, 3Hs, $-\text{OCH}_3$; mass spectrometry, see Table 1.

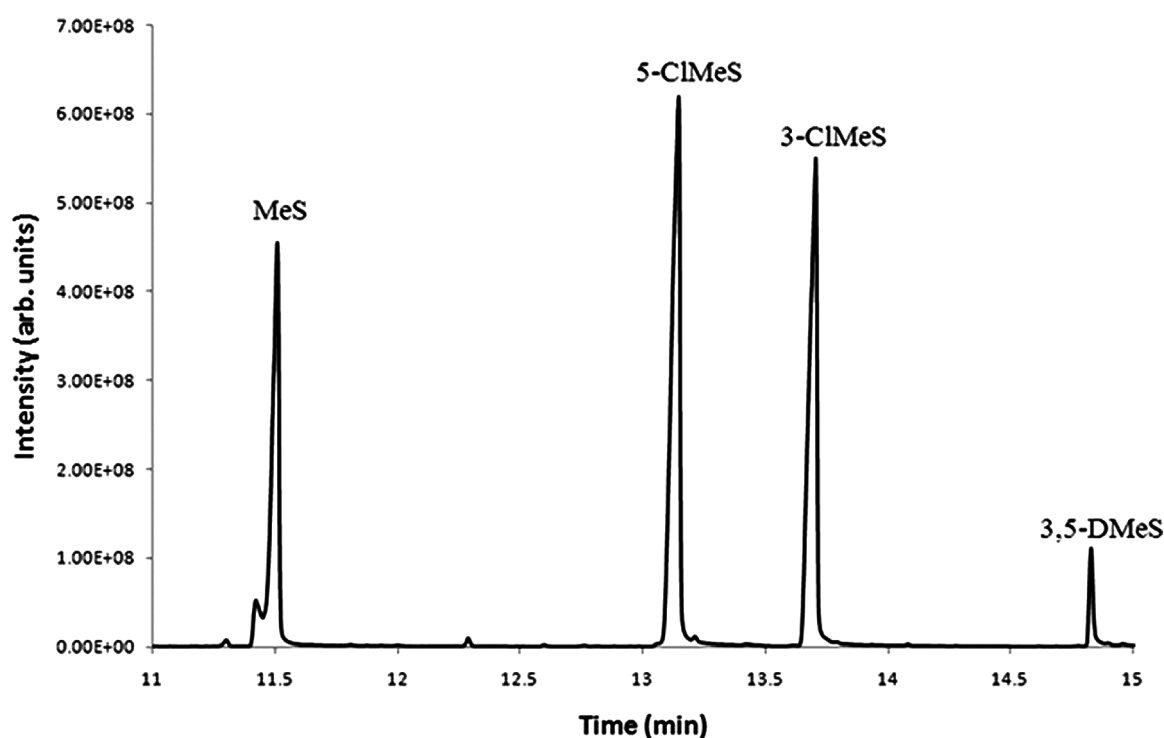
Vortexing 0.5 mL of MeS with 10.0 mL of hypochlorite for 15 s produced a moderate exotherm (comfortably warm to the touch) and formation primarily of 5-ClMeS, which was identified by its mass spectrum and by the splitting patterns observed for the aromatic protons in the ^1H NMR spectrum. A lesser component of the product mixture gave the same mass spectrum as 5-ClMeS and was identified as 3-ClMeS from the splitting patterns in the aromatic ^1H NMR signals. Figure 1 displays the total ion current from a GC-MS analysis with the major components identified. The elution order was verified by methylation of the purchased, authentic chlorosalicylic acids. Figure 2 shows mechanisms proposed to rationalize the formation of the products observed.

It is a noteworthy sidelight that the odd-electron (m/z 188, 190, and 192) fragments in the mass spectra of the chlorosalicylate esters are produced in amounts larger than the even-electron (m/z 189, 191, and 193) fragments formed by loss of the $-\text{OMe}$ group from the esters to form an acylium ion. Yeo and Williams¹³ reported preponderant loss of CH_3OH from the molecular ion of MeS, presumably favored by a concerted cyclic process to form an extensively delocalized product as illustrated in Figure 3. Comparing the intensities of the $[\text{M}-31]^+$ ions to those of the respective corresponding $[\text{M}-32]^+$ fragments in Table 1 reveals a consistent trend of decreasing relative intensity of the $[\text{M}-31]^+$ fragment with increasing substitution by chlorine

Table 1. Relative Intensities of Ions Measured in the 70 eV Electron-Impact Ionization Mass Spectra of Four Esters of the Series *o*-HOC₆H_{4-n}Cl_nCO₂Me

<i>n</i> =		% Intensity ^a of Ions Scaled to Base Peak =100% (<i>m/z</i>)			Ratio of Relative Intensity to Relative Intensity of Common Isotopomers ^b of [M-32] ⁺ Ion	
		M ⁺	M ⁺ -31	M ⁺ -32	M ⁺ /M ⁺ -32	M ⁺ -31/M ⁺ -32
0	H	35.0 (152)	19.1 (121)	100 (120)	0.35	0.19
1	3-Cl	24.0 (186)	13.8 (155)	100 (154)	0.24	0.14
		10.0 (188)	4.6 (157)	32.2 (156)	0.31	0.14
2	5-Cl	32.9 (186)	14.0 (155)	100 (154)	0.33	0.14
		9.7 (188)	4.8 (157)	33.9 (156)	0.27	0.14
		21.5 (220)	8.8 (189)	100 (188)	0.22	0.09
2	3,5-Cl ₂	17.9 (222)	6.4 (191)	60.2 (190)	0.30	0.11
		2.0 (224)	0.9 (193)	9.4 (192)	0.22	0.09

^a Intensities are corrected only for ¹³C satellite contributions. ^b Separate signals are listed for isotopomeric species having different representation of ³⁵Cl and ³⁷Cl, and the ratios of intensities measured among the isotopomers are consistent with the natural abundance ratio of chlorine.

**Figure 1.** Total ion current chromatogram for methyl salicylate and the primary chlorinated products: MeS, 5-ClMeS, 3-ClMeS, and 3,5-DMeS ($t_R = 11.51, 13.14, 13.70,$ and 14.83 min respectively).

and a weaker parallel trend toward destabilization of the molecular ion. A $-Cl$ substituent on an aromatic molecule is a weak, deactivating, ortho-para-directing group, whose effect is generally attributed to inductive withdrawal in the ground state and resonance release of electron density into the cationic intermediate by the $-Cl$ residue. The rationalization depicted in Figure 3 distributes the molecule's electron deficiency into the conjugated π -electron system. The aryl ring is arbitrarily represented as intact in the $[M]^+$ ion and in that form will be cross conjugated to the charge centers of the $[M-31]^+$ ion, which is consistent with a concerted elimination mechanism and possibly greater relative stabilization of the $[M-32]^+$ ion by successive replacements of $-H$ by $-Cl$, as suggested by the trends in Table 1.

Effect of Temperature, Reaction Time, Stoichiometry, and pH. To determine the baseline reactivity of MeS with hypochlorite, reactions were run at stoichiometric ratios of 1:1 and 1:2 (2 equivalents of hypochlorite). The evolution of EAS products, 5-ClMeS, 3-ClMeS, and 3,5-DMeS, coincided with removal of MeS. In reactions at 1:2 equivalents, the additional hypochlorite drives the reaction with MeS farther. The time course of the exotherm (Figure 4) shows that the reaction occurs on the scale of 10–20 min with hypochlorite alone, and in a minute or two in 20% aqueous methanol; however, the small amount of 3,5-DMeS continues to increase gradually for several hours.

Reactions run at or below pH 10 resulted in lower yields of chlorinated products, presumably due to decreased amounts of the phenolate anion alone or in combination with the equilibrium shift

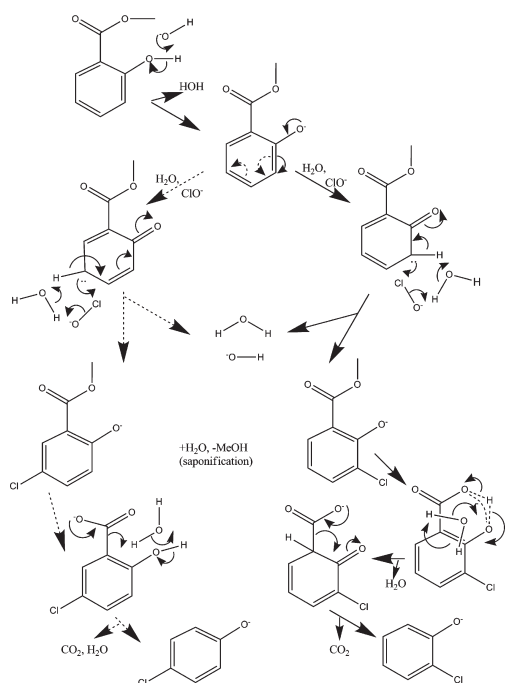


Figure 2. Proposed mechanism for EAS, saponification, and decarboxylation.

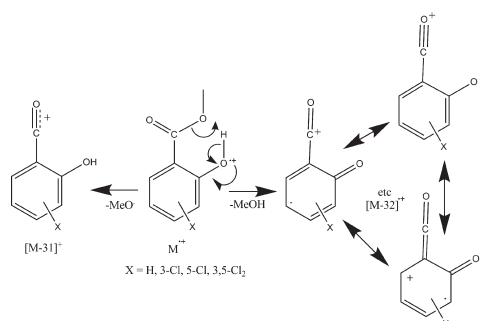


Figure 3. Possible concerted mechanism for the formation of $[M-32]^+$ at 70 eV.

from hypochlorite to hypochlorous acid.^{14–16} By varying the stoichiometry of the reactants—0.5, 1.0, 2.0, and 5.0 mol equivalents of hypochlorite to 1.0 equivalent of MeS—at pH 11, it was found that both monochloro isomers eventually formed at all four ratios, but at least 2.0 mol equivalent of hypochlorite were required to produce appreciable levels of 3,5-DMeS. Reactions that were not controlled reached 30–40 °C for up to 5 min and yielded predominantly 5-ClMeS. The reaction held at ~0 °C for 10 min revealed only partial conversion of MeS to yield approximately equal amounts of the two monochloro isomers. A possible interpretation is that 3-ClMeS forms as a kinetic product at low temperature but is slightly disfavored thermodynamically. Both monochloro isomers appear to be precursors to 3,5-DMeS when sufficient hypochlorite is available, and that the second chlorination step is slower than the first is also predictable because the Cl— substituent is deactivating.

Reactions on Textiles. Protective fabrics are a common medium on which to evaluate the effects and course of contamination and decontamination processes. Colorimetric reactions,

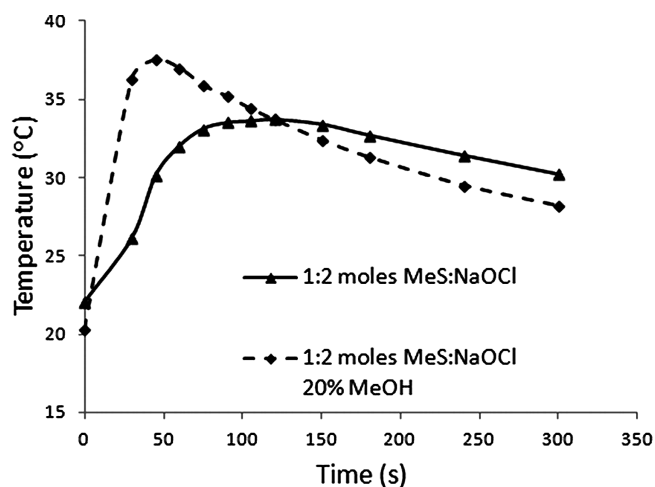


Figure 4. Exotherms for the reaction of MeS with hypochlorite demonstrating the effect of a cosolvent on the rate of reaction.

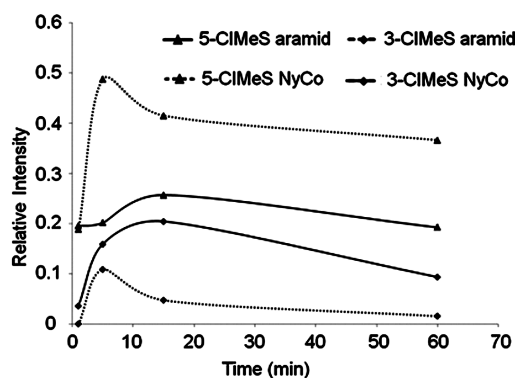


Figure 5. Reactions of MeS and hypochlorite on NyCo and meta-aramid at 1:1 equivalent ($n = 3$).

such as the formation of quinones, are favored in such applications because they provide an immediate visual indication of change. The anticipated oxidation to intensely colored quinones was not observed, but a faint yellow spot was visible on the white cotton fabric after application of the hypochlorite and MeS. There were no notable differences in EAS product formation on any of the three fabrics tested. Observed products from droplet tests on NyCo and meta-aramid (Figure 5) show the relative peak heights of the two monosubstituted products as a function of duration of exposure to hypochlorite at constant loading of MeS. Only monochloro-substituted esters were detected on the two textile types. The data reveal rapid formation of the EAS products, which reach maxima between 5 and 15 min. The subsequent steady decrease of product concentration is presumably due to saponification (Figure 2) followed by a slower decarboxylation step to produce detectable amounts of 2-chloro-, 4-chloro- and 2,4-dichloro-phenol. Figure 2 shows two possible mechanisms, both promoted by the phenolic oxygen center—tautomerization to a β -keto acid and β -elimination of CO_2 or a concerted cyclic elimination that includes a water molecule. Additionally, extraction efficiency may affect the analysis, as differences in surface energies of the materials influence the affinity of the substrate for the reactant and product esters;

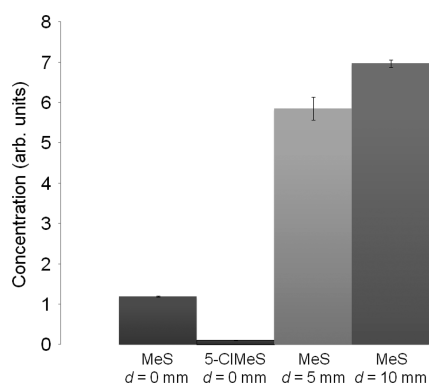


Figure 6. Reaction of MeS and hypochlorite on NyCo (1:1 equivalent) for 1 h. Three conditions investigated were direct contact with both reagents ($d = 0$), partial contact ($d = 5$ mm), and isolation ($d = 10$ mm) ($n = 3$).

therefore, one cannot say that the conversion into chlorinated esters is favored for either substrate.

Fractional coverage of CWA droplets on a surface by the application method used to deliver a decontaminant will limit the efficacy of a neutralization treatment—complete neutralization requires complete coverage. Although a color reaction was not realized, extraction and quantification of the ratio of MeS to chlorinated products by a GC or GC-MS method using t_{RS} and integrated areas will provide a measure proportional to the fraction of the contaminated zones that were covered by the neutralizant. In a final experiment to illustrate this principle, nine $1 \mu\text{L}$ droplets of MeS were deposited on individual swatches of NyCo, and a drop of hypochlorite was applied directly to ($d = 0$ mm) three MeS droplets and to six spots remote (three each at $d = 5$ and 10 mm) from the remaining MeS droplets. Once the droplets had absorbed into the textile, the 5 mm spaced reactants overlapped roughly 20% of the total wetted area. The data in Figure 6 reveal exclusively para-chlorination of MeS with EAS reactions detectable only when the droplets were superimposed. No EAS products were detected for the remotely placed droplets; however, there was a 17% reduction in MeS recovered from $d = 5$ mm droplets compared to the controls, indicating that some MeS was either consumed or retained when the respective droplets were placed in partial contact. This result suggests that reactivity of hypochlorite neutralizants delivered onto a substrate is strongly diffusion limited, an observation likely to be useful as a generalization for all liquid neutralizants.

Other Oxidants. When it became evident that hypochlorite was incapable of oxidizing MeS, MeS was treated with a small excess of potassium peroxydisulfate (Oxone), an oxidant with a higher standard reduction potential ($E^0 = 1.82$ V)¹⁷ than hypochlorite ($E^0 = 0.89$ V), to determine if a more powerful oxidant could convert MeS into a colored quinone, as was our original intent. MeS was not oxidized by Oxone after a 1 h exposure at 50 °C; therefore, it is unlikely that any oxidant compatible with a practical decontamination process will be capable of this conversion.

CONCLUSION

The data reveal that MeS consumes Cl^+ from hypochlorite to form identifiable products via electrophilic substitution, and that the carboxylate substituent both attenuates the reactivity of the phenol nucleus toward electrophilic substitution and confers

resistance to oxidation on the electron-rich MeS molecule. The initial step is presumed to be a Lewis acid–Lewis base interaction, similar to the initial step in many oxidation reactions; however, the subsequent mechanisms are grossly different. Electrophilic nuclear chlorination of MeS is activated by the presence of the hydroxyl group, which is a strong ortho–para director. Monochloro substituents at both activated sites on the aryl ring serve to weakly deactivate the aromatic system, consistent with the slower substitution of a second chlorine at the activated position still unsubstituted, to form 3,5-DMeS.

Quantitative analysis of the products is complicated by the competing process of saponification of the esters to chlorophenols, and by possible surface interactions with different substrates. Failure to realize a clear color test and slowing of the reactions at 0 °C limit the practical utility of MeS as a reactive simulant to qualitative analyses because it must be applied in a moderately warm environment that includes minimal laboratory capability. Once residual hypochlorite is quenched by the addition of sodium thiosulfate, EAS ceases and the byproduct hydroxide ion accelerates hydrolysis of both the product and reagent esters. Thus it will likely be necessary to establish system-specific standard conditions to make this practicable as a method for routine analysis. However, the presence of solubilizing agents in typical oxidative neutralizants will facilitate the rate of conversion of MeS.

A simple protocol for fabric testing is proposed—requiring only a minimal chemical kit to apply MeS followed by the decontamination reagent to be evaluated—to deliver and collect a small amount of extraction solvent, and to inject it into a portable GC. Extent of conversion in reactions carried out on textiles was much lower in similar time frames than in reactions in solution, due at least in part to severely limited mass transport of one or both reactants and possibly to losses of oxidant into the fabric matrix. Reactants that were in direct contact yielded a small degree of conversion into the para-isomer (5-ClMeS), whereas no chlorinated ester products were detected in the remotely placed droplets, which functioned as untreated controls. These data indicate that, for evaluation of the performance of hypochlorite-containing neutralizing agents, one can expect MeS, like the far more hazardous surrogate 2-CEES, to react stoichiometrically with the hypochlorite it encounters, which portends its utility as a surrogate for HD (and possibly VX) in such systems. Specifically, the extent of coverage of the surrogate on a fabric can be directly and quantitatively measured by hypochlorite or another EA substituting decontaminant. However, the proportionality between surrogate and agent will have to be measured in side-by-side experiments. Similar reactivity toward other electrophilic neutralizing agents is likely but also remains to be demonstrated.

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