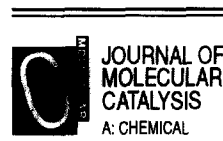




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# Reactions of the mustard simulant 2-chloroethyl phenyl sulfide with self-decontaminating sorbents. A $^{13}\text{C}$ MAS NMR study

George W. Wagner<sup>a,\*</sup>, Philip W. Bartram<sup>b</sup>

<sup>a</sup> Geo-Centers, Inc., Gunpowder Branch Box 68, Aberdeen Proving Ground, MD 21010-0068, USA

<sup>b</sup> Research and Technology Directorate, U.S. Army Edgewood RDEC, Aberdeen Proving Ground, MD 21010-5423, USA

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## Abstract

Decomposition reactions for the mustard simulant 2-chloroethyl phenyl sulfide ( $^{13}\text{C}$ -labelled, CEPS\*) sorbed on  $\gamma$ -alumina, polydivinylbenzene (impregnated with NaOH, polyethylene glycol and polyethylenimine) (DVB/NaOH), and Ambergard<sup>®</sup> XE-555, were characterized in situ using  $^{13}\text{C}$  MAS NMR. CEPS\* hydrolyzes on  $\gamma$ -alumina to form 2-hydroxyethyl phenyl sulfide. On DVB/NaOH, CEPS\* eliminates HCl to yield vinyl phenyl sulfide. No products were observed on XE-555, where the applied CEPS\* was spectroscopically observed to adsorb entirely within the micropores of the carbonaceous resin component of this material. Toxicities of the mustard products analogous to the degradation products observed for CEPS\* are discussed.

## 1. Introduction

Sorbents which can decontaminate chemical warfare agents (CWAs) [1] have received considerable attention in recent years. Such self-decontaminating sorbents (SDAs) are being considered as both a non-corrosive alternative to the current U.S. Army decontaminating solution DS2 (70% diethylenetriamine, 28% ethylene glycol monomethyl ether, and 2% NaOH), and as a next-generation replacement for a currently fielded material, Ambergard<sup>®</sup> XE-555. XE-555

is a non-irritating skin decontaminant that is also useful for decontaminating personal equipment. XE-555 and DS2 are formulated for use in battlefield situations where rapid decontamination is essential.

Two promising SDA candidates are  $\gamma$ -alumina and polydivinylbenzene impregnated with NaOH, polyethylenimine and polyethylene glycol (DVB/NaOH). Although more sophisticated approaches for introducing reactivity into polymeric sorbents were attempted [2], such as covalently-attaching iodosobenzoates [3] and other reactive groups, the resulting materials were less effective than DVB/NaOH. Also, the thermal stability of functionalized polymers is a concern. For example, the quaternary ammo-

\* Corresponding author. Tel.: +1-410-6718468; fax: +410-6713764; e-mail: gwwagner@cmail.apgea.army.mil.

nium groups of strong-base ion exchange resins are unstable above 60°C<sup>1</sup>.

In DS2, mustard (HD)<sup>2</sup> eliminates HCl to form divinyl sulfide [1]. However, hydrolysis occurs in aqueous solutions [1,4]. Besides the major product, thiodiglycol, complex sulfonium ion aggregates also form due to intermolecular reactions [4]. Similar degradation pathways are possible for the 2-chloroethyl phenyl sulfide (ClCH<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>, CEPS) simulant on the candidate sorbents.

Previously, we have utilized <sup>31</sup>P MAS NMR for the in situ study of the reactions of a VX<sup>3</sup> simulant, *O,S*-diethyl phenylphosphonothioate [(CH<sub>3</sub>CH<sub>2</sub>O)(CH<sub>3</sub>CH<sub>2</sub>S)P(O)(C<sub>6</sub>H<sub>5</sub>)] (DEPPT), with XE-555,  $\gamma$ -alumina, and DVB/NaOH [5]. In addition to delineating the reaction chemistry occurring on the sorbents, NMR also provided information about various sorption processes. For example, DEPPT could be spectroscopically observed [6] to slowly adsorb into the micropores of the carbonaceous resin component of XE-555. Additionally, on  $\gamma$ -alumina, NMR detected both a 'liquid' phase and a rather immobile 'monolayer' phase for sorbed DEPPT. The disappearance of the mobile 'liquid' phase coincided with a sudden, dramatic slowing of the reaction rate.

In the present study, we use <sup>13</sup>C MAS NMR to examine reactions of a <sup>13</sup>C-labelled CEPS (CEPS\*) [7], with the same candidate sorbents. Products are easily identified directly from the MAS NMR spectra. The results are compared with those previously found for DEPPT. Finally, the CEPS\* products observed enable the prediction of the HD products expected to form on the sorbents, and the toxicities of these compounds are discussed.

## 2. Experimental methods

### 2.1. Materials

<sup>13</sup>C-labelled 2-chloroethyl phenyl sulfide (CEPS\*) was provided by Professor Douglas F. Taber, University of Delaware. The compound is labelled only at the methylene positions and is actually a 50–50 mixture of C<sub>6</sub>H<sub>5</sub>-S-<sup>13</sup>CH<sub>2</sub>CH<sub>2</sub>Cl and C<sub>6</sub>H<sub>5</sub>-S-CH<sub>2</sub>-<sup>13</sup>CH<sub>2</sub>Cl [7]. The  $\gamma$ -alumina (Selexsorb CD<sup>®</sup>, Alcoa) was obtained in the form of 1/8 inch beads, and is reported in company literature to have a surface area of 400 m<sup>2</sup>/g. The beads were crushed to a fine powder before use. Ambergard<sup>®</sup> XE-555 (Rohm and Haas), a mixture of a high surface area carbonaceous resin and strong-acid and strong-base ion exchange resins [1], was used as received. The polydivinylbenzene (DVB) used to prepare the impregnated sorbent was synthesized by Dr. Gus Ibay and Mr. Philip E. Arnold, Southern Research Institute. The impregnated DVB sorbent was obtained from Dr. Ralph Spafford, Southern Research Institute, which was prepared by sorbing a methanol solution of NaOH, polyethylenimine and polyethylene glycol onto the DVB, followed by drying under a vacuum. The sample was used as received.

### 2.2. NMR

<sup>13</sup>C MAS NMR spectra were obtained using a Varian XL200 NMR spectrometer equipped with a Doty Scientific 7 mm high speed MAS probe. The spinning speed was 3000 Hz. Typically, 128 scans were taken using 90° observe pulses, high-power proton decoupling, and 5 s delays between accumulations. Chemical shifts were referenced to external TMS.

### 2.3. Kinetic runs

The CEPS\* loading was 5 wt% for all the sorbents. Reactions were run by adding a measured volume of CEPS\*, via a syringe, into the middle of a column of the sorbent (5 mm × 15

<sup>1</sup> Material Safety Data Sheet for Amberlite<sup>®</sup> IRA-900 Resin (Rohm and Haas).

<sup>2</sup> Mustard (or HD), a blister agent, has the structure: Cl-CH<sub>2</sub>CH<sub>2</sub>-S-CH<sub>2</sub>CH<sub>2</sub>-Cl.

<sup>3</sup> VX, a nerve agent, has the structure: (CH<sub>3</sub>CH<sub>2</sub>O)(CH<sub>3</sub>)P(O)SCH<sub>2</sub>CH<sub>2</sub>N(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>.

mm) contained in a 7 mm MAS NMR rotor. The rotor was then sealed using teflon tape [8].  $^{13}\text{C}$  MAS NMR spectra were acquired periodically to monitor reaction progress and product formation. The conversion of CEPS\* was calculated using the NMR peak areas of the CEPS\* and product(s), and is expressed as the %CEPS\* reacted.

### 3. Results

#### 3.1. $\gamma$ -alumina

Selected  $^{13}\text{C}$  MAS NMR spectra obtained for 15  $\mu\text{l}$  CEPS\* added to 0.3308 g  $\gamma$ -alumina at the indicated times are shown on the left side of Fig. 1. Using an estimated molecular area<sup>4</sup> of 39  $\text{\AA}^2$  for CEPS\* and the 400  $\text{m}^2/\text{g}$  surface

area of the  $\gamma$ -alumina, the amount of CEPS\* added corresponds to about 1/5 of a monolayer. Two peaks are evident in the spectra for the  $^{13}\text{C}$ -labelled methylene groups of CEPS\* at 43.3 and 36.6 ppm. These peaks are broadened compared to neat CEPS\* liquid, but remain unshifted. Over time, the peaks broaden slightly but remain unshifted with respect to the solution values. The broadening is attributed to the spreading of the CEPS\* throughout the sorbent, resulting in reduced mobility. As indicated in the spectra, two product peaks also appear at 61.1 and 36.3 ppm due to the formation of 2-hydroxyethyl phenyl sulfide ( $\text{C}_6\text{H}_5\text{-S-CH}_2\text{CH}_2\text{OH}$ , HEPS\*). No other products (i.e., sulfonium ions [4]) are detected. The initial region of the reaction profile is shown in Fig. 2, Fig. , and Fig. , and the conversions of CEPS\* at the time intervals of interest are given in Table 1.

#### 3.2. XE-555

Selected  $^{13}\text{C}$  MAS NMR spectra obtained for 10  $\mu\text{l}$  CEPS\* added to 0.2256 g XE-555 at the

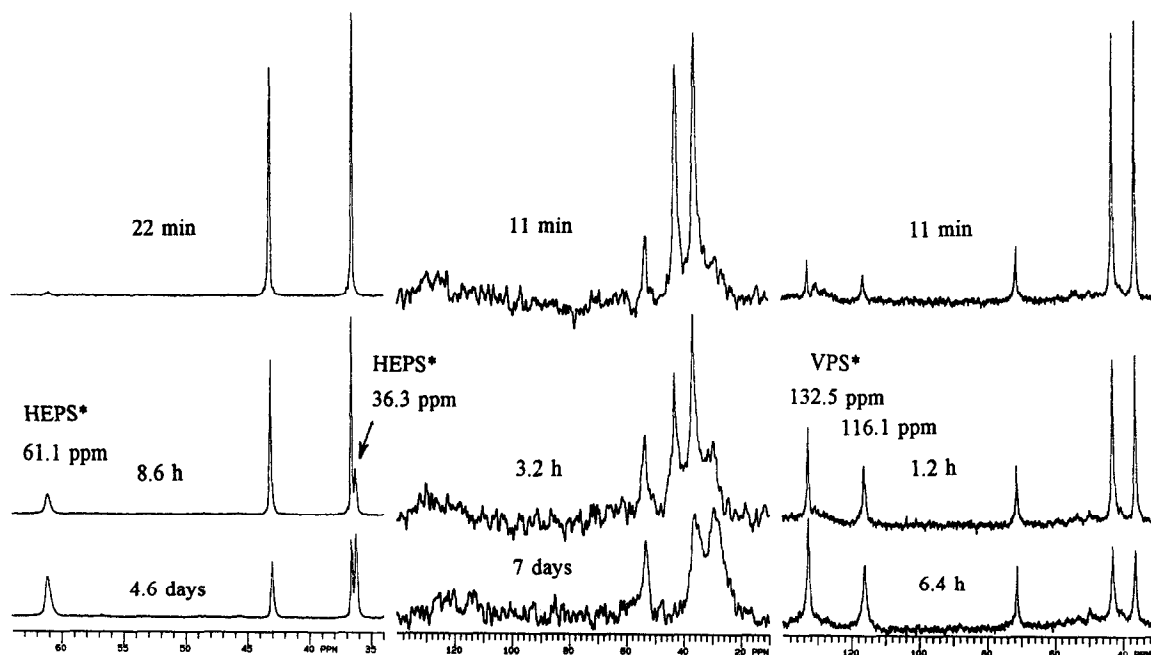


Fig. 1. Selected  $^{13}\text{C}$  MAS NMR spectra obtained for CEPS\* sorbed on  $\gamma$ -alumina (left), XE-555 (middle) and DVB/NaOH (right), at the indicated reaction times. The peaks detected for the HEPS\* and VPS\* products are indicated.

<sup>4</sup> Calculated using the equation [9]  $a_m = f(M/(\rho_L/L))^{2/3}$ , where  $a_m$  is the molecular area,  $f$  is the surface packing factor (1.091),  $M$  is the molecular weight of CEPS (172.7 g/mol),  $\rho_L$  is the liquid density (1.182 g/ml), and  $L$  is the Avogadro constant ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ).

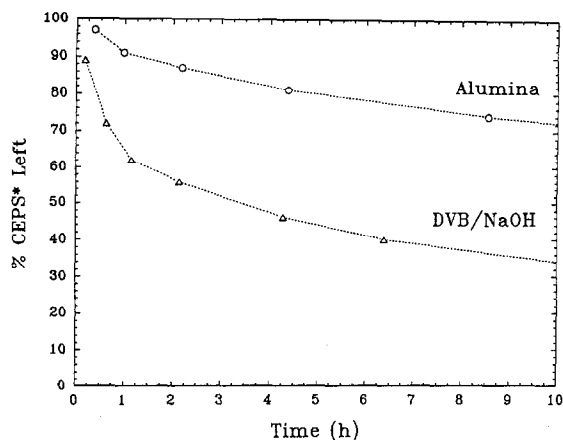


Fig. 2. Reaction profiles for CEPS\* sorbed on  $\gamma$ -alumina and DVB-NaOH.

indicated times are shown in the middle of Fig. 1. The two peaks for CEPS\* are at 43.0 and 36.5 ppm. The constant sharp peak evident in the spectra at 53.3 ppm is due to the trimethylammonium groups of the strong-base ion exchange resin component of XE-555 [8]. Within 24 h, the sharp CEPS\* peaks are slowly replaced by a broad pair of peaks at 36.0 and 29.0 ppm. The broadening and ca. 7 ppm upfield shift of the two peaks is indicative of adsorption of the applied CEPS\* into the micropores of the carbonaceous resin component of XE-555. Such micropore adsorption has previously been observed for this simulant applied to activated charcoal [6]. On charcoal,  $^1\text{H}$  and  $^{13}\text{C}$  MAS NMR peaks detected for adsorbed CEPS and CEPS\*, respectively, are broadened and shifted upfield by about 5.5 ppm. On XE-555, micropore

Table 1  
CEPS\* conversions<sup>a</sup> on sorbents

Time	XE-555	$\gamma$ -alumina	DVB/NaOH	DVB/NaOH <sup>b</sup>
10 min	< 10 <sup>c</sup>	< 3	< 10	< 5
2 h	< 10 <sup>c</sup>	13	44	12
24 h	< 10 <sup>c</sup>	38	71	50

<sup>a</sup> %CEPS\* reacted as measured from  $^{13}\text{C}$  MAS NMR peak areas of reactant and product.

<sup>b</sup> Exposed to air for 7 h before reaction.

<sup>c</sup> No product detected, estimated detection limit stated.

adsorption is the only observable process occurring for applied CEPS\*. No products are detected, even after 7 days. Since no products are observed, a reaction profile is not shown in Fig. 2. However, an upper limit for the CEPS\* conversion (< 10%) is reported in Table 1, which reflects the estimated detection limit for any product(s), if present.

### 3.3. DVB/NaOH

Selected  $^{13}\text{C}$  MAS NMR spectra obtained for 9  $\mu\text{l}$  CEPS\* added to 0.1984 g DVB/NaOH at the indicated times are shown on the right side of Fig. 1. The sharp, constant peak at 71.2 ppm is due to polyethylene glycol. The two sharp peaks initially detected for unreacted CEPS\* at 43.2 and 36.5 ppm become quite broadened over time, but remain unshifted. As in the case of  $\gamma$ -alumina, the peak broadening is also attributed to the spreading of the CEPS\* throughout the sorbent, but it is much more pronounced on DVB. Two product peaks emerge over time at 132.5 and 116.1 ppm due to the elimination product, vinyl phenyl sulfide ( $\text{CH}_2=\text{CH}-\text{S}-\text{C}_6\text{H}_5$ , VPS\*), which are indicated in Fig. 1. No other products are detected. The product peaks also tend to broaden with time, but remain unshifted, suggesting that the VPS\* spreads across the sorbent along with the unreacted CEPS\*. The initial region of the reaction profile is shown in Fig. 2, Fig. , and the CEPS\* conversions are reported in Table 1.

It was found that the reactivity of DVB/NaOH towards CEPS\* is diminished on exposure of the sorbent to air. Shown in Table 1 are the CEPS\* conversions for a sample of DVB/NaOH exposed to air for 7 h prior to adding the CEPS\*. The applied CEPS\* still eliminated HCl to form VPS\*, but the reaction was considerably slower.

## 4. Discussion

The current results show that the order of sorbent reactivity is the same for CEPS\* as

previously found for DEPPT [5]: DVB/NaOH >  $\gamma$ -alumina  $\gg$  XE-555. However, some subtle differences do exist between the overall sorption/reaction processes observed for CEPS\* and DEPPT. CEPS\* applied to XE-555 is completely adsorbed within the micropores of the carbonaceous adsorbent within 24 h, whereas some DEPPT remains outside the micropores, distributed among the ion exchange resin components, even after 5 days. Also, like DEPPT, very little CEPS\* conversion occurs on XE-555 within 24 h (< 10%). On  $\gamma$ -alumina, two distinct  $^{31}\text{P}$  MAS NMR resonances were initially observed for adsorbed DEPPT, which were attributed to 'liquid' and 'monolayer' phases [5]. The disappearance of the liquid phase DEPPT peak coincided with a sudden slowing of the reaction rate, consistent with very slow diffusion in the monolayer phase. In contrast to the behavior of DEPPT, no distinct peaks are observed for monolayer adsorbed CEPS\*; the unshifted peaks merely broaden as the liquid presumably spreads into a monolayer. Also, no sudden slowing of the reaction rate is observed for CEPS\*, which is consistent with facile diffusion within the monolayer. Both CEPS\* and DEPPT are hydrolyzed on  $\gamma$ -alumina. Unlike HD in aqueous solutions [4], no sulfonium ions are detected for CEPS\* on  $\gamma$ -alumina. On DVB/NaOH, CEPS\* decomposes by elimination of HCl and not hydrolysis or methanolysis<sup>5</sup> as seen for DEPPT. This degradation mechanism for CEPS\* is perhaps not unexpected since the DVB/NaOH formulation is reminiscent of DS2 [1]. As with  $\gamma$ -alumina, no sulfonium ions [4] are detected for CEPS\* on DVB/NaOH.

The deactivation of DVB/NaOH by air is attributed to the reaction of the hydroxide with  $\text{CO}_2$ . This is a well-known problem for strong-base ion exchange resins which slowly convert from the hydroxide form to the bicarbonate

form on exposure to air [8]. The prolonged air exposure suffered by the sample of XE-555 examined in this study may have resulted in the deactivation of the strong-base ion exchange resin component.

The fact that CEPS\* hydrolyzes to form HEPS\* on  $\gamma$ -alumina, but eliminates HCl to yield VPS\* on DVB/NaOH is significant, since the analogous HD products possess widely different toxicities. Available literature toxicities ( $\text{LD}_{50}$ , mouse, IV) for HD and its hydrolysis products, chlorohydrin ( $\text{Cl}-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-\text{OH}$ ) and thiodiglycol ( $\text{HO}-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-\text{OH}$ ), are 8.6, 35 and 2000 mg/kg, respectively [10]. The toxicities for the HD elimination products, 2-chloroethyl vinyl sulfide ( $\text{Cl}-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}=\text{CH}_2$ ) and divinyl sulfide ( $\text{CH}_2=\text{CH}-\text{S}-\text{CH}=\text{CH}_2$ ) are reportedly identical, 71 mg/kg [11]. Clearly, complete hydrolysis of HD to TDG, which is expected to occur on  $\gamma$ -alumina, is the preferred reaction for a SDA.

## 5. Conclusions

Of the sorbents examined, DVB/NaOH possesses the best reactivity towards CEPS\*. CEPS\* eliminates HCl to form vinyl phenyl sulfide. The analogous HD product is divinyl sulfide which is still quite toxic. DVB/NaOH suffers a loss of activity when exposed to air, apparently due to the reaction of hydroxide with  $\text{CO}_2$ .  $\gamma$ -alumina is about 50% less reactive than DVB/NaOH in a 24 h period, but is air-stable. CEPS\* is hydrolyzed on  $\gamma$ -alumina to form 2-hydroxyethyl phenyl sulfide. The analogous HD product is non-toxic thiodiglycol. Due to the absence of products, XE-555 shows no detectable reactivity towards CEPS\*, even after 7 days.  $^{13}\text{C}$  MAS NMR reveals that the applied CEPS\* liquid adsorbs completely within the micropores of the carbonaceous adsorbent component of XE-555 within 24 h.

<sup>5</sup> Residual methanol or methoxide on DVB/NaOH resulted in the methanolysis of sorbed DEPPT [5].

## Acknowledgements

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