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IDENTIFICATION OF DEGRADATION PRODUCTS OF 2-CHLOROETHYL ETHYL SULFIDE BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

Gas chromatography–mass spectrometry under both electron impact and methane chemical ionization conditions has been used to detect impurities and degradation products present in the mustard simulant 2-chloroethyl ethyl sulfide, with a detection limit of 0.05 area percent. After one and two years of storage at ambient temperatures, the primary degradation product was 1,4-dithiane formed from the degradation of dimeric sulfonium ions. Oxidation and hydrolysis products were not detected.

INTRODUCTION

The vesicant, bis(2-chloroethyl) sulfide or mustard, has recently been identified on the Iran/Iraq battlefield by a United Nations team of experts[1]. The international significance of this incident points to the need for specific and sensitive means to detect such compounds. In addition, knowledge of the impurities and degradation products may help pinpoint the source and age of the contamination. Such information could also be useful to teams charged with verifying treaty compliance or for scanning manufacturers of new stores of such chemicals.

Little published research exists for the degration of mustard and 2-chloroethyl sulfides[2]. Such research was aimed at specific identification of the parent compound without regard to the nature of degradation products or the mechanism by which they form. In our laboratory we have used gas chromatography–mass spectrometry (GC–MS) under both electron impact (EI) and chemical ionization (CI) conditions to identify the degradation products of a mustard simulant, 2-chloroethyl ethyl sulfide (CEES). The simulant has a single chlorine which should simplify spectra and interpretation with respect to the degradation mechanism.

EXPERIMENTAL

The CEES samples were doubly-distilled products from Farfield Chemical Company and were stored at ambient conditions. The three samples of different ages

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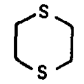
TABLE I

GC–MS IDENTIFICATION AND QUANTITATION OF CEES IMPURITIES (AREA %)

Retention time (s)	*Structure*	*Fresh**	*1-Year old**	*2-Year old**
54	$ClCH_2CH_2Cl$	–	0.2	0.2
57	$CH_3CH_2SCH_2CH_3$	–	0.2	0.2
79	$C_5H_{12}S$**	0.5	0.6	0.4
79	$CH_3SCH_2CH_2Cl$	0.8	0.2	0.2
92	$CH_2=CHSCH_2CH_2Cl$	0.2	0.1	0.1
106	$CH_3CH_2SCH_2CH_2Cl$	97.6	94.4	94.9
121	$CH(CH_3)_2SCH_2CH_2Cl$	0.6	1.1	1.0
144	$CH_3CH_2CH_2SCH_2CH_2Cl$	–	0.3	0.8
157	MW 156 (2 Cl)	–	0.4	0.3
167		–	1.7	0.9
237	$S(CH_2CH_2Cl)_2$	–	0.06	0.05
247	$CH_3CH_2SCH_2CH_2SCH_2CH_3$	–	0.1	0.1
423	$CH_3CH_2SCH_2CH_2SCH_2CH_2Cl$	–	0.1	0.5

* The samples were separately acquired at one-year intervals and analyzed at the same time.
** Perhaps $C_2H_5SC_3H_7$.

were analyzed by GC–MS techniques using both EI and CI methods to identify the impurities. The samples were analyzed on a Finnigan Model 5100 GC–MS instrument using a 15 m × 0.252 mm I.D. SE-54 capillary column with a split ratio of 50:1. The injector temperature was 200°C, the interface temperature was 230°C, the ion source temperature was 100°C and the oven was programmed from 60°C to 160°C at 10°C/min. The mass range was scanned from 60 to 450 a.m.u. for CI and from 30 to 450 a.m.u. for EI at one scan per s. Methane (0.6 Torr) was used as the chemical ionization reagent gas.

Spectral identifications were obtained by direct comparison to existing spectra or on the basis of combined EI/CI fragmentation*. Quantitation (expressed as area percent) was obtained by integration of the areas under the total ion chromatogram peaks and represents only an approximation of the relative quantities present. Sufficient quantity (0.05 μl) of neat sample was injected to observe sample components at the 0.05% concentration level.

RESULTS AND DISCUSSION

Degradation pathways

Table I lists the quantities of compounds found in freshly distilled and the one- and two-year old samples. One interesting result is the absence of oxidation products, *i.e.*, sulfone or sulfoxide in the aged samples. Second, it appears that 1,4-dithiane is

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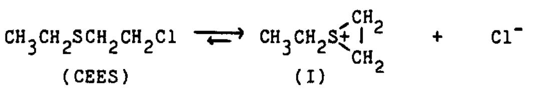
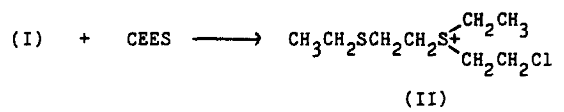
* National Bureau of Standards 39000 compound mass spectral data base and a user library of mustard derivatives generated in-house.

the major degradation product and a characteristic marker for an aged sample. A number of thioethers and alkyl halides were also formed during aging.

The presence of such compounds in aged samples can be accounted for by assuming that degradation of CEES occurs through formation of dimeric sulfonium ions. The initial step in the degradation is the formation of the reactive ethylene sulfonium ion intermediate I via an S_N1 mechanism (eqn. 1). The reactive intermediate I then reacts with any available nucleophile. In water or base, the reaction would lead to the formation of 2-hydroxyethyl ethyl sulfide (HEES). Under our conditions the principal nucleophile is CEES itself which leads to the stable ethyl 2-chloroethyl thiodiethyl (ECT) sulfonium ion II (eqn. 2).



(1)

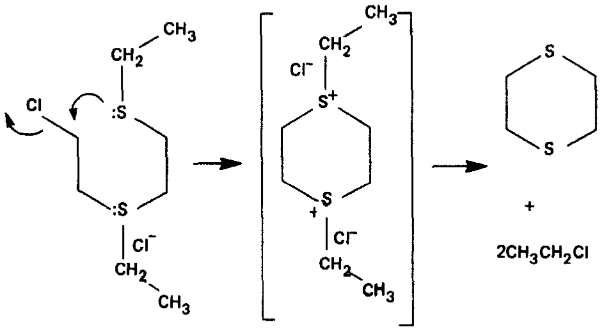


$$(I) + CEES \longrightarrow CH_3CH_2SCH_2CH_2\overset{+}{S}\begin{matrix}CH_2CH_3\\ CH_2CH_2Cl\end{matrix} \quad (II)$$

(2)

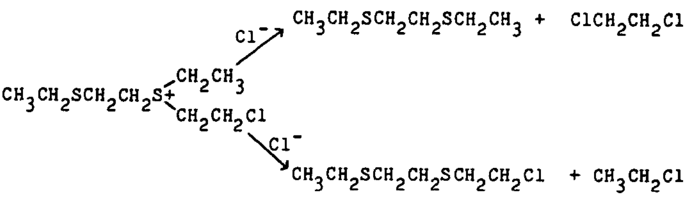
With time II decomposes very slowly in the aged sample to form 1,4-dithiane of a six-membered ring structure, linear sulfides, and alkyl halides as shown in Table I.

The decomposition mechanism of II is proposed in eqns. 3–5 (refs. 3 and 4).



(3)

(III)



$$CH_3CH_2SCH_2CH_2\overset{+}{S}\begin{matrix}CH_2CH_3\\ CH_2CH_2Cl\end{matrix} \xrightarrow{Cl^-} CH_3CH_2SCH_2CH_2SCH_2CH_3 + ClCH_2CH_2Cl \quad (4)$$

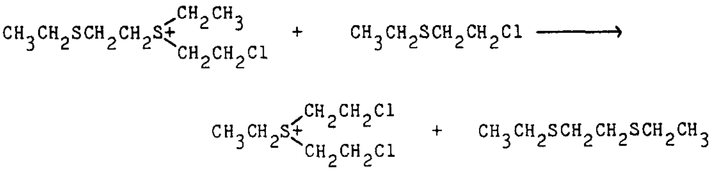
$$CH_3CH_2SCH_2CH_2\overset{+}{S}\begin{matrix}CH_2CH_3\\ CH_2CH_2Cl\end{matrix} \xrightarrow{Cl^-} CH_3CH_2SCH_2CH_2SCH_2CH_2Cl + CH_3CH_2Cl \quad (5)$$

(4)

(5)

Ethyl chloride was not detected in these samples probably because of loss due to extreme volatility. Attempts to identify sulfonium ion II directly by NMR were not successful. However, in binary mixtures of CEES and water, direct NMR identification of ethyl 2-hydroxyethyl thiodiethyl (EHT) sulfonium ion (product of I and HEES) has been reported[5]. We believe II can slowly hydrolyze to form EHT in the presence of water. Presumably EHT can also cyclize to form 1,4-dithiane if sufficient acid (H^+) is present in the aged sample to protonate the hydroxyl group as a first step[5,6]. However, the formation of dithiane from II or EHT is a slow process at room temperature and occurs only in aged samples. As reported previously, EHT forms from protonated HEES[5]. A solution containing EHT and hydrochloric acid decomposes under our GC–MS conditions (200°C injection port) to form primarily CEES and HEES, while 1,4-dithiane is absent[7]. This also suggests that 1,4-dithiane is not produced as an artifact of the analysis. Ethylene sulfide was not detected in these samples*. This suggests that the preferred reaction route for I is the formation of dimeric sulfonium ions; rather than decomposition to ethylene sulfide, as was previously reported for 2-haloethyl sulfide derivatives[8].

Although the amount of mustard detected was small it was positively identified by comparing the spectrum and retention time to that of a standard. We believe mustard is a decomposition product of ethyl dichloroethyl sulfonium cation III which is transformed from II by nucleophilic attack of CEES (eqn. 6). Similarly, II can form other secondary sulfonium ions.

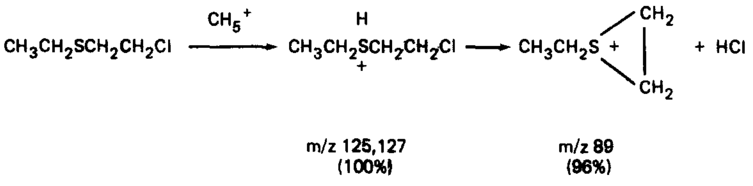


$$CH_3CH_2SCH_2CH_2\overset{+}{S}\begin{matrix}CH_2CH_3\\CH_2CH_2Cl\end{matrix} + CH_3CH_2SCH_2CH_2Cl \longrightarrow CH_3CH_2\overset{+}{S}\begin{matrix}CH_2CH_2Cl\\CH_2CH_2Cl\end{matrix} + CH_3CH_2SCH_2CH_2SCH_2CH_3 \qquad (6)$$

(III)

CI fragmentation pathways

Listed below are the major CI fragmentation pathways observed for CEES and CEES dimerization products. As shown, the protonated molecular ions readily undergo cleavage in the ionization source to form the cyclic sulfonium ion fragments. The numbers listed in parentheses represent the percentage of base peak.



(7)

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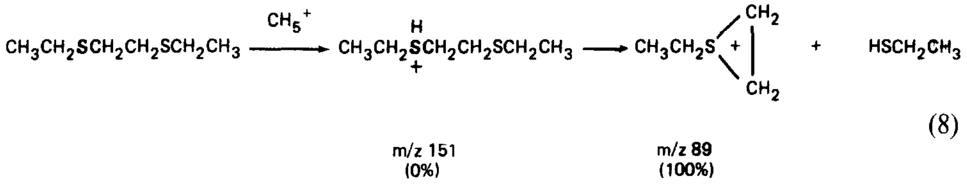
* Although ethylene sulfide is reactive and tends to polymerize, our method has been used to identify ethylene sulfide as a degradation product from other compounds successfully.



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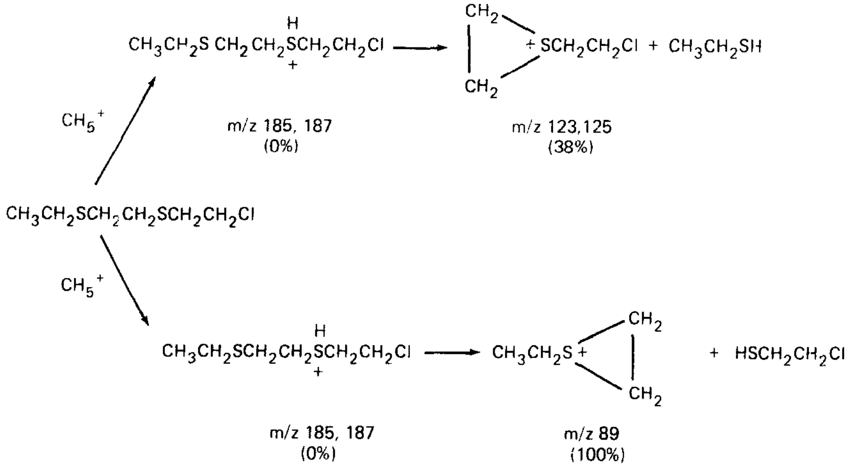

(9)

(10)

Worthy of note is the peak observed in the CI spectrum of CEES in all three samples at *m/z* 213 (2% of base peak), which corresponds to the dimeric sulfonium ion II.

CONCLUSION

Our results are consistent with a degradation mechanism in which dimeric sulfonium ions are formed as CEES ages. These ions transform slowly to 1,4-dithiane as a primary product. No oxidation or hydrolysis products were detected in the aged samples. The same mechanism for degradation at a slower rate is proposed for mustard, since it forms the reactive ethylene sulfonium ion less readily than CEES[9].

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