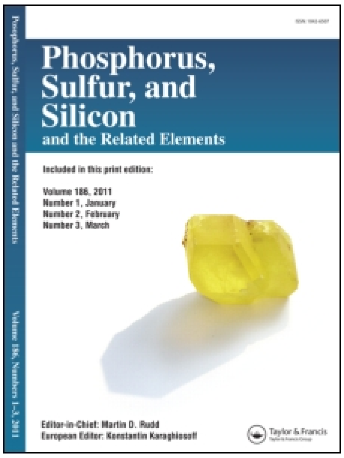

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THERMAL DEGRADATION OF BIS (2-CHLOROETHYL) SULFIDE (MUSTARD GAS)

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The thermal degradation of mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$, "HD"), with and without 5% added water, is examined. GC/MS, LC/MS and NMR were employed to comprehensively analyze the products. After 75 days at 90°C, 91% HD remains (80% with 5% water). After 40 days at 140°C, 30% HD remains (24% with 5% water) and black "tar" precipitates form. The apparent E_a is 22.4 kcal/mol. Major products include Q ($ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$), 1,2-dichloroethane, polysulfides and 1,4-dithiane. With 5% water, oxygenates such as 1,4-thioxane and 2-chloroethanol are produced as are numerous sulfonium ions, including *S*-(2-chlorethyl)-1,4-dithianium, a major component of "mustard heels." The decomposition does not go to completion due to the equilibrium nature of the reaction at these temperatures.

Keywords: mustard; mustard gas; mustard heels; thermal degradation; sulfonium ions

INTRODUCTION

The propensity of mustard gas, a viscous, oily liquid with a boiling point of 217°C (henceforth referred to by its military designation "HD"), to thermally degrade has been known for several decades,[1,2] although only recently have modern analytical techniques allowed for a comprehensive analysis of the range of products. An early mechanism proposed in 1927[1]

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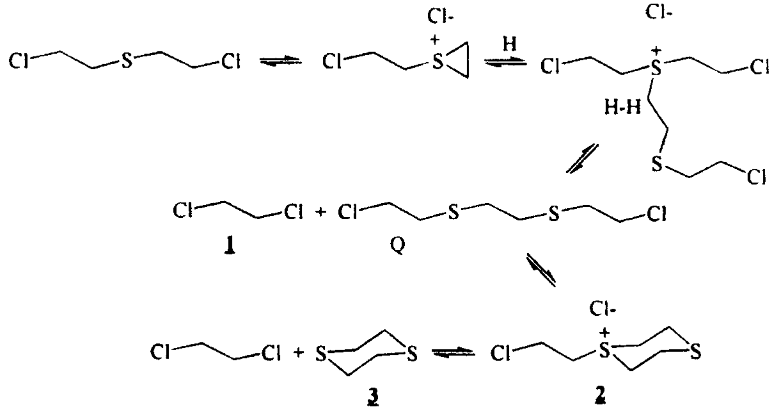
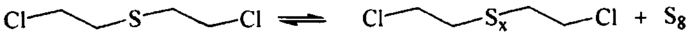
adequately accounts for the major products found for thermally degraded HD and for aged HD in ton containers (Scheme 1).[3]



SCHEME 1

The major products are 1,2-dichloroethane (**1**), 1,4-dithiane (**3**) and 1,2-*bis*(2-chloroethylthio) ethane (Q). A precipitate also forms which is partially ascribable to higher MW (Q-like) polyethylene sulfides.[1,4] Although not detected in earlier studies amoung the insoluble material,[1,2,4] the key intermediate **2**, a known compound,[5] was recently found as a major constituent of "mustard heels."[3] By extension of the same basic mechanism, the formation of longer chain polyethylene sulfides and sulfonium ions during HD decomposition is similarly explained (see below, Scheme 2).[1,4]

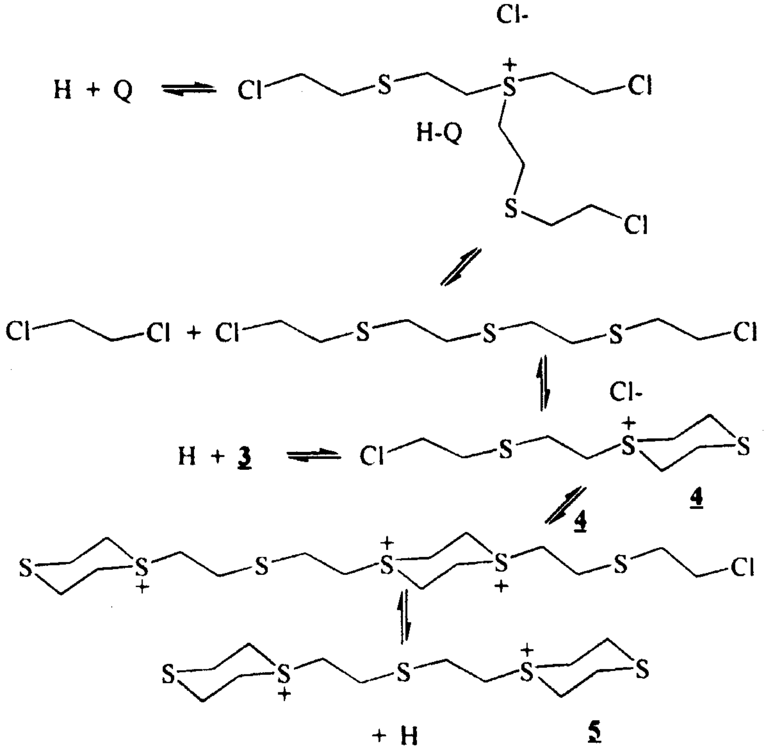
Another degradation pathway, which is most significant in air and at higher temperatures, involves the formation of polysulfides via free radical reaction mechanisms and elemental sulfur to yield a black, tar-like residue:[2,6,7]



x = 2 (HDS_2), 3 (HDS_3), 5 (HDS_5)

The purpose of this study is to investigate the rate and products of thermal degradation of HD at moderately elevated temperatures of 90 and

140°C. It is also our objective to examine the effect of air and a small amount of water on the rates and products of the thermal degradation of HD. In an earlier study,[3] it was discovered that in the absence of heat, air and moisture, HD degraded to mainly **2** under prolonged storage in ton containers at ambient temperatures. We attempt to compare the mechanism of thermal degradation of HD with that of the slow degradation of HD in ton containers. NMR, GC-MS and LC-MS are employed to comprehensively analyze the products.



SCHEME 2 (polysulfide growth/degradation)

EXPERIMENTAL

NMR spectra were obtained on Varian INOVA 200 and Unityplus 300 NMR spectrometers. Spectra were referenced to external TMS (0ppm, ^1H)

and $CDCl_3$ (77.0ppm, ^{13}C). GC-MS analyses were performed on a Hewlett Packard 5890 gas chromatograph coupled to a 5970 mass selective detector. The instrument was equipped with a 30m × 0.25mm HP-5 capillary column with a film thickness of 1.0μm. The injection port and detector temperatures were 225°C. The carrier gas was helium at a flow rate of ca. 1ml/min. The column oven temperature was programmed from 70°C to 270°C at 10°C/min, with a 2 min post-injection interval and a 5 min upper limit interval. Results are reported as a percentage of the total ion chromatogram and represent only an approximation of the relative quantities present. LC-MS analyses were performed by dissolving the sample in methanol and analyzing by electrospray ionization (ESI) on a Finnigan TSQ-7000 GC/MS/MS. ECI conditions were as follows: spray voltage 4.5kV, spray current 0.5mA, capillary temperature 200°C, sheath gas (nitrogen) 70psi, scan range 100–400amu, scan time 0.7sec, mobil phase methanol, methanol flow rate 0.2ml/min. Authentic standards of **2**, **4**, **7**, **8**, and **11** were prepared as described elsewhere.[8, 9] Thermal degradations were carried out at either 90° or 140°C by placing 2ml of HD in 12ml capacity screw-cap (teflon-faced cap liner) or autoclave vials, respectively. The vials were stored in thermostated ovens. Periodically, the vials were removed and cooled to room temperature for analysis. 5vol% water was added to some samples, thus forming aqueous and organic layers in the vials. For these samples, the aqueous layers were decanted from the organic layers and examined separately by NMR and LC-MS to characterize the water-soluble ionic degradation products.

RESULTS AND DISCUSSION

The ^{13}C NMR and GC-MS results for the thermal degradation of HD at 90° and 140°C are shown in Table I, and the corresponding decomposition profiles are shown in Figure 1. ^{13}C NMR and LC-MS analyses of the aqueous layer from the 5vol% H_2O sample are shown in Table II. Various detected products are identified in the reaction schemes below.

The major products detected, Q, **1** and **3**, are in agreement with earlier studies.[1, 2, 4] With water present, additional major products form, including 2-chloroethanol (**6**) and 1,4-thioxane (**10**), and sulfonium ions **2**, **7** and **8**. At extended reaction times HDS_2, HDS_3 (and presumably higher polysulfides and sulfur) and the black tar form, also consistent with the earlier studies.

TABLE I Analyses of HD Thermal Degradation

90°C

^{13}C *NMR*[a]	*Day*	*Day 14*			*Day 46*			*Day 75*			*Day 110*[d]			*Day 147*[e]		
	0	*Ar*	*Air*	H_2O[c]	*Ar*	*Air*	H_2O	*Ar*	*Air*	H_2O	*Ar*	*Air*	H_2O	*Ar*	*Air*	H_2O
HD	97.0	96.6	96.7	[c] 91.9	91.8	92.6	86.8	90.5	91.7	79.8	85.1	84.5	70.6	80.7	79.8	59.9
Q	-	0.3	0.5	1.0	1.0	1.1	2.2	1.7	1.2	3.4	2.2	2.0	3.9	2.8	2.4	4.9
1	0.2	0.7	0.7	1.9	2.7	2.6	5.7	4.7	4.1	9.8	7.3	7.9	13.7	9.5	10.0	19.2
3	1.4	1.4	1.2	1.5	1.8	1.8	3.7	2.6	2.6	5.5	3.5	3.8	7.8	5.0	5.3	11.3
6	-	-	-	0.2	-	-	0.5	-	-	0.5	-	-	0.6	-	-	0.4
10	-	-	-	0.3	-	-	0.5	-	-	0.7	-	-	0.7	-	-	0.7
HDS_2	-	-	-	-	-	-	-	-	-	-	0.1	0.1	0.2	0.1	0.2	0.2
other	1.5	1.0	0.9	3.0	1.9	1.4	1.0	0.5	0.4	0.2	1.8	1.7	2.7	2.0	2.4	3.4

GC-MS[b]	*Day*	*Day 46*			*Day 75*			*Day 110*[d]		
	0	*Ar*	*Air*	H_2O[c]	*Ar*	*Air*	H_2O	*Ar*	*Air*	H_2O
HD	94.64	88.07	90.38	84.61	84.73	87.66	81.12	82.18	87.55	76.87
Q	-	2.71	2.68	5.49	3.81	4.06	7.00	3.45	3.60	8.44
1	-	2.53	2.72	5.67	3.89	3.32	8.42	5.68	6.05	10.82

3	2.76	3.62	3.87	7.03	4.61	5.25	9.24	5.95	5.84	12.00
6	-	-	-	0.89	-	-	0.74	-	-	1.13
HDS_2	-	-	-	0.40	0.30	0.33	0.89	0.35	0.51	0.59
$ClCH_2CH_2SCH_2CH_2CH_2Cl$	0.39	0.47	0.46	0.42	0.41	0.49	0.30	0.37	0.39	0.33
$ClCH_2CH_2CH_2SCH_2CH_2CH_2Cl$	0.41	0.51	0.55	0.33	0.49	0.43	1.01	0.39	0.43	0.95
$CH_3ClCHCH_2SCH_2CH_2CH_2Cl$	0.45	0.48	0.47	0.22	0.38	0.37	0.45	0.33	0.33	0.00
$ClCH_2CH_2SCH_2CH_2CH_2CH_2Cl$	1.35	1.61	1.58	1.49	1.37	1.41	0.00	1.31	1.36	0.82

140°C

^{13}C *NMR*^{a}	*Day 2*		*Day 6*^{d}		*Day 40*^{e}		*GC-MS*^{b}	*Day*	*Day 2*		*Day 6*^{d}		*Day 40*^{e}	
	Air	H_2O^c	*Air*	H_2O	*Air*	H_2O		*0*	*Air*	H_2O	*Air*	H_2O	*Air*	H_2O
HD	92.4	80.9	83.0	57.4	30.2	24.2		92.0	83.5	71.1	73.6	50.3	60.8	40.2
Q	1.6	3.5	2.8	5.2	6.4	6.8		0.4	4.8	8.4	6.1	10.8	9.8	10.3
1	2.6	7.1	8.3	21.4	44.7	49.8		0.2	13.1	7.0	8.0	15.6	12.5	21.1
3	1.7	4.1	4.2	11.7	15.8	15.0		2.9	3.2	6.2	6.5	13.8	10.9	21.0
6	-	0.7	-	0.9	-	-		-	-	0.9	-	1.0	-	0.6
10	-	0.4	-	0.7	-	0.1		-	-	0.8	-	1.3	-	0.9
HDS_2	0.3	0.3	0.3	0.5	0.3	0.4		-	0.6	0.9	1.2	1.6	1.8	1.5

HDS_3	-	-	-	-	0.3	0.3		-	-	-	-	-	-	-
other	1.5	2.9	1.4	1.9	2.4	3.3	$CH_3ClCHCH_2CH_3$	-	-	-	-	0.3	-	0.5
							$ClCH_2CH_2OCH_2CH_2Cl$	-	-	0.4	-	0.8	-	0.7
							$CH_3C(O)CH{=}C(CH_3)_2$	-	-	-	-	-	0.8	0.5
							$CH_3C(O)CH_2C(OH)(CH_3)_2$	-	1.7	1.5	1.4	1.5	1.0	0.8
							$ClCH_2CH_2SCH_2CH_2CH_2Cl$	0.8	0.6	-	0.4	0.2	-	-
							$ClCH_2CH_2CH_2SCH_2CH_2CH_2Cl$	1.5	0.6	0.2	0.4	-	0.4	-
							$CH_3ClCHCH_2SCH_2CH_2CH_2Cl$	2.3	1.8	1.3	1.6	0.6	1.2	0.2
							Unknown, MW=166	-	-	1.3	-	0.8	-	0.4
							Unknown, MW=211	-	-	-	-	0.4	0.3	0.3
							Unknown, MW=285	-	-	-	0.6	0.9	0.5	0.8

[a]Mol%. [b]Area%. [c]5vol% H_2O added, organic layer. [d]Black tar formed. [e]Aqueous layer vanished.

Longer chain polyethylene sulfides and sulfonium ions form and degrade via extension of the same mechanism outlined in the Introduction (Scheme 2).

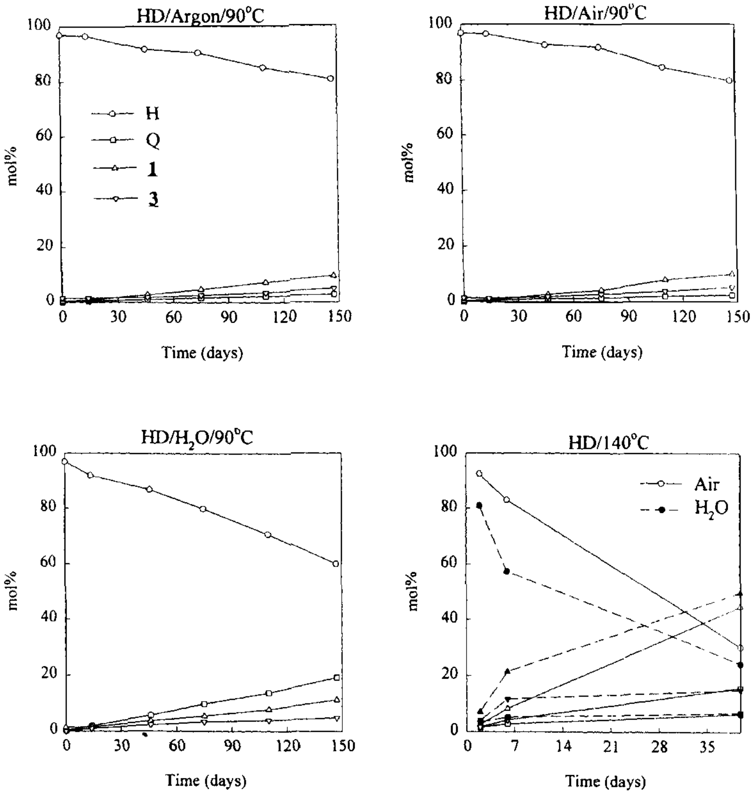


FIGURE 1 Thermal Decomposition Profiles for HD and Major Products

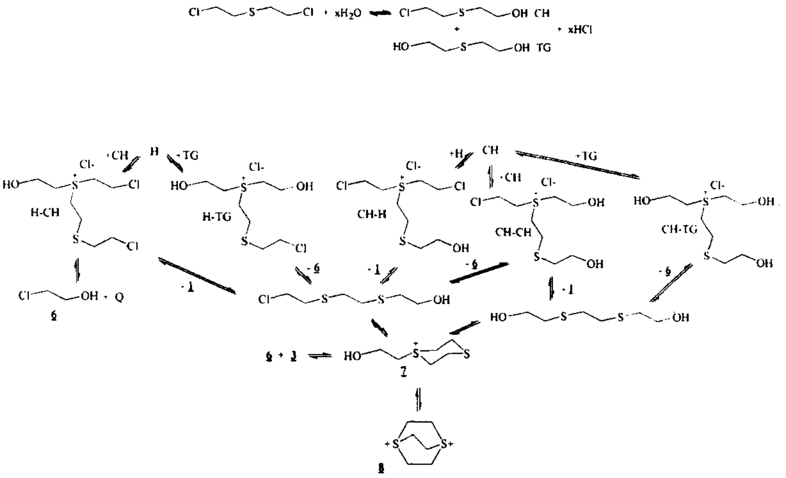
Although polyethylene sulfides/ethers higher than Q were not detected by GC-MS, possibly due to low volatility, LC-MS did detect minor amounts of **4** in the aqueous phase during the HD/5vol% H_2O decomposition at 90°C (see Table II). The transient nature of **4** is reflected by the instabilities of the two authentic samples, possessing either Cl^- or BF_4^- counterions. Authentic **4** (Cl^-) decomposed to form HD and **3**,[10] but authentic **4** (BF_4^-) further reacted with itself to form **5**[9,11] and HD as shown in Scheme 2. A minor amount of the oxygenated analog of **4** was also detected by LC-MS (m/z=227, Table II).

TABLE II ^{13}C NMR and LC-MS Analysis of HD + 5vol% H_2O Degradation at 90°C (Aqueous Layer)[a]

Compound	*^{13}C NMR Shifts*	*m/z*	*Day 46*	*Day 75*	*Day 105*
$Cl\text{-}CH_2CH_2\text{-}OH$ (**6**)	62.5, 46.4[b]	-	27.3	30.3	30.5
$S(C_2H_4)_2S^+CH_2CH_2OH$ (**7**)	56.3, 42.8, 37.3, 23.1[b]	165	28.2	29.6	29.0
$S(C_2H_4)_2S^+CH_2CH_2Cl$ (**2**)	42.7, 38.1, 37.3, 23.1[b]	183	19.1	15.3	15.1
$^+S(C_2H_4)_3S^+$ (**8**)	25.5[b]	-[c]	3.6	3.2	2.4
other[d]			22.0	21.7	23.0
$S(C_2H_4)_2S^+CH_2CH_2SCH_2CH_2Cl$ (**4**)	44.3,40.7,37.3,34.2,26.2,23.6[e]	243			
$O(C_2H_4)_2S^+CH_2CH_2Cl$ (**11**)	65.1, 37.3, 45.8, 40.6[f]	167			
$S(C_2H_4)_2S^+CH_2CH_2OCH_2CH_2Cl$		227			
$O(C_2H_4)_2S^+CH_2CH_2OH$ (**9**)		149			
H-TG		245			

[a] Mol% by ^{13}C NMR. [b] In aqueous layer of HD/5vol% H_2O; ref. to external $CDCl_3$(77.0ppm). [c] Decomposes under LC-MS conditions. [d] Includes the following sulfonium ions detected by LC-MS. [e] Authentic sample in CD_3CN; ref. to internal solvent peak at 1.30ppm. [f] Authentic sample in D_2O; ref. to *external* TSP/D_2O (0ppm).

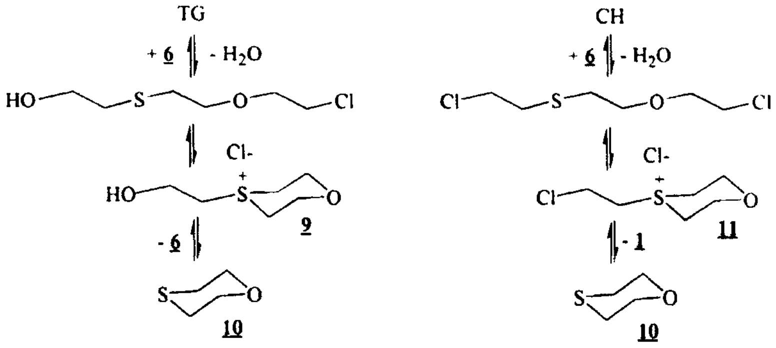
Oxygenated products form in the presence of water where, following initial hydrolysis to chlorohydrin (CH) and thiodiglycol (TG),[12] production may be envisioned to occur in a manner similar to Scheme 1, yielding various alcohols (Scheme 3), and ethers via acid-catalyzed dehydration of the alcohols (Scheme 4).



SCHEME 3 (hydrolysis/alcohol production)

Sulfonium ions **7**, **8**, **9** and **11** were detected in the water layer, with **7** being the most abundant, even greater than **2** (Table II). The reaction of HD with boiling water is known to produce **8**,[13] as does treatment of TG with HCl[5] or H_2SO_4,[14] via the intermediate **7**. As with neat HD, production of longer chain polyethylene sulfides/ethers and sulfonium ions occurs via similar mechanisms.

Consistent with the equilibrium nature of the decomposition at the current temperatures, the reaction does not go to completion. Complete decomposition has been reported[2] at the much higher temperature of 450°, where major products include HCl, ethylene, H_2S, vinyl chloride and the black, tar-like residue.



SCHEME 4 (dehydration/ether production)

CONCLUSIONS

Due to the equilibrium existing between HD and products, thermal degradation does not go to completion at the temperatures examined. Much higher temperatures (ca. 450°) are needed for complete decomposition. The addition of water promotes a greater extent of decomposition, causing the formation of oxygenates and various sulfonium ions.

Acknowledgements

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[11] The ^{13}C NMR shifts for **5** in a degraded sample of **4** are 40.1, 37.3, 25.7, 23.6 (CD_3CN), and LC-MS showed the expected m/z = 164 ion peak.

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