

Chemistry of Chemical Agents

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ABSTRACT

The Department of Defense Explosives Safety Board (DDESB) oversees the Demilitarization and Disposal of Chemical Warfare Agents. One such group of agents of interest, that have been stockpiled and are still being uncovered in buried munitions, are *bis-(2-chloroethyl) sulfide* (sulfur mustard, H/HD) and *tris-(2-chloroethyl) amine* (nitrogen mustard, HN-3). Although H/HD was originally used in World War I, it has reemerged as a major threat around the world due to its ease of manufacture and can be a first choice if a country were to undertake chemical warfare development. Sulfur mustards were first developed in the early-to-mid-1800s and were introduced as chemical warfare agents in 1917 during World War I. Nitrogen mustards were first developed in the late 1920s and the early 1930s. This class of chemical warfare agents are vesicants. The term mustard has been used interchangeably whereas “H” is not distilled with 20-30% impurities; “HD” is distilled or purified form; and “HN-3” is nitrogen mustard. An overview of the chemistry of *bis-(2-chloroethyl) sulfide* (H/HD) and *tris-(2-chloroethyl) amine* (HN-3) and related physical properties will be discussed.

INTRODUCTION

The chemical warfare agents *bis-(2-chloroethyl) sulfide* (sulfur mustard, H/HD) and *tris-(2-chloroethyl) amine* (nitrogen mustard, HN-3) are very reactive vesicants that damage the skin, eyes, respiratory and the immune system. Sulfur mustard was first developed in 1822 and nitrogen mustards were developed in the late 1920s and the early 1930s. Sulfur mustard is a colorless oily liquid at 25°C and odorless in its pure form. HN-3 nitrogen mustard is one of three nitrogen blistering agents that include *bis-(2-chloroethyl) ethylamine* (HN-1) and *bis-(2-chloroethyl) methylamine* (HN-2). HN-3 is a colorless to pale yellow oily liquid at 25°C, has a faint almond odor and is the most stable of the nitrogen mustard agents. Their physical properties are shown in Table 1.^{1,2}

Table 1. Physical Properties of Chemical Agents

| Name | <i>Bis-(2-chloroethyl) sulfide (H/HD)</i> | <i>Tris-(2-chloroethyl) amine (HN-3)</i> |
|---------------------------|---|--|
| CAS | 505-60-2 | 555-71-1 |
| Molecular Formula | C ₄ H ₈ Cl ₂ S | C ₆ H ₁₂ Cl ₃ N |
| Molecular Weight | 159 | 204 |
| Density | 1.24 g/cc | 1.27 g/cc |
| Decomposition Temperature | 180 °C | 150 °C |
| Melting Point | 14 °C (52.7 °F) | -4 to-3.7 °C (24.8 to 25.3 °F) |
| Boiling Point | 217 °C (422.6°F) | 256 °C (492.8°F) |
| Appearance | Colorless to pale oily liquid | Pale yellow oily liquid |
| Vapor Pressure | 0.072 mmHg @ 20°C | 0.016 mm Hg @ 20°C |

SYNTHESIS

There are several processes to manufacture *bis*-(2-chloroethyl) sulfide. The typical synthetic method used in the United States is the Levinstein method³ shown in Figure 1. *Bis*-2-chloroethyl sulfide is prepared from ethylene and sulfur monochloride (S_2Cl_2) or dichloride (SCl_2) in an atmosphere of ethylene via 2-chloroethylsulfenyl chloride intermediate (**I**). This process affords a yield of 70% with byproducts of polysulfides $(ClCH_2CH_2)_2S_x$ of approximately 30% yield. The polysulfides vary in stability and formula which is a side reaction from the process and is not shown in Figure 1.

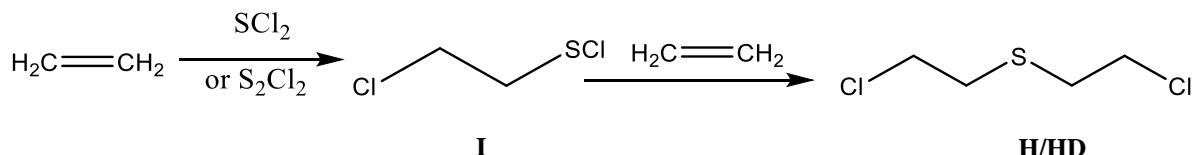


Figure 1. Synthesis of *Bis*-(2Chloroethyl) sulfide

Tris-(2-Chloroethyl) amine is easily synthesized from the triethanolamine as shown in Figure 2. Triethanolamine can be obtained by the condensation of the appropriate alkyl halide and dialkanolamine, not shown. The reaction in Figure 2 proceeds by the substitution of the hydroxyl groups of triethanolamine with a chlorinating agent such as thionyl chloride ($SOCl_2$) or phosphorous pentachloride (PCl_5).^{4,5}

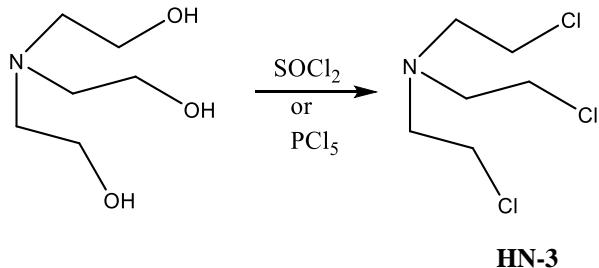


Figure 2. Synthesis of *Tris*-(2-Chloroethyl) amine

DEGRADATION via HYDROLYSIS

One method that has often been investigated for the demilitarization of mustard agents is hydrolysis. Hydrolysis is the chemical breakdown of a compound due to reaction with water. It is reported in the literature^{6,7} that *bis*-(2-chloroethyl) sulfide undergoes a slow hydrolysis to form *bis*-(2-ethylhydroxyl) sulfide (**III**) as the major product with the liberation of hydrogen chloride gas at 25°C, Figure 3. The rate of H/HD hydrolysis is very slow but can be increased with increasing temperature and is not complete even after several days unless a base is present.

Hydrolysis is not a complete solution as it yields toxic compounds such as 2,2'-(chloroethylhydroxyl) sulfide (**II**) and bis-(2-ethyl-hydroxyl) sulfide (**III**). When recovered, the sulfur mustard in sealed canisters or munitions is relatively unchanged. This is attributed to a slower rate of degradation due the absence of moisture, minimal thermal cycling, and the presence of stabilizers, such as hexamethylene tetramine.

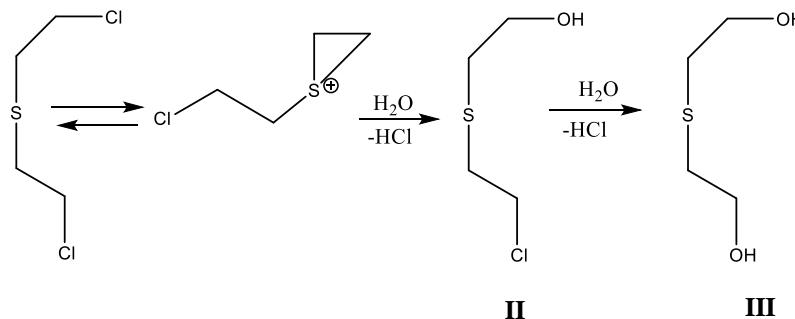


Figure 3. Hydrolysis of Bis-(2-Chloroethyl) sulfide

The hydrolysis of HN-3 proceeds in a similar manner as sulfur mustard, in that it is a stepwise process of chlorine displacement by hydroxyl groups. It is reported in the literature⁸ that the hydrolysis of *tris*-(2-chloroethyl) amine leads to the formation of triethanolamine (**V**) via a cyclic unstable intermediate that is attacked to form an alcohol and hydrochloric acid at 25°C, Figure 4. Hydrolysis proceeds with the loss of the first chlorine after approximately the first 15 minutes, the second chlorine after approximately 4 hours with approximately 90-95% completion after 24 hours at 25 °C. It should be noted that the hydrolysis process yields toxic compounds such as bis-(2-chloroethyl)-2-ethylhydroxyl amine (**IV**) and triethanolamine (**V**) that still pose a risk and can be transferred to the skin. When, recovered, the nitrogen mustard in sealed canisters or munitions is relatively unchanged. This is attributed to a slower rate of degradation due the absence of moisture and minimal thermal cycling.

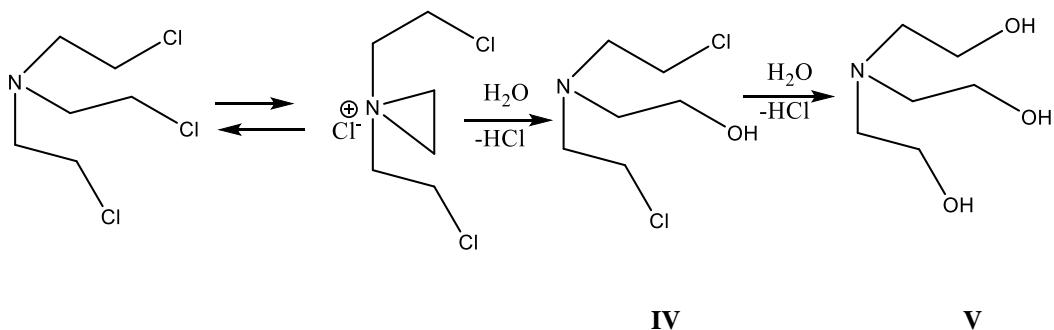


Figure 4. Hydrolysis of *Tris*-(2-Chloroethyl) amine

THERMAL DEGRADATION

Thermal degradation is an efficient method of destruction for sulfur mustard and HN-3 nitrogen mustard that ensures complete destruction including that of the agents, their intermediates and byproducts. As shown in Figures 3 and 4, sulfur mustard and HN-3 nitrogen mustard can exist in equilibrium to form the corresponding cyclic intermediates which have similar properties to the chemical agent. For sulfur mustard stored at 25°C in steel canisters, in the absence of heat, water and moisture, the sulfur mustard slowly degrades (Figure 5) to mainly 1,2-bis-(2-chloroethylthio)ethane (**VI**), 1,2-dichloroethane (**VII**) and 1,4-dithiane (not shown). It has been determined that a temperature of 500 °C must be reached to ensure complete degradation of the chemical agent, its intermediates and byproducts.

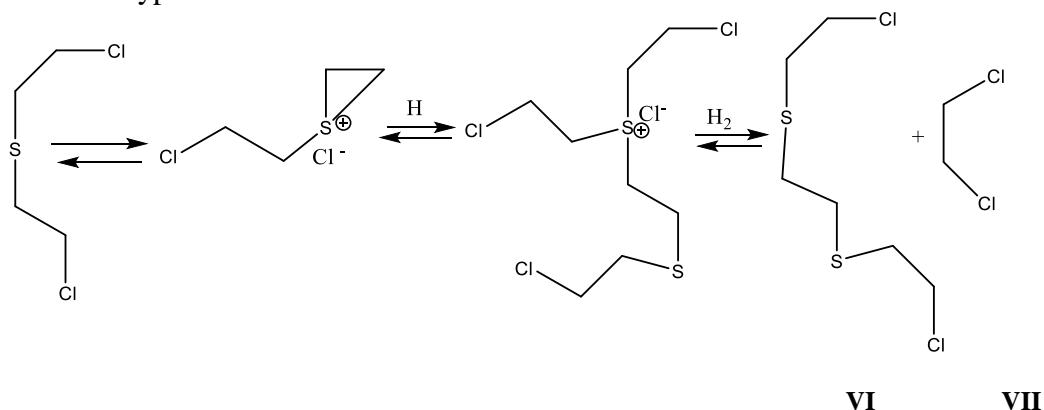


Figure 5. Degradation of Bis-(2-Chloroethyl) sulfide

To date, the decomposition of HN-3 mustard has not been as fully studied as that of sulfur mustard. It is plausible, at 25 °C in steel canisters or in munitions HN-3 may exist in equilibrium with its intermediates. It may undergo a very slow degradation process overtime which involves the elimination of hydrochloride gas to form N,N-bis-(2-chloroethyl) ethenamine (**VIII**), N-(2-chloroethyl)-N-vinylethenamine (**IX**) and trivinylamine (**X**), Figure 6. As is common for the thermal treatment of sulfur mustard, a temperature of 500°C must be reached in order to ensure complete degradation of the chemical agent, its intermediates and byproducts.

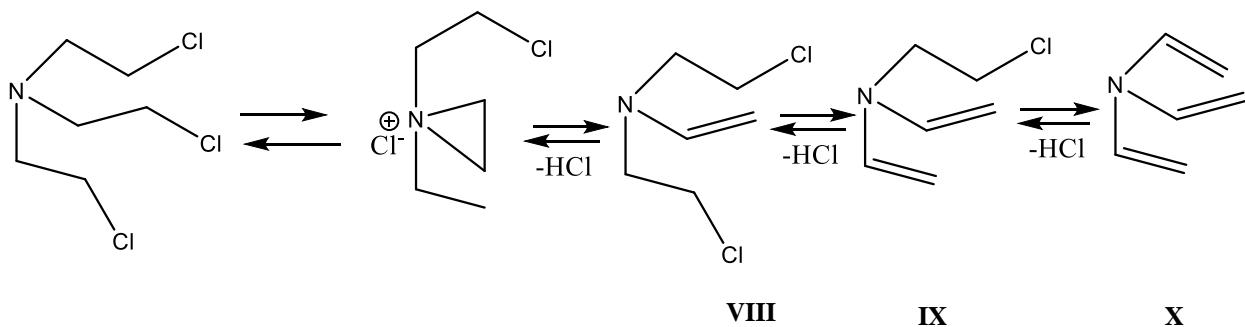


Figure 6. Degradation of *Tris*-(2-Chloroethyl) amine

ACUTE EXPOSURE GUIDELINE LEVELS (AEGLs)

The acute exposure guideline levels (AEGLs) are established to protect workers and the general population from harmful effects of a short-term (8 hours or less) exposure to chemical agents. Three types of AEGLs have been developed and they are AEGL-1, AEGL-2 and AEGL-3. AEGL-1 is an airborne concentration (expressed as mg/m³ [milligram per cubic meter]) of a substance above what is predicted that the general population may experience notable discomfort, irritation or non-disabling effects. AEGL-2 is an airborne concentration (expressed as mg/m³ [milligram per cubic meter]) of a substance above what is predicted that the general population may experience irreversible or other serious long lasting effects or impaired ability to escape. AEGL-3 is an airborne concentration (expressed as mg/m³ [milligram per cubic meter]) of a substance above what is predicted that if released in the general population may result in life threatening effects or death. The AEGLs for H/HD are listed in Table 2. The AEGL-1 values range from 0.40 mg/m³ for a 10 minute exposure to 0.008 mg/m³ for an 8-hour exposure. The AEGL-2 values range from 0.60 mg/m³ for a 10 minute exposure to 0.013 mg/m³ for an 8-hour exposure. The AEGL-3 values range from 3.9 mg/m³ for a 10 minute exposure to 0.27 mg/m³ for an 8-hour exposure⁹.

Table 2. AEGLs for *Bis-(2-Chloroethyl) sulfide (H/HD)*

| H/HD | 10 minutes | 30 minutes | 1 Hour | 4 Hours | 8 Hours |
|--------|------------------------|------------------------|-------------------------|-------------------------|-------------------------|
| AEGL-1 | 0.40 mg/m ³ | 0.13 mg/m ³ | 0.067 mg/m ³ | 0.017 mg/m ³ | 0.008 mg/m ³ |
| AEGL-2 | 0.60 mg/m ³ | 0.20 mg/m ³ | 0.10 mg/m ³ | 0.025 mg/m ³ | 0.013 mg/m ³ |
| AEGL-3 | 3.9 mg/m ³ | 2.7 mg/m ³ | 2.1 mg/m ³ | 0.53 mg/m ³ | 0.27 mg/m ³ |

The AEGLs for HN-3 are listed in Table 3. There are no AEGL-1 recommended values for HN-3 currently due to insufficient data. The AEGL-2 values range from 0.13 mg/m³ for a 10 minute exposure to 0.0028 mg/m³ for an 8-hour exposure. The AEGL-3 values range from 2.2 mg/m³ for a 10 minute exposure to 0.047 mg/m³ for an 8-hour exposure.¹⁰ It should be noted that the AEGL-2 values are approximately 4.5 times higher for H/HD than HN-3 at all intervals. This would suggest that HN-3 is more toxic than H/HD.

Table 3. AEGLs for *Tris-(2-Chloroethyl) amine (HN-3)*

| HN-3 | 10 minutes | 30 minutes | 1 Hour | 4 Hours | 8 Hours |
|--------|------------------------|-------------------------|-------------------------|--------------------------|--------------------------|
| AEGL-1 | NR ¹ | NR | NR | NR | NR |
| AEGL-2 | 0.13 mg/m ³ | 0.044 mg/m ³ | 0.022 mg/m ³ | 0.0056 mg/m ³ | 0.0028 mg/m ³ |
| AEGL-3 | 2.2 mg/m ³ | 0.74 mg/m ³ | 0.37 mg/m ³ | 0.093 mg/m ³ | 0.047 mg/m ³ |

1. NR: Insufficient data

DEMILITARIZATION AND DISPOSAL

In recent years, the destruction of these stockpiles and their technologies that are safe, environmentally friendly and readily available have received much attention. DoD Manual 6055.09 Volumes 6 and 7 Enclosures 4 set forth the standards for protecting workers and the general public from harmful effects of chemical agents and munitions associated with research, testing, training, preservation and maintenance operations, storage and chemical safety submissions. Also, demilitarization at laboratories, manufacturing plants, and depots as well as other DoD component agent operations, exclusive of combat training and operations. Regardless of the disposal technology chosen, the chemical agent handling will have similar safeguards. All chemical agents will be placed in containers, then monitored for leaks before handling, after moving and off-loading to the disposal plant and again within the disposal plant system. A selected list of technologies that are approved by the DDESB are shown below for the disposition of chemical agents:

1. Static Detonation Chamber (SDC 1200CM)¹¹
2. Detonation of Ammunition Vacuum Integrated Chamber (DAVINCH™ USA DV-60)¹²
3. Explosive Destruction System (EDS Phase II Units)¹³

CONCLUSIONS

Bis-(2-chloroethyl) sulfide and *tris*-(2-chloroethyl) amine are of interest because they had been previously stockpiled or improperly discarded and are in need of remediation. Generally, the vapor pressure is lower with increasing molecular weight, and since HN-3 has a higher molecular weight, the vapor pressure for HN-3 mustard is ten times (10x) lower than the HD/H mustard. Given that the rate of evaporation is slower for HN-3 and is a heavier vesicant, it is therefore more persistent and more toxic than H/HD mustard. Both chemical agents, *bis*-(2-chloroethyl) sulfide and *tris*-(2-chloroethyl) amine, upon heating will begin decomposition to hydrochloric acid and toxic gases. The decomposition processes of the chemical agents do not proceed to completion as they can exist in equilibrium with their corresponding intermediates which have similar toxicity to the chemical agent themselves. It has been determined that a temperature of 500 °C must be reached to ensure complete degradation of the chemical agent, its intermediates and byproducts.

Both agents can also decompose at lower temperatures by reacting with water through hydrolysis. The rate of degradation in water is faster for HN-3 which is attributed to the higher number of chlorine atoms in HN-3 (3-Cl atoms) compared to sulfur mustard (2 Cl-atoms). However, storage in sealed steel canisters or munitions for both chemical agents are relatively unchanged over 50 years. This is attributed to a slower rate of degradation due the absence of moisture, minimal thermal cycling, and the presence of stabilizers. In the disposal of munitions containing sulfur and nitrogen mustard, one could argue for the use of lower temperature treatments, such as hydrolysis, but that would require the removal of the chemical warfare agent from the munition. This additional and unnecessary handling of the munition increases the overall risk of the process. It also creates dangerous byproducts that would require further mitigation. Thus DDESB approved technologies that are currently being used take into account that 500 °C must be reached to ensure safe destruction of the chemical agents, their intermediates and byproducts.

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