Chemistry of Chemical Warfare Agents

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SLIDES ONLY

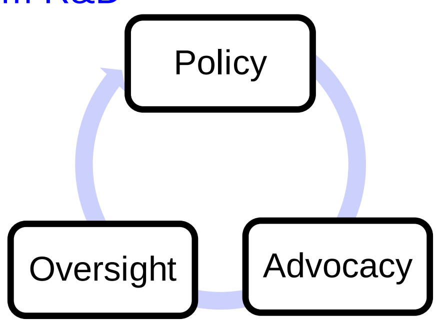
NO SCRIPT PROVIDED

Kirstin F. Warner Ph.D.
Department of Defense Explosives Safety Board

The DoD Explosives Safety Board (DDESB)

MAJOR FUNCTIONS

- Develop and maintain the DoD Explosives Safety Program
- Support Combatant Commanders Mission where DoD Munitions are involved
- Support Multinational Organizations and Operations (NATO, UN, and State Dept)
- Support Joint Staff Assessments
- Develop and maintain DoD Explosives Safety Policy and Regulations
- Evaluate Explosives Safety Programs
- Perform R&D




Flash of Shells in Night
Long Symphony of Terror

ORIGIN: Established in 1928 by Congress after a major disaster at the Naval Ammunition Depot, Lake Denmark, New Jersey in 1926. The accident virtually destroyed the depot, causing heavy damage to adjacent Picatinny Arsenal and the surrounding communities, killing 21 people, and seriously injuring 53 others.

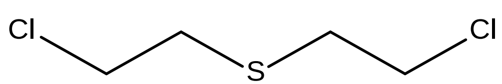
DoD Manual 6055.09 Volumes 6 and 7 Enclosures 4:

- Set forth the standards for protecting workers and the general public from harmful effects of chemical agents and munitions
- Chemical Safety Submissions
- Demilitarization

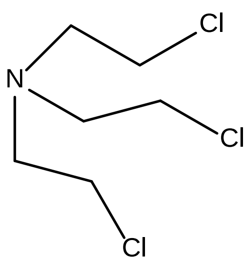
Background

- One such group of agents of interest, that have been stockpiled and are still being uncovered in buried munitions
  - *Bis*-(2-chloroethyl) sulfide **(Sulfur mustard, H/HD)**
  - *Tris*-(2-chloroethyl) amine **(Nitrogen mustard, HN-3)**

- The Chemical Weapons Convention entered into force on April 29,1997
  - The world's stockpiled chemical weapons must be destroyed



***Bis*-(2-chloroethyl) sulfide (H/HD)**

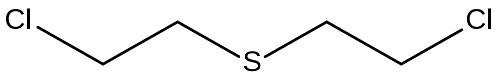


***Tris*-(2-Chloroethyl) amine (HN-3)**

Background

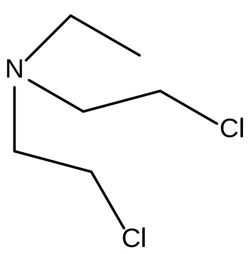
Chemical warfare agents sulfur mustard and nitrogen mustard are highly reactive vesicants or blistering agents that have been previously stockpiled or improperly discarded and are in need of remediation

- Sulfur mustards were first developed in 1822

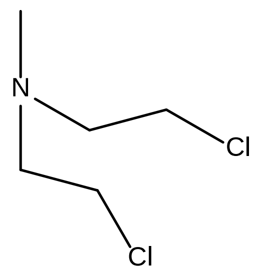


***Bis*-(2-chloroethyl) sulfide (H/HD)**

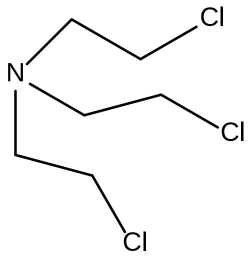
- Nitrogen mustards were first developed in the late 1920s and early 1930s.
- HN-3 is the most stable of the three nitrogen blistering agents



Bis-(2-Chloroethyl) ethylamine (HN-1)



Bis-(2-Chloroethyl) methylamine (HN-2)

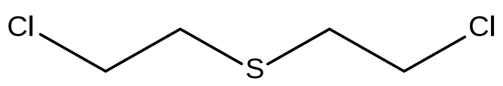


***Tris*-(2-Chloroethyl) amine (HN-3)**

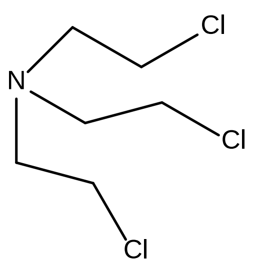
- References
- Agency for Toxic Substances and Disease Registry; Blister Agents
- http://www.bt.cdc.gov/agent/nitrogenmustard/erc555-771-1pr.asp CDC HN-3 Nitrogen Mustard Emergency Response Card (NIOSH) ERC 555-77-1

Physical Properties

- HN-3 has a higher molecular weight, the vapor pressure for HN-3 mustard is ten times (10x) lower than the HD/H mustard
  - The rate of evaporation is slower for HN-3 and is a heavier vesicant, it is therefore more persistent than H/HD mustard



***Bis*-(2-chloroethyl) sulfide (H/HD)**

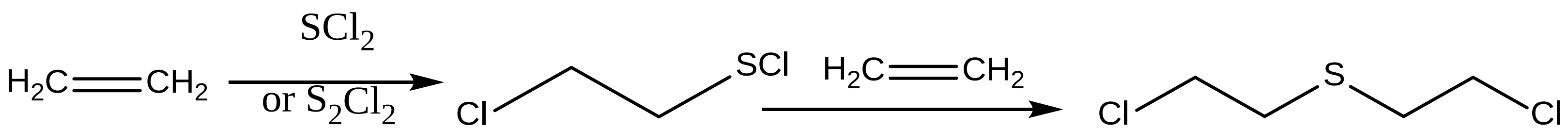


***Tris*-(2-Chloroethyl) amine (HN-3)**

Name	H/HD	HN-3
CAS	505-60-2	555-71-1
Molecular Formula	$C_4H_8Cl_2S$	$C_6H_{12}Cl_3N$
Molecular Weight	159	204
Density	1.24 g/cc	1.27 g/cc
Decomposition Temperature	180 ^oC	150 ^oC
Melting Point	14 ^oC (52.7 ^oF)	-4 to-3.7 ^oC (24.8 to 25.3 ^oF)
Boiling Point	217 ^oC (422.6^oF)	256 ^oC (492.8^oF)
Appearance	Colorless to pale oily liquid	Pale yellow oily liquid
Vapor Pressure	0.072 mm Hg @ 20^oC	0.016 mm Hg @ 20^oC

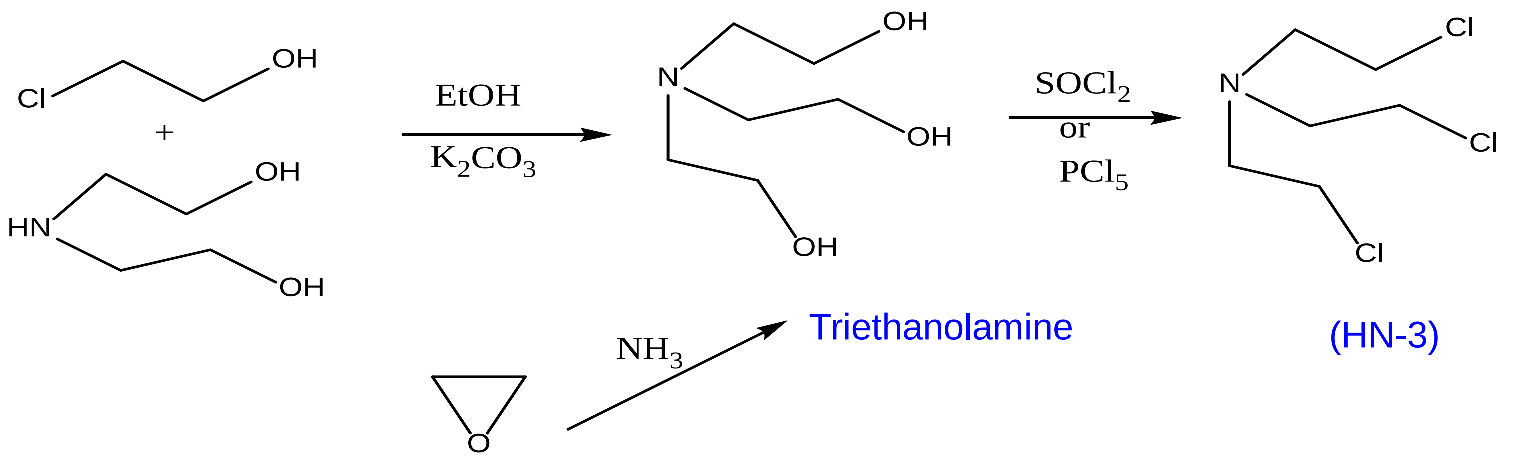
References
- Agency for Toxic Substances and Disease Registry; Blister Agents
- http://www.bt.cdc.gov/agent/nitrogenmustard/erc555-771-1pr.asp CDC HN-3 Nitrogen Mustard Emergency Response Card (NIOSH) ERC 555-77-1

Levinstein Method



2-chloroethylsulfenyl chloride
(Intermediate)

(H/HD)



Triethanolamine

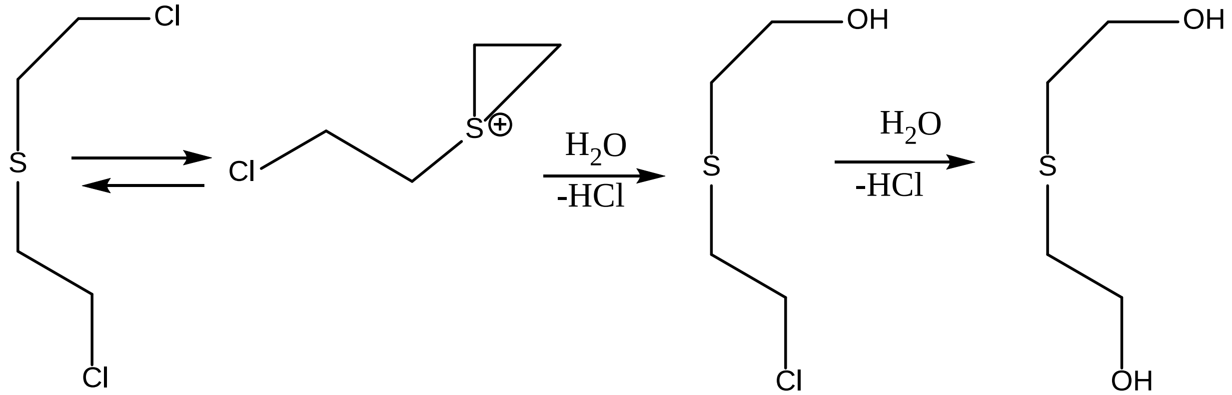
(HN-3)

References

- H/HD: Fusion, R.C. *et al.; J. Org. Chem.* **1946**, 11 (5) 504-509
- HN-3: Wilson, E. *et al*.; *J. Am. Chem. Soc*. **1951**, 73 (8) 3635-3641
- HN-3: Frauenkron, Matthias *et al.;* Ullmann's Encyclopedia of Industrial Chemistry, 2001 *Ethanolamines and Propanolamines,* https://doi.org/10.1002/14356007.a10_001

Degradation via Hydrolysis of H/HD

25ºC: Hydrolysis is the chemical breakdown of a compound due to reaction with water.



I **II**

- 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.

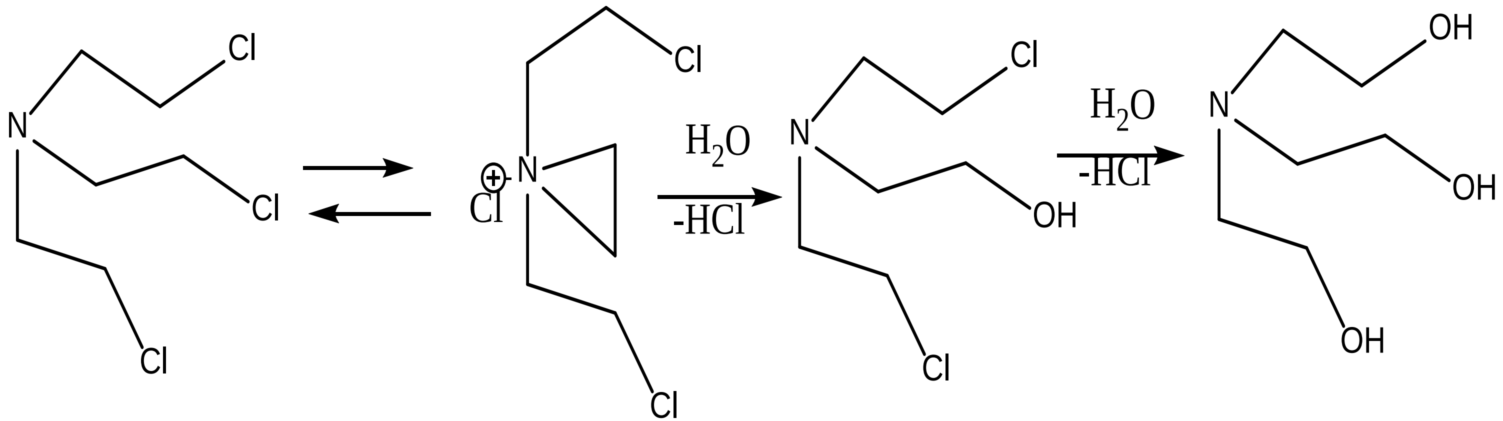
- Hydrolysis is not a complete solution as it yields toxic compounds such as 2,2'-(chloroethylhydoxyl) sulfide **(I)** and *bis*-(2-ethylhydroxyl) sulfide **(II).**

- However, recovered 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.

References
- Malhota, R.C. *et al.; Defence Sci. J.* **1999**, 49 (2) 97-116
- Wagner, G. W. *et al.; Phosphorous Sulfur and Silicon* **1999**, 152 65-76

Degradation via Hydrolysis of HN-3

25ºC: Hydrolysis is the chemical breakdown of a compound due to reaction with water.



I **II**

- 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.

- It should be noted that the hydrolysis process yields toxic compounds such as bis-(2-chloroethyl)-2-ethylhydroxyl amine **(I)** and triethanolamine **(II)** that still pose a risk and can be transferred to the skin.

- However, recovered 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.

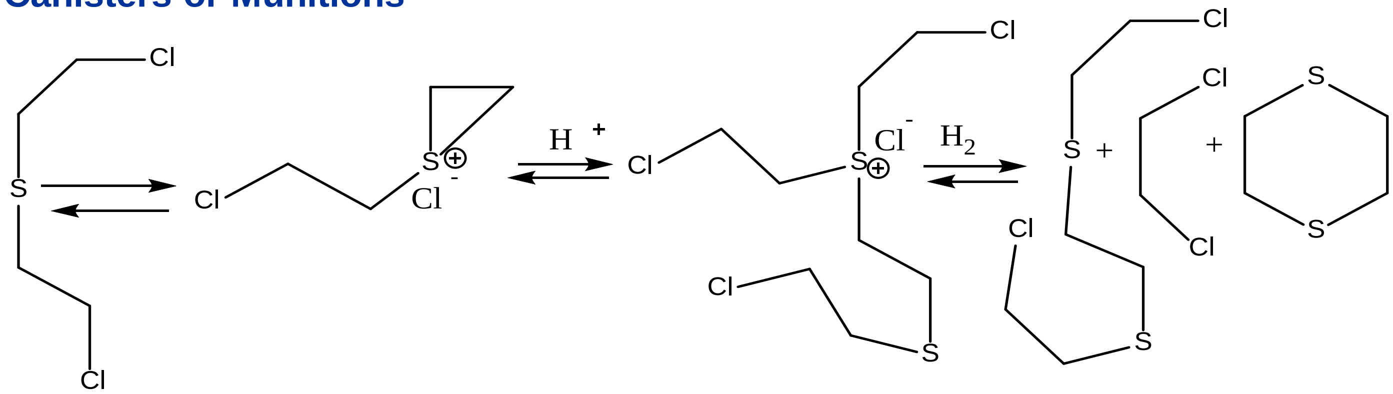
Reference

- Chatterji, D.C.; *J. Pharm. Sci.* **1980**, 69 (7) 859-861

Thermal Degradation of H/HD

Thermal degradation is an efficient method of destruction for sulfur mustard that ensures complete destruction including that of the agents, their intermediates and byproducts.

Sealed Canisters or Munitions



I **II** **III**

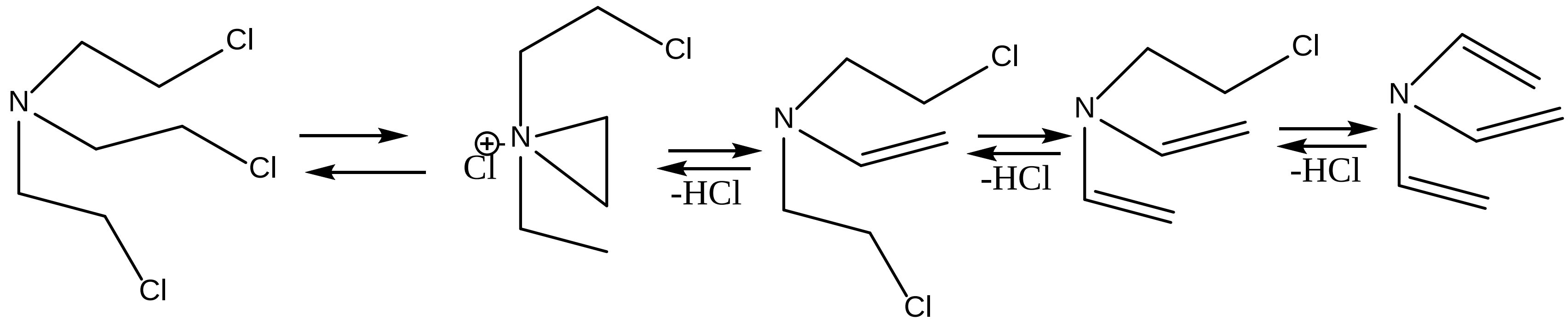
- Sulfur mustard can exist in equilibrium to form the corresponding cyclic intermediates which have similar properties to the chemical agent.

- At 25°C sulfur mustard, stored in steel canisters, in the absence of heat, water and moisture, the sulfur mustard slowly degrades to mainly 1,2-*bis*-(2-chloroethylthio) ethane **(I)**, 1,2-dichloroethane **(II)** and 1,4-dithiane **(III).**

- 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.

Thermal Degradation of HN-3

Sealed Canisters of Munitions



I

II

III

- It is plausible, at 25 ^{o}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 **(I)**, N-(2-chloroethyl)-N-vinylethenamine **(II)** and trivinylamine **(III)**.
- As is common for the thermal treatment of sulfur mustard, a temperature of 500^{o}C must be reached in order to ensure complete degradation of the chemical agent, its intermediates and byproducts.

ACUTE EXPOSURE GUIDELINE LEVELS (AEGLs) for H/HD and HN-3

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.

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

HN-3	10 minutes	30 minutes	1 Hour	4 Hours	8 Hours
AEGL-1	NR	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

- AEGL-1 is an airborne concentration (expressed as mg/m^3 [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 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 of a substance above what is predicted that if released in the general population may result in life threatening effects or death.

References
- https://www.epa.gov/sites/production/files/2014-11/documents/tsd45.pdf
- Gupta, R.C.; Handbook of Toxicology of Chemical Warfare Agents pp. 81

Approved Technology

Photo: Dynasafe

Photo: Kobelco

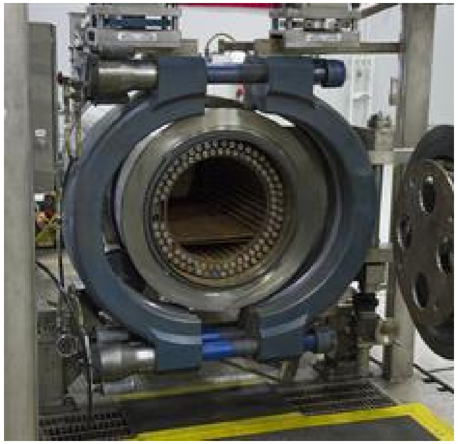


Photo: U.S. Army Chemical Materials Activity

- In the Static Detonation Chamber (SDC) munitions are fed through an automated loading system into the gas-tight detonation chamber, where they are heated until they burn, deflagrate or detonate.
- The process gases are cleaned by separate Dynasafe Off-Gas Treatment (OGT) systems.
- Remaining metal scrap as resulting from the destruction process in the SDC is after discharging guaranteed free of explosives as well organic material and safe for recycling.

- The DAVINCH (Detonation of Ammunition in a Vacuum Integrated Chamber) will be used to destroy chemical munitions where they are destroyed by the detonation of the donor explosives surrounding the munitions.
- Off- gas system employs a cold plasma oxidizer which converts carbon monoxide to CO_2. Off- gas is monitored for agent prior to release to the carbon filters.
- Scrap metal and liquid waste are treated and disposed of in compliance with applicable federal and state regulations.

- The Explosives Detonation System (EDS) is used to destroy chemical munitions as an alternative to detonation. The EDS uses cutting charges to open the metal shell, exposing the chemical agent and the burster explosives.
- A chemical reagent is used to destroy the chemical agent and decontaminate the resulting scrap metal parts.

- DDESB-PE Memorandum dated 6 October 2010, Subject: DDESB Approval for the Static Detonation Chamber (SDC) 1200 CM
- DDESB-PE Memorandum dated 2 August 2011, Subject: DDESB Approval for the Detonation of Ammunition in a Vacuum Integrated Chamber DAVINCH ™ USA DV-60
- DDESB-PE Memorandum dated 14 March 2014, Subject: DDESB Final Approval for the Explosive Destruction System (EDS) Phase 2 Units

Conclusions

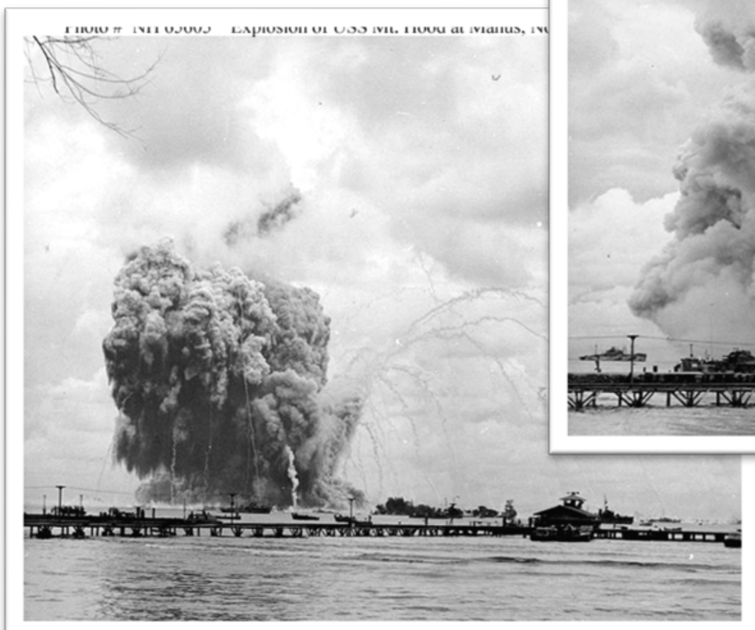
- Since HN-3 has a higher molecular weight, the vapor pressure for HN-3 mustard is ten times (10x) lower than the HD/H mustard
  - The rate of evaporation is slower for HN-3 and is a heavier vesicant, it is therefore more persistent and more toxic than H/HD mustard

- Both 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)
  - This would require the removal of the chemical warfare agent from the munition, unnecessary handling and increases the overall risk of the process
  - Intermediates and byproducts would require mitigation

- 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 ^{o}C must be reached to ensure complete degradation of the chemical agent, is intermediates and byproducts.

- Storage in sealed steel canisters or munitions for both chemical agents are relatively unchanged over 50 years.
  - Slower rate of degradation due the absence of moisture, minimal thermal cycling, and the presence of stabilizers.

Questions?



Explosion of the USS Mt. Hood (AE-11), Admiralty Islands, 10 November 1944. While moored at the Manus Naval Base, Admiralty Islands, the Mount Hood's cargo ~2.3M pounds of munitions detonated. Damage and casualties were inflicted on ships anchored as far as 2000 yards away. Personnel casualties on Mount Hood and on other vessels totaled 45 known dead, 327 missing and 371 injured. Over 30 large ships damaged, including the USS Mindanao (ARG-3), pictured above. 13 small boats and landing craft were sunk, destroyed or damaged beyond repair and 33 were damaged but reparable.