Analysis and Structural Studies of Complex Sulfur-Mustard Mixtures by Sulfur-33 NMR

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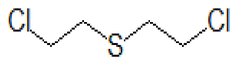
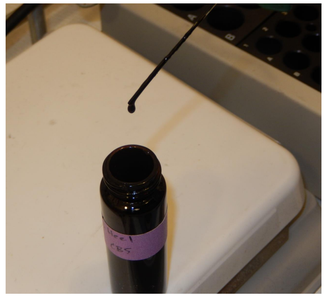
Introduction

Bulk containers and chemical munitions containing Mustard (Bis(2-chloroethyl)sulfide) are still being found around the world as unexploded ordinance, in undocumented burial locations, as well as in weapon stockpiles of various nations. The safe and complete destruction of these hazardous materials represents an important task for the organizations charged with decontaminating them.

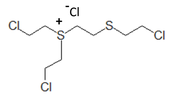


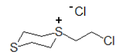
Mustard

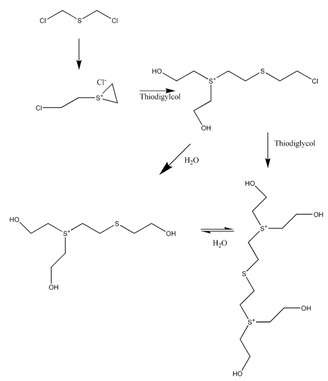
When Mustard is stored for long periods of time, chemical reactions may occur. A variety of sulfur-containing compounds can be formed that dramatically change the physical and chemical state of the material. Sulfonium ions may form and, being charged species, will fall out of solution. Depending on the other inorganic compounds present and other conditions of the reaction, solid or semi-solid material known as the "mustard heel" may form. The consistency of the heel varies, and can be a tarry, viscous material, or a more crusty, solid material.



Example sulfonium ions that may be formed in Mustard storage containers:



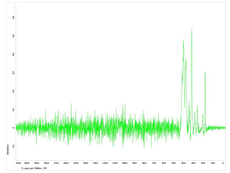


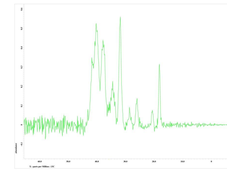


Complex reaction pathways can take place between mustard and breakdown products present in the containers.

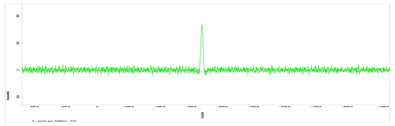
NMR Spectra

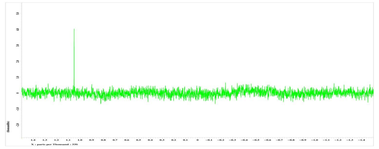
Complex C-13 NMR spectra of Mustard Heel Samples:





S-33 NMR Spectrum of CS_2 Standard material and mustard heel:





Conclusion

Chemical analysis of mustard heel material presents a difficult and ongoing challenge. Sulfur-33 combines the difficulties of low natural abundance, a small gyromagnetic ratio, and a quadrupolar magnetic spin, making it one of the most difficult nuclei to study by NMR. (Wagler, et Al. J. Mag. Res. 161 (2003) 191-197) The DEPTH2 experiment showed some promise is obtaining interpretable spectra, and continuing work will focus on alternative pulse sequences that will improve the instrument performance. The high iron content found in mustard samples can present challenges to NMR analysis, but also allows for rapid cycling of experiments due to very short T1 relaxation times. Continuing work on these experiments will be needed before Sulfur-33 NMR can be effectively used to analyze the complex mixtures found in mustard heel.

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