Investigation of Polysulfide Mustard Analogues and Reactive Intermediates from Levinstein Mustard by Density Functional Theory (DFT)

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1. INTRODUCTION
Sampling and analysis of environmental and biomedical samples are key elements of the verification regime of the Chemical Weapons Convention (CWC) as it is the only way to prove the presence (or absence) of chemicals relevant to the Convention. The OPCW Laboratory constantly aims to improve the toolkit available to the Organisation by investigating new analytical methods and by (re)investigating and improving exposure of chemical warfare agents. Methods to obtain chemical signatures that point to production methods or sources of raw materials of agents (for example by impurity) may then be used in the field and have received renewed interest as an important part of Chemical Forensics.

Recently, an OPCW Fact Finding Mission (FFM) was able to confirm “with utmost confidence” that at least two people were exposed to sulfur mustard in the town of Marra in Syria during an attack on 21 August 2015 allegedly carried out by a non-state actor. The OPCW has also recently worked with Iraqi authorities leading to the confirmation of the use of sulfur mustard in the Kirkuk Region of Iraq.

As thiodiglycol (TDG), the main precursor for the production of highly pure sulfur mustard, is a highly regulated chemical (Schedule 2.B.13 of the CWC) and is on the export control list of the Australia Group, non-state actors might turn to alternative production methods that result in an impure but still highly toxic form of “crude” sulfur mustard. One of these alternative methods is the Levinstein Process.

2. LEVINSTEIN MUSTARD
Sulfur mustard was first used in combat by German troops near Ypres in July 1917. Germany employed the Meyer-Clarke Process in which TDG is the key precursor component and that resulted in a product of high purity. As key intermediates in this process were not available from the Allied chemical industries at short notice, the UK and the USA employed an alternative route known as the Levinstein Process in which sulfur monochloride is reacted with dry ethylene under controlled conditions to directly yield sulfur mustard.[1]

The final product is an impure mixture containing about 70% sulfur mustard (HD). The two main impurities (ca. 10% ± 5% of each depending on the reaction conditions and age of the sample) are the di- and trisulfide analogues of sulfur mustard: Bis(2-chloroethyl) disulfide (HS₂Cl₂S₂) and Bis(2-chloroethyl) trisulfide (HS₂Cl₂S₃). These compounds and the higher poly sulfides are also known as the “Levinstein Mustards”. Because of their large relative amounts HS₂Cl₂S₂ and HS₂Cl₂S₃ might lead to significant amounts of degradation/reaction products in the environment resulting in a unique chemical signature. Therefore, the reactivity and potential reaction pathways of HS₂Cl₂S₂ and HS₂Cl₂S₃ are of significant interest but were not subject of intense study since the 1940s[2].

Levinstein Mustard

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
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</thead>
<tbody>
<tr>
<td>S₂Cl₂</td>
<td>ca. 70%</td>
</tr>
<tr>
<td>CH₂Cl₂S₂Cl₂</td>
<td>ca. 10%</td>
</tr>
<tr>
<td>CH₂Cl₂S₂Cl₂S₂</td>
<td>ca. 10%</td>
</tr>
<tr>
<td>Others (lower poly sulfides)</td>
<td>ca. 10%</td>
</tr>
</tbody>
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3. DENSITY FUNCTIONAL THEORY
Density Functional Theory (DFT) is a method to determine the quantum mechanical ground state of a many-electron system (such as atoms and molecules) based on the location dependent electron density. DFT is founded on the Hohenberg-Kohn Theorem that states that the ground-state of a system of N electrons is fully described by the location-dependent electron density ρ(r). All other properties of the system, for example the total energy, can be derived from the density. These other properties are therefore functionals (functions of functions) of the density. DFT is among the most popular methods in computational chemistry and one of its theoretical pioneers, Walter Kohn, was awarded the Nobel Prize in Chemistry in 1998.

This work was carried out using the software Amsterdam Density Functional (ADF) 2016 employing the OLYP functional and the TZ2P basis set.

REFERENCES

4. REACTIVITY OF SULFUR MUSTARD

The chemistry of HD is dominated by the polar carbon-chlorine bonds and the ability of the sulfur atom to stabilize a reactive episulfonium ion which is an effective electrophile and reacts with numerous nucleophiles (including the mildly nucleophilic sulfur atoms of other HD molecules).

The electron density for HD (red = high density; blue = low density).

[2093x420](ADF)

5. EPSILONUM IONS OF HS₂ AND HS₃

Starting from the optimized structure of HS₂ the abstraction of chloride from the molecule and subsequent geometry optimization also leads to formation of the episulfonium ion (the electrophile). Visual inspection of the LUMO clearly shows orbital lobes at the two cyclic carbon atoms, allowing attack of the mustard at these sites.

A similar procedure for HS₃ leads to an episulfonium ion with orbital lobes for the LUMO almost exclusively located at the sulfur atoms but not at the ring carbons.

6. ORBITAL ENERGY LEVELS

Analysis of the MO energy levels of the episulfonium ions of HD vs. HS₂ and HS₃ reveals that the sulfur-centered LUMOs for HS₂ and HS₃ are the LUMO+1 for the HD ion. As a result of the more polar sulfur atoms therefore leads to a stabilization of the MOs with a strong sulfur component due to the possibility to delocalize the charge over the polarsulfur atoms.

7. OTHER EPSILONUM IONS

8. CONCLUSIONS

The presence of significant quantities of HS₂, HS₃, and higher polysulfides in Levinstein Mustard and the differences in the electronic structure of reactive intermediates gives new markers of destructive degradation products. For example, the cyclic sulfonium ions with five-, six- or even seven-membered rings can undergo elimination reactions leading to the sulfur-sulfur heterocycles 1,2,3-Thiatriola, 1,2,3,4-Tetrahydro-1,2,3,4-Pentafluorophene respectively. These three compounds were found during analysis of old Levinstein Mustard from artillery shells in the USA prior to destruction.

While knowledge of degradation and reaction products from old munitions after decades of storage is important to prevent potential possible reactions of Levinstein Mustard, very little is available in the open literature regarding the formation of such polysulfides from fresh Levinstein Mustard in common matrices such as soil, building materials, vegetation and water. Finding specific markers of the polysulfide mustards would enhance the verification mechanism in an Investigation of Alleged Use in general but might also yield markers with long half-lives that would allow post-incident analysis for prolonged periods of time.