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Photochemical Approaches to Decontamination

Joint Services Scientific Conference on Chemical and Biological Defense Research.

November 20th, 2003
Report Documentation Page

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Overview

Six month project to:

- evaluate singlet oxygen, superoxide and hydrogen abstraction for reaction with chemical weapons simulants.
- Identify principal products and reaction pathways.
- Determine approximate conversion to products.
- Evaluate reaction confined to a surface.
Visible through near infrared (200 nm – 800 nm).
- Colorless systems.
Low power requirement, typically 0.01 – 0.1 W/m²
Energy and electron transfer control
Organic and inorganic
Sensitizers for:
- Singlet oxygen
- Superoxide
- Hydrogen abstraction
- Redox
## Chemical Weapon Simulants

<table>
<thead>
<tr>
<th>CW Agent</th>
<th>Simulant</th>
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<tbody>
<tr>
<td>Sarin (GB)</td>
<td>Dimethyl methylphosphonate (DMMP).</td>
</tr>
<tr>
<td></td>
<td>![Sarin (GB) Chemical Structure]</td>
</tr>
<tr>
<td>Soman (GD)</td>
<td>Ethyl dichlorophosphate</td>
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<tr>
<td></td>
<td>![Soman (GD) Chemical Structure]</td>
</tr>
<tr>
<td>Tabun (GA)</td>
<td>Diethyl chlorophosphate</td>
</tr>
<tr>
<td></td>
<td>![Tabun (GA) Chemical Structure]</td>
</tr>
<tr>
<td>VX</td>
<td>2-(Butylamino)ethanethiol</td>
</tr>
<tr>
<td></td>
<td>![VX Chemical Structure]</td>
</tr>
<tr>
<td>Mustard gas</td>
<td>2-Chloroethyl ethyl sulfide</td>
</tr>
<tr>
<td></td>
<td>![Mustard gas Chemical Structure]</td>
</tr>
</tbody>
</table>
Photochemical Technology Product Identification

10 fold excess simulant

Before illumination

After illumination

Time (minutes)
Photochemical Technology: Singlet Oxygen

- Photosensitized activation of oxygen to form singlet oxygen
- Very short lived:
  - 5 µs in water
  - 30 µs in THF
- Can be generated at most wavelengths (250nm – 750nm)
- Examples:
  - Thioxanthone (I)
  - Perinaphthenone (II)
  - Phthalocyanines
- Powerful electrophilic oxidant
Singlet Oxygen reaction with Half Mustard

Initial reaction is oxidation of the sulfur and/or HCl elimination.

Carbon sulfoxide bond cleaves and coupling (radical) products are generated.

Electrophillic nature of oxidant prevents sulfone formation.

Overall ~90% conversion to products in 15 mins.

Surface coatings and neat CEES gives ~80% removal in 60 minutes.
Singlet Oxygen Reaction with Malathion (VX)

- Initial reaction is loss of P-S bond.
- Sulfur is lost and oxidizes to sulfonic acids.
- Phosphorous oxidizes to phosphoric acids.
- Overall conversion is still being determined
Singlet Oxygen reaction with Phosphonates (Sarin/Tabun/Soman)

- No reaction was found between singlet oxygen and any of the G agent simulants.
- G agents are based around a ‘fully oxidized’ phosphorous so unlikely to be reactive with electrophillic oxidant.
- Singlet oxygen could be used to generate hydroperoxides or similar to provide reactivity with G agents.
Photochemical Technology: Superoxide

- Photosensitized electron transfer.
- Superoxide is longer lived (seconds to minutes) than singlet oxygen species.
- Can be generated at most wavelengths (300nm – 700nm).
- Examples
  - Curcumin (I)
  - Thioxanthone + amine/amide (II)
- Powerful oxidant and base.

![Superoxide diagram](Image)
Superoxide Reaction with Half Mustard

- Reaction products are similar to singlet oxygen
  - Oxidation of sulfur and/or HCl elimination
  - Cleavage of carbon sulfoxide bond and coupling products.
  - Greater HCL elimination due to basicity of superoxide.
- Overall ~90% conversion to products in 15 minutes
- Surface coatings and neat CEES gives ~50% removal in 60 minutes.
Superoxide Reaction with Malathion (VX)

- Superoxide systems tried to date have led to loss of Malathion but products could not be identified (product and sensitizer overlap).
- Other sensitizer systems being evaluated.
Superoxide Reaction with Phosphonates (Sarin/Tabun/Soman)

- Initial results for dimethyl methyl phosphonate indicate that G agents are probably not reactive towards superoxide.
- Ethyl dichlorophosphate and dichloroethylphosphosphate are still under evaluation.
Photochemical Technology: Hydrogen Abstraction/Redox

- Careful sensitizer selection or structural manipulation provides redox or hydrogen abstraction.
- Examples:
  - Polyoxometallates
  - Ketones
  - Semiconductors
- Powerful reductants, oxidants, and biocides.
Hydrogen Abstraction with Half Mustard

- Coupling products dominate as compared to singlet oxygen and superoxide where oxidation of the sulfur predominates.

- Polyoxometalate:
  - High concentration ~90% < 5 mins.
  - Sensitive to conditions (attacks solvents etc.)
  - Product analysis run at high substrate concentration and short time.
  - Surface reaction gives ~50% in 60 minutes.

- Ketone:
  - ~90% in 15 mins.
  - Similar product distribution to polyoxometalate.
Hydrogen Abstraction with Malathion (VX)

• Initial reaction is loss of P-S bond.
• Sulfur is lost and oxidizes to sulfonic acids.
• Phosphorous oxidizes to phosphoric acids.
• Overall conversion is still being determined
Hydrogen Abstraction with Phosphonates (Sarin/Tabun/Soman)

Reaction appears to lead to rapid loss of either a halogen or methoxy group.

Groups appear to continue to be lost and phosphate is likely end product.

Conversion to products:
- ~90% in <6 minutes with polyoxometalate and DMMP.
- ~50% in 30 minutes for chlorophosphates*

R = Me or Et
R’ = Me or OEt or Cl
X = Cl or OMe

* Preliminary results
Photochemical Technology
Photobase

- Generates basic moieties such as amines, hydroxyl etc.
- Can generate base in aprotic media.
- Sensitizers between 250nm and ~450nm.
- Examples:
  - Triphenyl carbinol
  - Malachite green (I)
- Strong base and nucleophile.
Photobase and Phosphonates (Sarin/Tabun/Soman)

Reaction apparently leads to loss of halogen or methoxide.

Initial evaluation did not determine if further reaction occurs.

\[
\begin{align*}
R & = \text{Me or Et} \\
R' & = \text{Me or OEt or Cl} \\
X & = \text{Cl or OMe}
\end{align*}
\]
**Photochemical Technology Review**

- **Phototechnology can provide a viable approach to the generation of reactive surfaces for decontamination.**
  - Singlet oxygen and superoxide are rapidly effective against simulants for VX and mustard.
    - Trapping all or part of these as hydroperoxides would likely provide activity on G agents.
  - Hydrogen abstraction is effective against all simulants tested.
    - More coupling reactions observed in addition to breakdown.
  - Photobase hydrolysis provides an alternative to hydrogen abstraction on G agents.

<table>
<thead>
<tr>
<th>Photochemistry</th>
<th>CWA Simulant</th>
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<tbody>
<tr>
<td></td>
<td>DMMP (Sarin)</td>
</tr>
<tr>
<td><strong>Singlet Oxygen</strong></td>
<td>✗</td>
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<tr>
<td><strong>Superoxide</strong></td>
<td>✗</td>
</tr>
<tr>
<td><strong>Hydrogen Abstraction</strong></td>
<td>✓</td>
</tr>
<tr>
<td><strong>Photobase</strong></td>
<td>✓</td>
</tr>
</tbody>
</table>
What Happens at Night?

- Photochemistry in the Dark:
  - Light activated generation of actives.
  - Continues to be reactive from seconds to hours after activation.
  - Activation takes seconds to minutes.
  - Actives include singlet oxygen, superoxide, radicals (H-abstraction) + other oxidants.
  - Functions in both aqueous and non-aqueous (e.g. silicone, perfluorinated solvent etc.) environments.
Phototechnology Advantages

- High activity against wide range of potential chemical weapons threats
  - Also will be effective against toxic industrial chemicals.
- Strong biocidal activity especially for superoxide and hydrogen abstraction.
  - Possible ‘one stop shop’ for chemical and biological weapons agents.
- Robust across all surfaces.
  - Can be used on sensitive equipment.
  - Likely safe on all materials.
- Aqueous or non-aqueous media.
- Photoactivation provides for decon in the dark!
- Can be used for decontamination or as reactive surface.
- Activity of coating can be easily checked using UV/Vis or fluorescence detection.
Potential Applications

- Equipment Decontamination (where light available).
- Sensitive equipment decontamination and decontamination solution cleanup.
- Decontamination powder/solution:
  - Photoactivate or use ambient light
    - area clean up,
    - equipment decon.
    - Personnel decon
    - Wound sterilization
- Surface reactive systems for sustained decontamination and cleaning.
  - Incorporation in paints and surface coatings.
  - User applied film for field use/reapplication.
    - In-use activity can be monitored by UV/vis or fluorescence.
    - Color change on reaction possible
    - In addition to potential activity for C&BWA could have more mundane application for keeping surfaces clean and antimicrobial e.g., tenting, clothing.
- Water purification
  - Lightweight polymer beads for water purification without tainting the water.
  - Coating on the interior of drinking utensils
- Air purification.
  - Packed bed stable until needed
Acknowledgements

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