Catalytic Oxidation of CW Agents
Using $H_2O_2$ in Ionic Liquids

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Illinois Waste Management & Research Center

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Structures of ionic liquids

cations:

\[
\begin{align*}
\text{N}^+ & : R^1/ \text{N}^+ R^3 \\
\text{P}^+ & : R^1/ \text{P}^+ R^3 \\
\text{S}^+ & : R^1/ \text{S}^+ R^3
\end{align*}
\]

anions:

\[
\begin{align*}
\text{BF}_4^- & , \text{PF}_6^- , \text{SbF}_6^- , \text{NO}_3^- , \text{CF}_3\text{SO}_3^- , (\text{CF}_3\text{SO}_3)_2\text{N}^- , \\
\text{ArSO}_3^- & , \text{CF}_3\text{CO}_2^- , \text{CH}_3\text{CO}_2^- , \text{Al}_2\text{Cl}_7^-
\end{align*}
\]
Common Cationic Surfactants

CTAB

N-alkylpyridinium halides

morpholinium salts

salts of alkyl-substituted pyridine
Micelles to Microemulsions

Rapid, Cheap
Selective
Microemulsion Formulations

- 69% H₂O
- 9% EtOH
- 11% [BMIM] BF₄
- 11% Cyclohexane
  o/w

- 5% H₂O
- 10% EtOH
- 5% [BMIM] PF₆
- 80% Cyclohexane
  w/o
Structures of HD, VX, GB, and GD

(1) HD, mustard; (2) VX; (3) GB or Sarin; (4) GD or Soman
Decontamination of Mustard and Phosphorous (V) Esters

- PhSCH₂CH₂Cl + H⁺, H₂O₂ → PhSCH₂CH₂Cl
- Ph₂P(OH)₂RSEt + H₂O₂ → Ph₂POH + EtSO₃⁻
Hydrogen Peroxide with added carbonate

CICH₂CH₂SEt → CICH₂CH₂SEt

H₂O₂ / Me₄NHCO₃ → O

[BMim] BF₄

Less than 2 minutes

2 mole equiv. Of H₂O₂

Hydrogen peroxide, bicarbonate, and organic cosolvents afford rapid, decontamination of CWA

### Solubility in a Microemulsion vs glycol/water

<table>
<thead>
<tr>
<th>Solubilizate</th>
<th>Microemulsion</th>
<th>3:1 PG/water</th>
</tr>
</thead>
<tbody>
<tr>
<td>paraoxon</td>
<td>470 mg/0.5 mL</td>
<td>215 mg/0.5 mL</td>
</tr>
<tr>
<td>half-mustard</td>
<td>75 mg/0.5 mL</td>
<td>b</td>
</tr>
</tbody>
</table>
**Bicarbonate-activated Peroxide (BAP)**

![Chemical structure of Bicarbonate-activated Peroxide (BAP)]
BAP oxidations in aqueous cationic micelles
Oxidation of sulfides to sulfoxides and sulfones with 30% $H_2O_2$

VX Decontamination by Bleach

Yang, Y.-C. et al. Chem. Rev. 1992, 92, 1729-1743
Rapid detoxification of HD using magnesium monoperoxyphthalate (MMPP)

Mustard oxidation in the microemulsion

- Reaction capacity is excellent
- Sulfoxide is formed quantitatively
- Microemulsions prepared from anionic, non-ionic, and cationic surfactants
Acknowledgements

This research is being Funded by the Army Research Office (ARO)
Wisdom on the journey…

He who can no longer pause to wonder and stand rapt in awe is as good as dead; his eyes are closed.

*Albert Einstein*