

P&G

*Photochemical
Approaches to Decontamination*

Joint Services Scientific Conference on Chemical
and Biological Defense Research.

November 20th, 2003

Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE 01 OCT 2005		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Photochemical Approaches to Decontamination				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Procter and Gamble Company				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM001851, Proceedings of the 2003 Joint Service Scientific Conference on Chemical & Biological Defense Research, 17-20 November 2003. , The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 24	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Overview

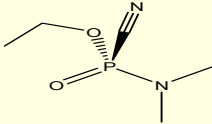
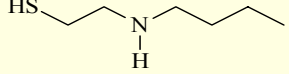
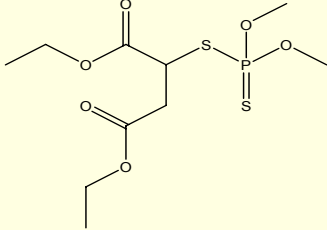
- Six month project to:
 - evaluate singlet oxygen, superoxide and hydrogen abstraction for reaction with chemical weapons simulants.
 - Identify principal products and reaction pathways.
 - Determine approximate conversion to products.
 - Evaluate reaction confined to a surface.

P&G Photochemical Technology

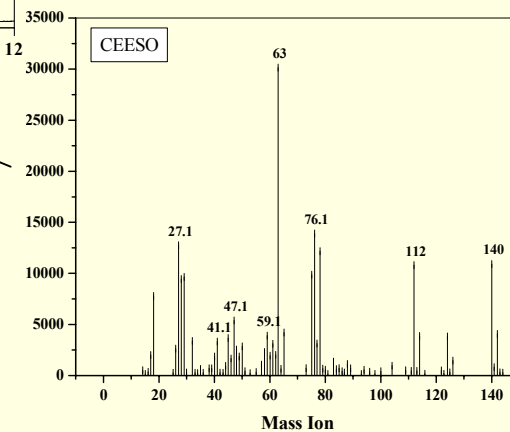
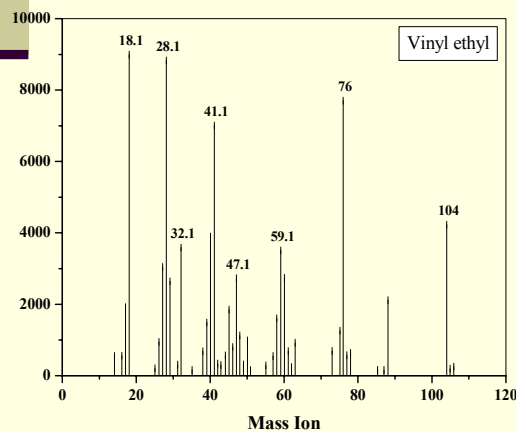
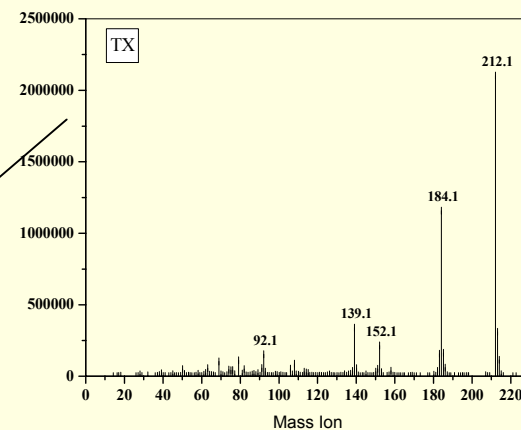
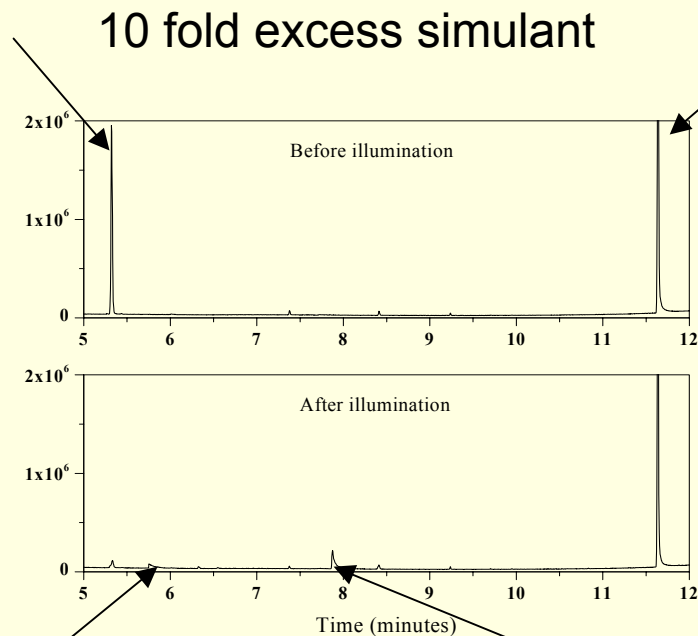
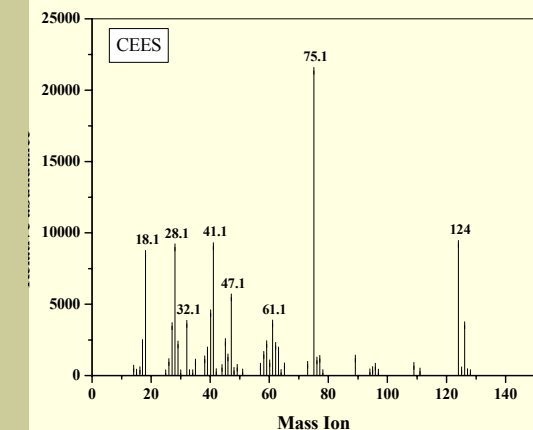
Background

- 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

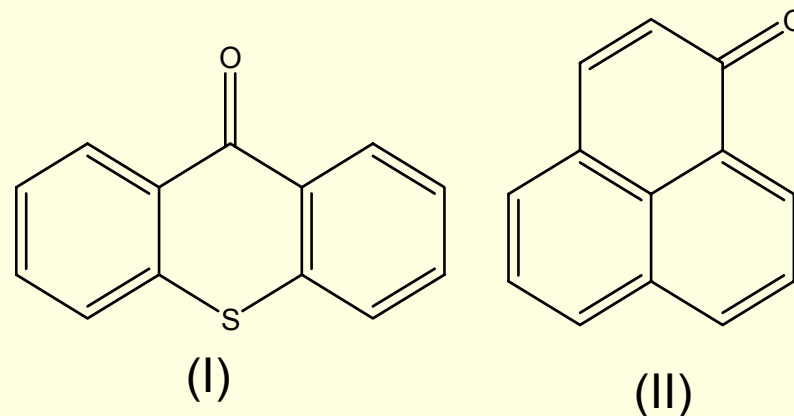
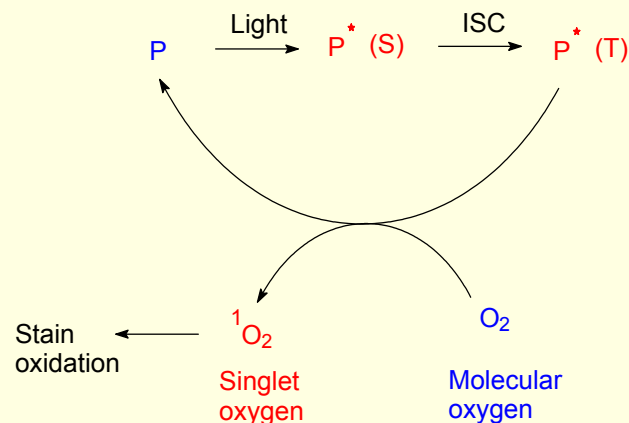
CW Agent	Simulant
Sarin (GB) $\text{CH}_3\text{O}-\text{P}(=\text{O})(\text{F})-\text{O}-\text{CH}(\text{CH}_3)_2$	Dimethyl methylphosphonate (DMMP). $\text{CH}_3\text{O}-\text{P}(=\text{O})(\text{CH}_3)-\text{O}-\text{CH}_3$
Soman (GD) $\text{CH}_3\text{O}-\text{P}(=\text{O})(\text{F})-\text{O}-\text{CH}(\text{CH}_3)-\text{C}(\text{CH}_3)_2$	Ethyl dichlorophosphate $\text{EtO}-\text{P}(=\text{O})(\text{Cl})_2$
Tabun (GA) 	Diethyl chlorophosphate $\text{EtO}-\text{P}(=\text{O})(\text{Cl})-\text{OEt}$
VX $\text{C}_2\text{H}_5\text{O}-\text{P}(=\text{O})(\text{CH}_3)-\text{S}-\text{CH}_2\text{CH}_2-\text{N}(\text{CH}_2\text{CH}_3)_2$	2-(Butylamino)ethanethiol 
	Malthion 
Mustard gas $\text{Cl}-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-\text{Cl}$	2-Chloroethyl ethylsulfide $\text{Cl}-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_3$

Photochemical Technology Product Identification

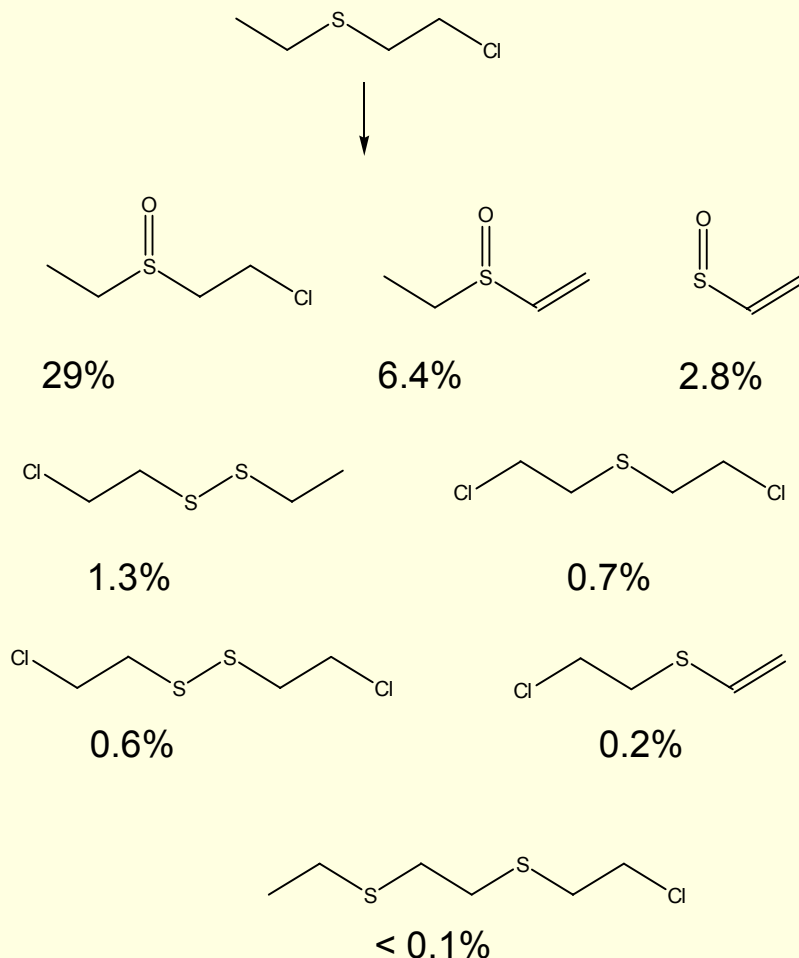


Photochemical Technology: Singlet Oxygen

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

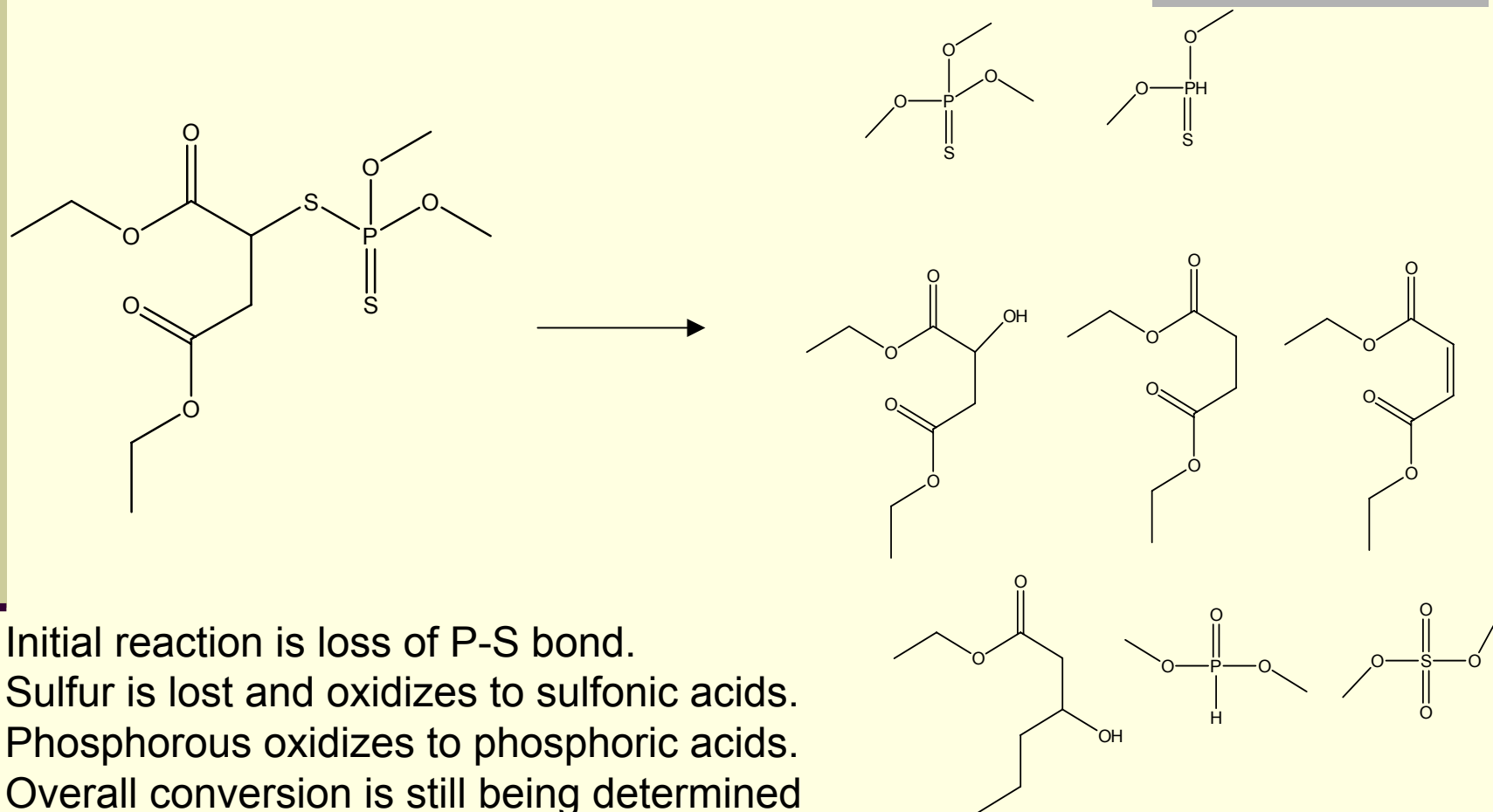


Singlet Oxygen reaction with Half Mustard



- Initial reaction is oxidation of the sulfur and/or HCl elimination.
- Carbon sulfoxide bond cleaves and coupling (radical) products are generated.
- Electrophilic 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)

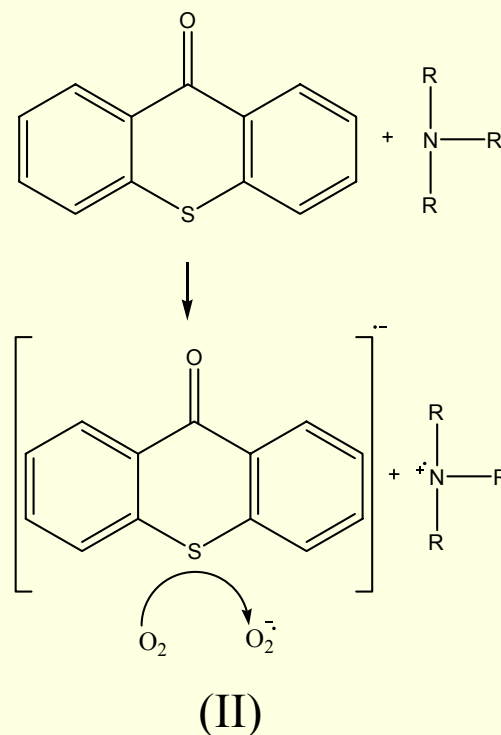
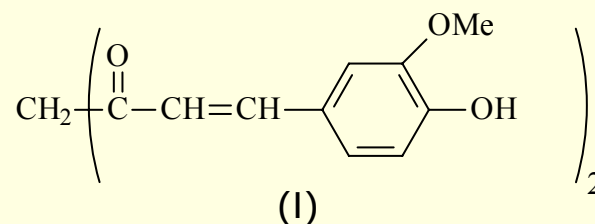


Singlet Oxygen reaction with Phosphonates (Sarin/Tabun/Soman)

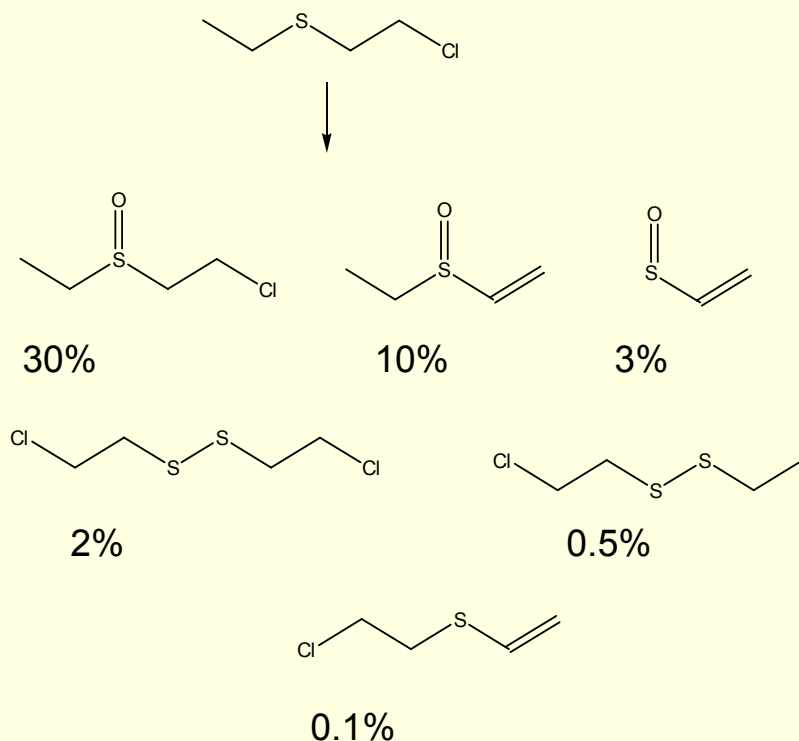
- No reaction was found between singlet oxygen and any of the G agent simulants.
- G agents are based around a 'fully oxidized' phosphorous so unlikely to be reactive with electrophilic oxidant.
- Singlet oxygen could be used to generate hydroperoxides or similar to provide reactivity with G agents.

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 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)

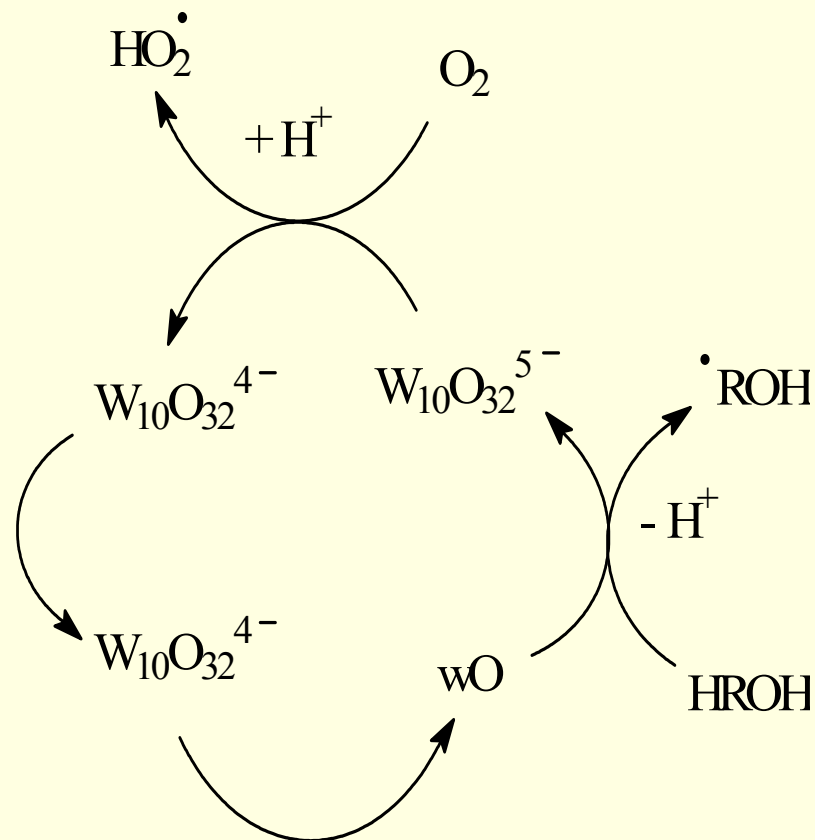
- Superoxide systems tried to date have led to loss of Malathion but products could not be identified (product and sensitizer overlap).
- Other sensitizer systems being evaluated.

Superoxide Reaction with Phosphonates (Sarin/Tabun/Soman)

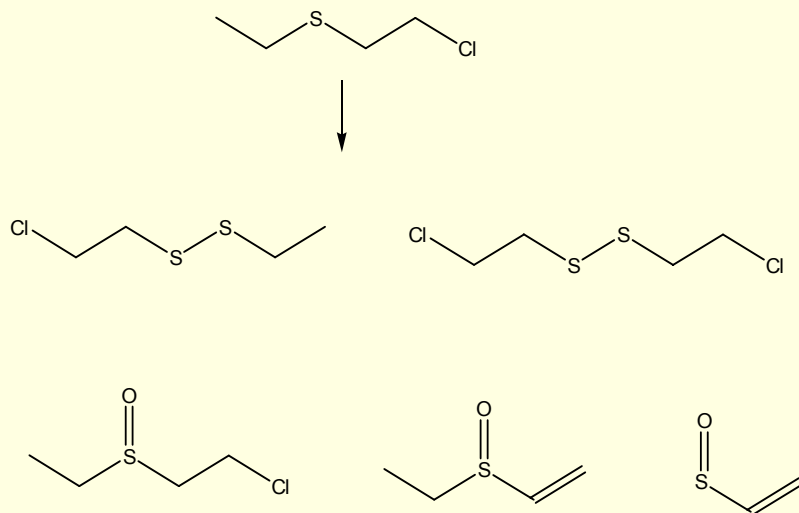
- Initial results for dimethyl methyl phosphonate indicate that G agents are probably not reactive towards superoxide
 - Consistent with literature: Aguila et al *J. Phys Chem. A* **2001**, 105, 7834
- Ethyl dichlorophosphate and dichloro ethylphosphate are still under evaluation.

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.

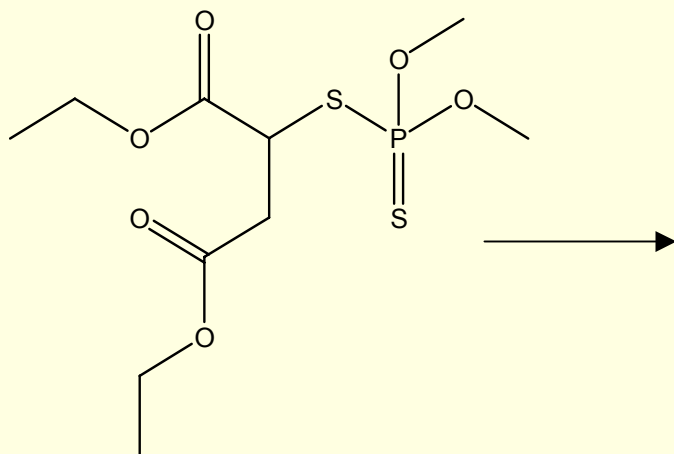


Hydrogen Abstraction with Half Mustard

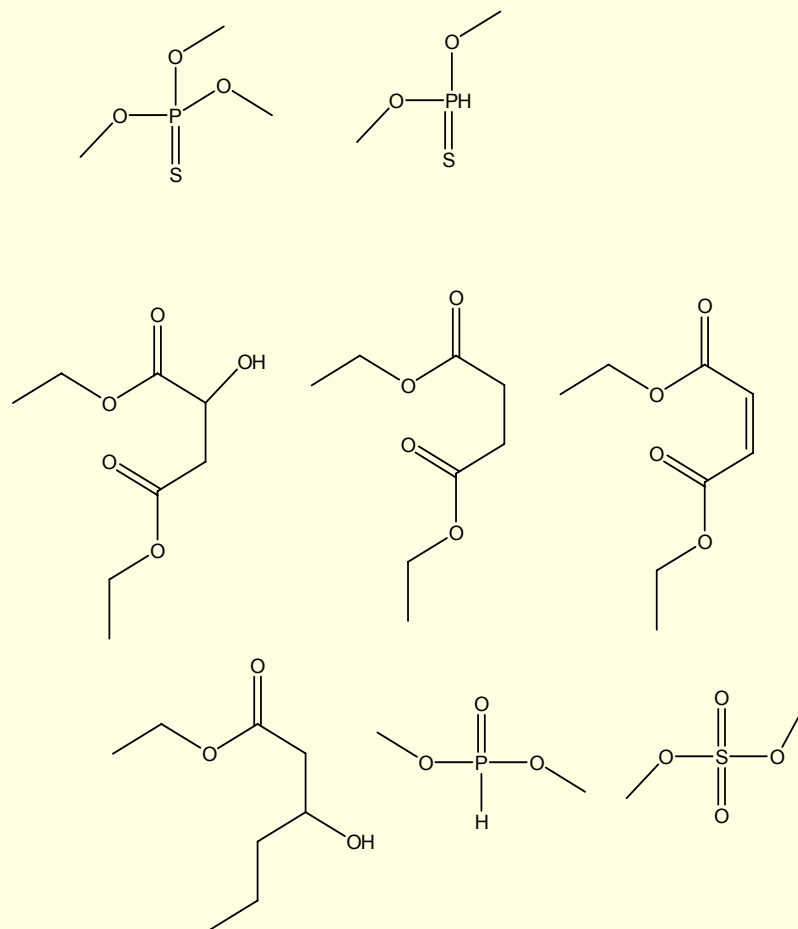


- Coupling products dominate as compared to singlet oxygen and superoxide where oxidation of the sulfur predominates.
- Polyoxometalate:
 - High concentration ~90% < 5 mins.
 - Sensitive to conditions (attacks solvents etc.)
 - Product analysis run at high substrate concentration and short time.
 - Surface reaction gives ~50% in 60 minutes.
- Ketone:
 - ~90% in 15 mins.
 - Similar product distribution to polyoxometalate.

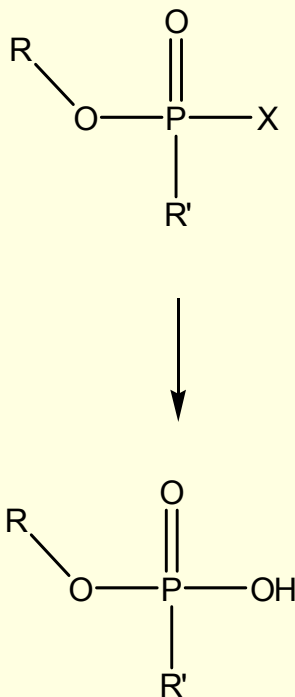
Hydrogen Abstraction with Malathion (VX)



- 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)



R = Me or Et

R' = Me or OEt or Cl

X = Cl or OMe

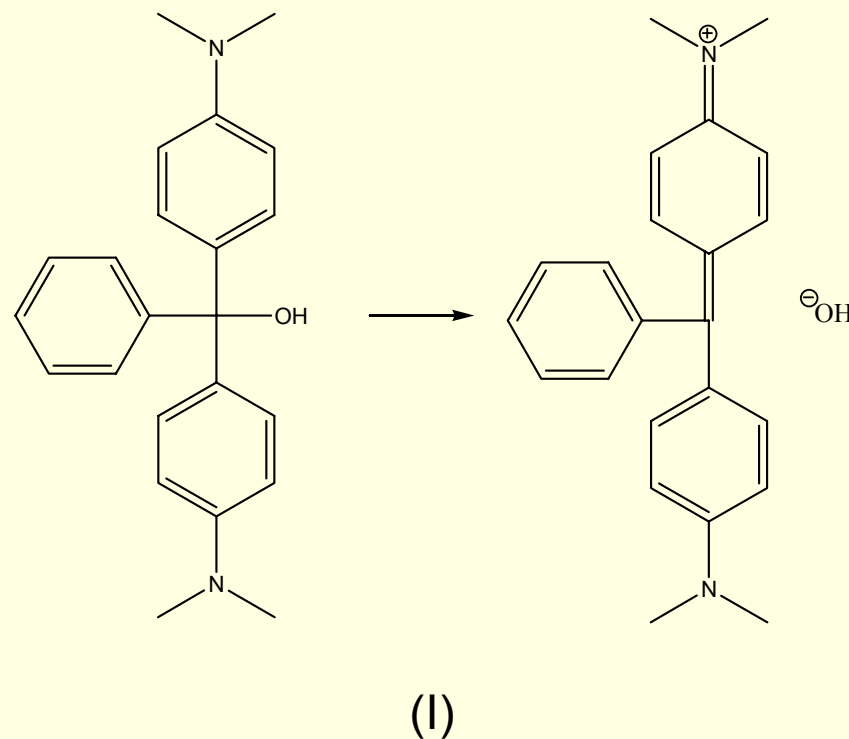
- Reaction appears to lead to rapid loss of either a halogen or methoxy group.
- Groups appear to continue to be lost and phosphate is likely end product.
- Conversion to products:
 - ~ 90% in < 6 minutes with polyoxometalate and DMMP.
 - ~ 50% in 30 minutes for chlorophosphates*

* Preliminary results

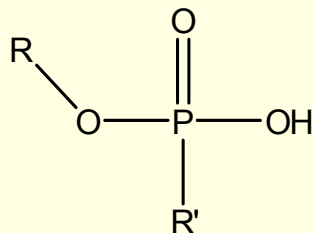
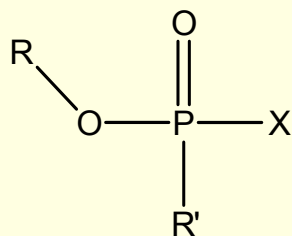
Photochemical Technology

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.

R = Me or Et

R' = Me or OEt or Cl

X = Cl or OMe

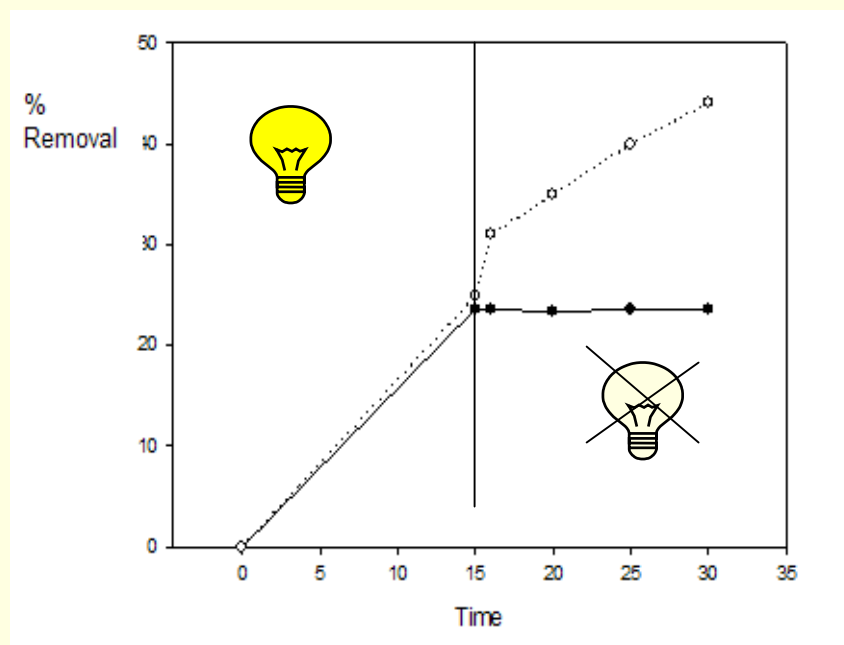
Photochemical Technology Review

Photochemistry	CWA Simulant					
	DMMP (Sarin)	Ethyl dichloro phosphate (Sarin/Tabun/ Soman)	Diethyl chloro phosphate (Sarin/Tabun/ Soman)	Malathion (VX)	Butylamino ethanethiol (VX)	Chloroethyl ethyl sulphide, CEES (Mustard)
Singlet Oxygen	✗	✗	✗	✓	✓	✓
Superoxide	✗			✓	✓	✓
Hydrogen Abstraction	✓	✓	✓	✓	✓	✓
Photobase		✓		✓	✓	

- **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

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 (wher 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

- Dr. Stephen Lee and the Army Research Office for supporting the work under Grant DAAD19-03—1-0089.
- Dr. James Tinlin and Mr. Bill Mueller.
- **Thank you for your time**