

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 02/10/06	3. REPORT TYPE AND DATES COVERED Final Report 20 May 03 - 30 June 04	
4. TITLE AND SUBTITLE Photochemically reactive Surfaces for Decontamination			5. FUNDING NUMBERS DAAD19-03-1-0089	
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER 45234.1-CH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The objective of the project was to evaluate the application of photochemical systems to the destruction of chemical warfare agent (CWA) simulants. A number of reactive species including singlet oxygen, superoxide and radicals were generated photolytically and their reaction with known CWA simulants was followed by GC-MS. By using solar simulators or low power UV (7%) lamps we were able to show removal of a mustard simulant with all three photolytic species. However, the same species were less successful with G agent and VX simulants. Only the radical approach showed some activity and this was slow and produced multiply by products. Preliminary investigation into whether these species could be prepared as photolytic ractive surfaces was initiallys succesful, showing reactivity towards the mustard simulant. However, reactivity was determined to be due to the rate at which the surface was dissolved into the simulant, creating a homolytic solution reaction.				
14. SUBJECT TERMS Phtocatalysis, singlet oxygen, superoxide, radical, photobleach,			15. NUMBER OF PAGES 4	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

PHOTOCHEMICALLY REACTIVE SURFACES FOR DECONTAMINATION

**Research Agreement No. DAAD19-03-1-0089
20 May 2003-30 June 2004**

Statement of the problem studied.

The purpose of this work was to investigate the viability of using photo-chemical processes in the decontamination of Chemical Warfare Agents (CWA's). The approaches investigated the formation, through chemical activation, of singlet oxygen, super-oxide, or radicals. A further approach involving photoacid/base chemistry was also initially investigated. Funding was limited to a six month period.

The method of generation of these active species is dependent on the initial photochemical chosen and on the wavelength of light required to activate the process.

A broad range of photochemicals were chosen for investigation including:

Singlet oxygen producers – paranaphthone, thioxanthone

Super-oxide producers – curcumin, silicon phthalocyanine,

Radical generators – decatungstate, benzophenone.

A number of light sources were chosen to excite the samples

A low power, low cost iguana lamp – used in reptile keeping ~370nm -initially used but later found to be too low in power to facilitate rapid decontamination.

A medium power solar simulator from oriel ~10x output from the sun used for the majority of this work unless otherwise stated.

A medium power Xenon arc lamp from oriel.

A high power 400W Mercury arc lamp

The majority of work involved the solution phase destruction of stimulants, however attempts were made to form films of these photochemicals in order to investigate the possibility of sunlight activated reactive surfaces.

Summary of the most important results - Homogeneous Reactions.

Method – Solutions containing different concentrations of sensitizer and simulant in acetonitrile were prepared. These were then illuminated using the required light source and simulant degradation was measured over time via GC and GCMS. Degradation studies predominantly involved sensitizer:simulant levels of 1 to 1, however a range of levels were also investigated from 1:10 to 10:1.

Photochemistry	G-Agent simulant	Mustard Simulant		VX simulant
		T _{15 min}	T _{60 min}	
Singlet oxygen	No identified loss	85%	90%	No identified loss
Super-oxide	No identified loss	65%	90%	No identified loss
Radical chemistry	Degradation (60% removal in 45min)	20%	60%	Evidence of P-S cleavage

Table 1 Summary of the amount of simulant removed by the photochemistry

G-agent simulants

The following chemicals were chosen as simulants to G-agents:

- Dimethyl methyl phosphate (DMMP)
 - No observable photochemical degradation via singlet oxygen, super oxide or radical approaches. Hydrolysis product was only produced at high pH's.
- Ethyl dichlorophosphate (EDCP) –
 - No identifiable losses with either singlet oxygen or super-oxide. Radical chemistry utilizing decatungstate derivatives showed some removal however, intermediate identification is not possible on HPLC-GC. Identification of hydrolysis products via ³¹P NMR was not investigated due to safety constraints.
 - Attempts to investigate whether a Photobase/Acid (malachite green) approach would work with EDCP were hampered due to the highly acidic nature of the stock chemical. The addition of the EDCP resulted in a rapid color change of the photobase with no loss of simulant. Similar results were found when curcumin was investigated. Further work is required.

Identifiable decontamination products.

GC Mass spec failed to elucidate possible intermediates from the radical attack of EDCP. It is believed that any formed would be unstable and react rapidly with hydroxides. These hydrolysis products would then fail to run on GC.

Mustard simulants.

A single chemical was chosen as the chemical to mimic the properties of Mustards.

- 2Chloroethyl ethyl sulfide (2CEES) –
 - Although the singlet oxygen approach was the most efficacious route there were observable losses via all three photochemical routes and via all chemicals investigated.

Identifiable decontamination products.

Both the singlet oxygen and super-oxide approaches rapidly remove 2CEES forming the majority product sulphoxide (2CEESO) and a further minor product which seems to be formed by an elimination of HCl (designated Vinyl ethyl sulphoxide (VESO)).

Of the two approaches singlet oxygen attack through formation from thioxanthone appears to be the best. The radical approach is considerably slower, and a large number of unidentified intermediates are formed.

VX simulant

The following chemicals were chosen as simulants to VX.

- 2-(butylaminol) ethanethiol (BAET) –
 - Initial losses were found to be a consequence of dimer formation. This dimer subsequently showed no removal via singlet oxygen or super-oxide. The radical approach using decatungstate removes 90% of this dimer in 30 minutes.

- The dimer formation problem of BAET prompted the sourcing of a better VX stimulant (Malathion)
- Malathion (MALT).
 - Initial losses using benzophenone (radical) and paranthone (singlet oxygen) showed rapid destruction of the malathion molecule producing molecules consistent with the cleavage of the phosphorous sulphur bond. This was later attributed to low wavelength photochemical destruction via the 400W mercury lamp (no loss when light source was filtered).
 - Repeated work using singlet oxygen and super oxide generators and benzophenone showed no removal of malathion when using a filtered solar simulator.
 - Decatungstate showed a small but noticeable loss of malathion (20 % in 45minutes when using the same light source. Intermediates were consistent of cleavage of the phosphorous sulphur bond.

Summary of the most important results - Heterogeneous Reactions.

Initial work focused on the preparation of stable films and their use in the removal of deposited simulant.

Method – a coating of the photosensitizer was applied to a ½ inch diameter glass disk, placed in a enclosure of 2ml volume and a known concentration of simulant was directly deposited onto the coating. The enclosure was sealed and illuminated for a fixed time depending on the photosensitizer. The coating and simulant were then extracted and run on GC MS to determine removal.

Sensitizers investigated

Singlet oxygen – paranthone

Super oxide – silicon phthalocyanine, curcumin

Radical – decatungstate with TBA counter ion

G agents simulant

There was no activity from any of the sensitizers in this heterogeneous state including decatungstate which had earlier working in the solution phase. It was noted that this may be caused by poor surface interaction.

Mustard simulant

Activity was ordered similar to that of the homogenous results, However, rates were reduced. In 60 minutes singlet oxygen had removed 80%, Superoxide 40% and radical 20%. Removal was due to the favorable dissolution of the film into the simulant creating a homogeneous reaction media. Reaction products were similar to those seen during the earlier homogeneous work.

VX simulant

There was no activity from any of the sensitizers investigated.

Conclusions

This work has shown the radical chemistry of the polyoxometalate decatungstate can successfully degrade all three simulated agents in the solution phase. Further work would be needed to develop a working coating. Radical chemistry produced a large number of products, determination of the toxicity of these was beyond the limits of the project. Much faster reactivity is achieved by the singlet oxygen or superoxide route, however, these only show activity towards the mustard simulant. It was decided that a DOD application was not viable and concerns over toxic byproducts prompted the non continuation of funding.