

## Preface

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The Army Research Office\* (ARO), The Defense Threat Reduction Agency (DTRA), The Edgewood Chemical and Biological Center (ECBC), and the Inorganic Division of the American Chemical Society sponsored the Symposium: “Sensing and Destroying Chemical Weapons and Pesticides” at the 238th American Chemical Society Meeting held in Washington, DC August 18–19, 2009. Dr. David McGarvey (DTRA), Prof. Daniel Williams (Kennesaw State University), and Prof. David Atwood (University of Kentucky) co-organized the Symposium. The presentations, shown on the following page, addressed the many challenges currently facing society with regards to problematic organophosphates (OPs) such as chemical weapon agents and pesticides. The articles in this Special Issue of *Main Group Chemistry* are based, in part, on presentations made at the Symposium. The majority of the articles focus on new reagents that can degrade and deactivate OPs. Importantly, however, several of the articles describe the basic chemistry taking place during degradation, providing the necessary foundation for the design of new mitigation and remediation reagents.

In the first article **Carol Brevett** and **Kenneth Sumpter** describe the rates, products, and mechanisms of how various CWAs, including VX, are degraded on environmental substrates. VX is one of the most problematic CWAs since it is slow to hydrolyze, can persist for weeks, and is a dermal-contact hazard. In the second article **Gary Groenewold** reveals that VX volatility is an additional hazard, and provides kinetic data on the degradation of VX and EA2192. Most simulants model the physical properties of chemical weapon agents but it is more difficult to find general simulants for CWA reactions since the mechanisms, rates, and product distribution should be similar to the “live” agent. **William Creasy** and coauthors provide information on reactive standards and the relative merits of HRMAS-NMR and Headspace GC-MS as standard analytical methods. The next seven articles in the Issue describe innovative means by which OPs may be deactivated. **George Wagner** describes a hydrogen peroxide-based system that is weakly basic and maintains activity for at least 12 hours. It is used to decontaminate VX, GD, and HD on non-porous surfaces to below acceptable levels. **Stan Brown and Alexei Neverov** review the history and recent advances in metal ion-promoted alcoholysis. Metals such as lanthanum, zinc, and copper are rapid catalysts for compounds containing P=O bonds but ineffective for those containing P=S bonding. **Louis Kuo** and coauthors describe interesting new reactivity of molybdenum metallocenes in the selective cleavage of P-S bonds in a VX simulant. **Kenneth Klabunde** provides a review of non-toxic metal oxide nanomaterials with chemically active surface functionality. He identifies metal-doped titanium dioxide as having the needed properties of being a destructive sorbent, catalytically active under ambient light, and with self-cleaning regenerable properties. **Daniel Williams** and coauthors from the ECBC also take advantage of electropositive, Lewis acidic metals by using aluminum sulfate and sodium aluminate to induce the hydrolysis of VX. Among other degradation products they identify an aluminum complex of EMPA by <sup>31</sup>P HRMAS-NMR. In further work with Lewis acidic elements, **David Atwood** and coauthors describe how group 13 chelates can combine with CWAs and pesticides to produce stable, deactivated OP-group 13 compounds. Demonstrating the breadth of potential degradation technologies, **Kallol Gosh** and coauthors review the use of micelles to catalyze the hydrolysis of CWA simulants and pesticides. Fortunately, significant new advances have been made in therapeutic treatments for human OP exposure. **Kamil Musilek** and coauthors present the results of a broad, systematic search for compounds capable of rapidly regenerating AChE activity and the identification of several promising candidates for OP detoxification.

The ACS Symposium and this issue of *Main Group Chemistry* demonstrate that many significant advances are being made to deal with the threat of OPs. There is a clear need for a better understanding of the Lewis basicity and electronic structure of OPs and their interactions with Lewis acids and the many other substrates and surfaces the OPs would contaminate when released. The United States Army has created the infrastructure necessary to fully characterize and understand the basic chemistry of OPs and to test new reagents and technologies for their degradation and deactivation. In addition to providing the means of responding to a CWA attack, much of

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this research and development will be directly relevant to the widespread contamination of soils and water with pesticides and related OPs. However, there is still no single system or reagent that is effective against all OPs. There remains a critical need for such a reagent or technology, and the fundamental knowledge of OPs that would guide their design.

**Sensing and Destroying Chemical Warfare Agents and Pesticides Symposium  
The 238th ACS National Meeting, Washington, DC, August 18–19, 2009**

1. Keynote: From bench to battlefield: Chemical and biological defense. Col. Michael O'Keefe
2. Metal ion-catalyzed alcoholysis as a strategy for the high loading destruction of CW organophosphorus agents. H. Dupont Durst, Kenneth Sumpter, R. Stan Brown, Alexei A. Neverov, Tamer Andrea
3. Development of metal ion-catalyzed alcoholysis as a rapid methodology for the destruction of organophosphorus CW agents, their simulants and pesticides. R. Stan Brown, Alexei A. Neverov
4. All-weather, hydrogen peroxide-based decontamination of CBRN contaminants. George W. Wagner
5. Greener methods for the destruction of phosphorus based chemical warfare agents. Daniel J. Williams, William R. Creasy, David J. McGarvey, Roderick A. Fry, Vicky L. H. Bevilacqua, H. Dupont Durst
6. Ricin and staphylococcal enterotoxin B stability: Heat and chlorine treatment. Vicky L. H. Bevilacqua, Janna S. Madren-Whalley, Jeffrey S. Rice, Lisa M. Reilly, Thomas J. Rogers, Amanda Schenning
7. Development of promising oximes against nerve agent and/or pesticide intoxication. Kamil Musilek, Ondrej Holas, Marketa Komloova, Jana Zdarova-Karasova, Miroslav Pohanka, Kamil Kuca
8. New insights into detoxification of chemical warfare simulants and pesticides using micellar mediated systems. Kallol K Ghosh, Shuchi Tiwari, Kamil Kuca, Jan Marek
9. Seeking simple solutions for the detection of chemical and biological warfare agents. Kim D. Janda
10. Nanoscale titanium oxide as a superior destructive adsorbent. Kenneth Klabunde, Shyamala Rajagopalan, Dambar B Hamal, Kennedy Kalebaila, Xiangxin Yang, Megan Winter, David Jones, Haidoo Kwen
11. Room temperature destruction of dimethyl methylphosphonate (DMMP) by ozone on oxide surfaces. Mark B. Mitchell, Viktor N. Sheinker, Woodrow W. Cox Jr.
12. Selective P-S bond scission in phosphonothioate hydrolysis by molybdenum metallocene complexes. Louis Y. Kuo
13. Organophosphonate binding with manganese-A2B-corrole and -A2B2-porphyrin systems and favorable pendant-amino metal chelation in VX model systems. David G. Churchill, Yoon Sup Lee, Kibong Kim, Indrajit Bandyopadhyay, Nilkamal Maiti, Inkoo Kim
14. Group 13 chelates in nerve agent and pesticide destruction. David A. Atwood
15. Optical and electrical detection of chemical warfare agents. Timothy M. Swager
16. Concentration, manipulation, and detection of chemical toxicants using porous photonic crystals based on silicon. Michael J. Sailor
17. Chemical warfare agent reaction studies using headspace GC/MS and high resolution magic angle spinning (HRMAS) NMR. William R. Creasy, David J. McGarvey, Roderick Fry, H. D. Durst
18. Degradation of the chemical warfare agents GD, thickened GD, HD and VX on ambient and moist operationally-relevant substrates. Carol A. S. Brevett, Kenneth Sumpter
19. Comparisons of reactivity of chemical weapons agents to agent simulants. David J. McGarvey, William R. Creasy, Roderick Fry, H. Dupont Durst

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