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13. ABSTRACT (Maximum 200 words) This final report summarizes the many accomplishments of this grant including (1) the development of versatile materials with catalytic activity for the effective decontamination of mustard (HD) analogs; (2) the development of effective catalytic HD decontamination catalysts that work using air (O ₂); (3) the detailed investigation and elucidation of the mechanisms of such new catalytic systems including the mechanism for O ₂ activation by reduced polyoxometalate (POM) clusters; and (4) the characterization of relevant reduced polyoxometalates. These results coupled with the compatibility of these systems with existing decontamination technology augur well for development of utilitarian decontamination catalysts.				
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Final Progress Report

By: Craig L. Hill (Principal Investigator)

Title of grant: Multifunctional Catalysts for Decontamination and Fuel Cells

Statement of the problem studied:

To design, synthesize, characterize and investigate both molecules and materials, particularly transition-metal oxygen-anion clusters (polyoxometalates or POMs for convenience) and/or their organic and polymeric derivatives, for the effective catalytic decontamination of chemical warfare agents, and in particular mustard (HD) and VX, or their simulants, under ambient conditions.

Summary of the most important results:

Significant accomplishments have been made on several fronts regarding the development of materials with catalytic oxidative decontamination activity that are also readily recoverable and reusable. The first systems that catalyze effective oxidations, including decontamination of chemical warfare agent simulants, using air/O₂ have been reported. New materials (POM-containing powders and cloths) that oxidatively decontaminate chemical warfare agent simulants catalytically and rapidly under ambient conditions have been reported. The detailed mechanism of some seminal POM redox processes has been elucidated. Many of the details are elaborated in the abstracts of the published papers given below.

List of publications (each publication with its abstract is given):

The first publication below is major review article on pertinent redox catalysis and POM chemistry that was published during this grant period. It is an authoritative and comprehensive review on chemistry that permeates our ARO funded research and impacts the research of many groups worldwide. The following is the Table of Contents from this article and enumerates the specific topics covered:

- Hill, C. L.; Prosser-McCartha, C. M. "Homogeneous Catalysis by Transition-Metal-Oxygen-Anion Clusters" *Coord. Chem. Rev.* **1995**, *143*, 407-455.

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• Gall, R. D.; Faraj, M.; Hill, C. L. "Scope, Kinetics, and Mechanism of Oxidation of Thioether HD Analogs by *t*-Butylhydroperoxide Catalyzed by H₅PV₂Mo₁₀O₄₀. The Role of Water in Polyoxometalate-Catalyzed Oxidations in Non-aqueous Media." Proceedings of the 1994 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research, US Army Armament, Munitions & Chemical Command, 1995.

Abstract: Hydrated H₅PV₂Mo₁₀O₄₀ (**1**) catalyzes the rapid oxidation of thioether HD analogs including tetrahydrothiophene (THT) to the corresponding sulfoxides by *t*-BuOOH at 25 °C in extremely high selectivity (>99.9%). This selectivity derives from an unusual mechanism for metal-catalyzed peroxide oxidations: **1** oxidizes the substrate thioether and *t*-BuOOH only reoxidizes the reduced form of **1**. The rate law for the reaction of **1** and THT is $v_0 = k[\text{THT}][\mathbf{1}][\text{H}_2\text{O}]^{-1}$ with $\Delta H^\ddagger = 8.06 \pm 0.64 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -29.7 \pm 0.18 \text{ e.u.}$ In the absence of water, the rate law becomes $v_0 = k'[\mathbf{1}]$.

- Harrup, M. K.; Hill, C. L. "Thermal Multielectron Transfer Catalysis by Polyoxometalates. Application to the Practical Problem of Sustained, Selective Oxidation of Hydrogen Sulfide to Sulfur." *J. Mol. Catal.* **1996**, *106*, 57-66.

Abstract: Novel polyoxometalate-based catalytic systems for the effective and selective aerobic oxidation of H₂S to S(0) are reported. The base stable catalysts TMA₉[Nb₃P₂W₁₅O₆₂], **1**, Li₃₃[H₇P₈W₄₈O₁₈₄], **2**, K₁₀[Zn₄P₂W₁₈O₆₈], **3**, and K₄[Nb₂W₄O₁₉] produce 17, 135, 5.7 and 8.8 turnovers of S₈, respectively (23 °C; 1.0 atm O₂; 4 h; sealed vessel). The stability of these catalysts during sulfide oxidation is evaluated. The redox potentials of these polyoxometalates and the primary fragmentation products pertinent to sulfide oxidation are given. Early time kinetics of the reduction of **1** by sulfide proceeds according to the rate law $+d[\text{Nb}_3\text{P}_2\text{W}_{15}\text{O}_{62}^{10-}]/dt = k[1][\text{HS}^-]$, with a complex pH dependence. The buffering agent is shown to be noninnocent and at parity of reaction conditions, the reduction of K₁₄[NaP₅W₃₀O₁₁₀], **4**, by sulfide in media buffered with PO₄³⁻, CO₃²⁻, B₄O₁₀²⁻, and OH⁻ (a blank) results in 40, 9.0, 49, and 10 turnovers of S₈, respectively.

- Chen, Q.; Hill, C. L. "A Bivanadyl Capped, Highly Reduced Keggin Polyanion, [PMo^V₆Mo^{VI}₆O₄₀(V^{IV}O)₂]⁵⁻" *Inorg. Chem.*, **1996**, *35*, 2403-2405.

Abstract: The hydrothermal reaction of Na₂MoO₄·2H₂O, VOSO₄·3H₂O, H₃PO₄, (C₂H₅)₃N·HCl, and H₂O at 180 °C, yields dark blue crystals of [(C₂H₅)₃NH]₅[PMo^V₆Mo^{VI}₆O₄₀(V^{IV}O)₂], TEA1, a bicapped, highly reduced vanadylpolymolybdophosphate Keggin complex. Redox titration, bond length based valence sum calculations, spectroscopy (infrared, electronic absorption, and ⁵¹V and ³¹P NMR on its degradation products) all confirm this assignment. TEA1 is inactive electrochemically on a glassy carbon electrode. It decomposes under anaerobic conditions via second order process at 25 °C ($k_2 = 1.83 \times 10^{-6} \text{ M}^{-1} \text{ min}^{-1}$ from a 25-point fit with R = 99.23%). Decomposition under aerobic conditions is very complicated exhibiting conventional kinetics followed by autocatalytic behavior. It is clear from this structure, and those of other Keggin polyoxometalates of any oxidation state with two vanadium capping units, that this vanadium capping phenomenon is fairly general and is controlled primarily by the charge on the Keggin moiety and the factors that dictate this charge.

- Gall, R. G.; Hill, C. L.; Walker, J. E. "Selective Oxidation of Thioether Mustard (HD) Analogs by *tert*-Butylhydroperoxide Catalyzed by H₅PV₂Mo₁₀O₄₀ Supported on Porous Carbon Materials." *J. Catal.* **1996**, *159*, 473-478.

Abstract: The polyoxometalate H₅PV₂Mo₁₀O₄₀ (**1**) supported on porous carbons forms selective and recoverable heterogeneous catalysts for the rapid room temperature oxidation of thioether mustard (HD) analogs. Both selectivities (95 to 99% for sulfoxide) and rates (~20%) vary with the carbon support at parity of all

other parameters. A 99% selectivity for the sulfoxide product, even at 75% conversion of the thioether substrate, is seen for the most selective system, 10 weight % **1** on Rohm and Haas Ambersorb (1/Ambersorb). Washing for 125 h in the solvent for catalysis, toluene, results in no significant loss in catalytic activity and a recovery and reusability study at high turnover also indicates that the catalysts are very stable. The polyoxometalate/carbon catalysts can be reactivated between uses by heating to ~ 80 °C. The oxidation of tetrahydrothiophene (THT) to THTO by *tert*-butylhydroperoxide (TBHP) catalyzed by 1/Ambersorb is first order in substrate and oxidant and proportional to the concentration of active sites on the 1/Ambersorb. The activation parameters for the process are $\Delta H^\ddagger = 11.4 \pm 0.05$ Kcal/mole and $\Delta S^\ddagger = -38.8 \pm 0.22$ cal/K mole.

- Gall, R. D.; Hill, C. L.; Walker, J. "The Selective Oxidation of Thioethers by *tert*-Butylhydroperoxide Catalyzed by Divanadododecamolybdophosphate Supported on Carbon Cloths and Powders." Proceedings of the 1995 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research, US Army Armament, Munitions & Chemical Command, 1996, pp 397-403.

Abstract: This study establishes that the carbon-supported polyoxometalate $H_5PV_2Mo_{10}O_{40}$ (**1**) is an effective and recoverable heterogeneous catalyst for selective oxidation of HD analogs to the corresponding sulfoxides. The order of activity for the three carbons studied was Maxsorb/**1** > Calgon/**1** > Ambersorb/**1** with conversions of 84%, 60%, and 57.5% respectively (94 min., 25 °C). The corresponding selectivities for the sulfoxide were 100 (Ambersorb/**1**) > 97 (Calgon/**1**) > 95 (Maxsorb/**1**). The catalyst was able to be recovered, washed, heated (70 °C) and reused.

- Gall, R. D.; Hill, C. L.; Walker, J. E. "Carbon Powder and Fiber Supported Polyoxometalate Catalytic Materials. Preparation, Characterization, and Catalytic Oxidation of Mustard (HD) Analogs." *Chem. Materials* 1996, 8, 2523 - 2527.

Abstract: We report here a prototype material for the sustained catalytic decontamination of mustard analogs with the ultimate goal being the fabrication of self-decontaminating clothing. $H_5PV_2Mo_{10}O_{40}$ (**1**) can be supported on carbon cloths as well as powders, with 1/Ambersorb 572 being the best material (high catalytic activity and low desorption of **1**). Evaluation of the desorption of **1** from six carbon supports indicates that the PPAN (Pyrrolyzed Polyacrylonitrile) and Ambersorb 572 materials are highly effective at retaining the immobilized **1** even under catalytic conditions (oxidation of tetrahydrothiophene, THT, by *tert*-butylhydroperoxide, TBHP). The products of THT oxidation, tetrahydrothiophene oxide (THTO) and *tert*-butyl alcohol (TBA), inhibit the reaction at high conversions; however, the catalytic activity can be restored by heating in a vacuum oven to 80 °C. The reactivity for oxidation of four different thioethers by TBHP catalyzed by **1** supported on hydrophobic (Ambersorb 563) and hydrophilic (Ambersorb 572)

- Hill, C. L.; Gall, R. D. "The First Combinatorially Prepared and Evaluated Inorganic Catalysts. Polyoxometalates for the Aerobic Oxidation of the Mustard Analog Tetrahydrothiophene (THT)." *J. Mol. Catal. A: Chem.* **1996**, *114*, 103 - 111. (Special Issue on Polyoxometalates in Catalysis, Hill, C. L., Ed.).

Abstract: The combinatorial synthesis and evaluation of inorganic catalysts is described. The catalysts are an array of early-transition-metal-oxygen-anion clusters (polyoxometalates) and the reaction is the aerobic oxidation of a mustard thioether analog, tetrahydrothiophene (THT). Selective oxidation of THT to the desired sulfoxide, THTO, was achieved in high selectivity (> 99%) and under relatively mild conditions (95 °C, 1.52 atm). Solutions with a molar ratio of 1:2 (phosphorus:vanadium) had the highest catalytic activity. ⁵¹V NMR and IR were used not only to identify the self-assembling polyoxometalates in several representative precursor combinations (columns in the combinatorial gallery of Figure 1) but also to assess the stability of one representative polyoxometalate catalyst, 1P:2V:10W, under catalytic conditions (no decomposition after 50 turnovers). Gas chromatography was sufficient to rapidly quantify the product (THTO) yields and selectivities of representative reactions. Application of combinatorial methods should be applicable to and provide the same advantages for discovery and optimization of catalysts as it has for pharmaceuticals.

- Hill, C. L.; Gall, R. D. "The First Combinatorially Prepared and Evaluated Inorganic Catalysts. Polyoxometalates for the Aerobic Oxidation of the Mustard Analog Tetrahydrothiophene (THT)." Proceedings of the 1996 U.S. Army Edgewood Research, Development and Engineering Center Scientific Conference on Chemical and Biological Defense Research, US Army Armament, Munitions & Chemical Command, 1997, pp 107-112.

Abstract: The combinatorial synthesis and evaluation of inorganic catalysts will be described. The catalysts are an array of early-transition-metal-oxygen-anion clusters (polyoxometalates) and the reaction is the aerobic oxidation of a mustard thioether analog, tetrahydrothiophene (THT). Selective oxidation of THT to the desired sulfoxide, THTO, was achieved in high selectivity (> 99%) and under relatively mild conditions (95 °C, 1.52 atm of O₂). Solutions with a molar ratio of 1:2 (phosphorus:vanadium) had the highest catalytic activity. ⁵¹V NMR and IR were used to identify the self-assembling polyoxometalates in representative precursor combinations and to assess the stability of one representative catalyst, 1P:2V:10W, under turnover conditions (no decomposition after 50 turnovers). GC was sufficient to rapidly quantify the product (THTO) yields and selectivities of representative reactions. Combinatorial methods should be applicable to and provide the same advantages for discovery and optimization of catalysts as it has for pharmaceuticals.

- Duncan, D. C.; Hill, C. L. "Mechanism of Reaction of Reduced Polyoxometalates with O₂ Evaluated by ¹⁷O NMR." *J. Am. Chem. Soc.* **1997**, *119*, 243-244.

Abstract: The O₂-based reoxidation mechanism of three representative reduced polyoxometalates (POMs), H₂[W₁₀O₃₂]⁴⁻ (1; two-electron reduced), [P₂W₁₈O₆₂]⁷⁻ (2; one-electron reduced), and H_{5+x}[PV₂Mo₁₀O₄₀]^{(5+x)-} (3; x-electron reduced where x = 1-2) was investigated using ¹⁷O-labeled O₂ with ¹⁷O NMR detection. The results presented here demonstrate that the dominant mechanism for reoxidation of the reduced POMs, 1 and 2, *does not* involve oxygen incorporation within the POM framework; consequently, the data argue strongly against intermediacy of covalent W-O bonds during the reoxidation of either 1 or 2. Additionally, preliminary evidence obtained for the reoxidation of 3 by O₂ also is consistent with this conclusion; however, the rapid oxygen exchange between water and 3 makes this assignment tentative.

- Zeng, H.; Hill, C. L.; Newkome, G. "Catalytically Decontaminating Dendrimers. Poly-tris Arborols Covalently Functionalized with Redox Active Polyoxometalates." Proceedings of the 1997 U.S. Army Edgewood Research, Development and Engineering Center Scientific Conference on Chemical and Biological Defense Research, US Army Armament, Munitions & Chemical Command, 1998, pp 351-357.

Abstract: A prototype of a new class of materials has been prepared and characterized, a dendrimer-like structure containing units that catalyze oxidative decontamination reactions. The dendrimer-like molecule is an arborol with terminal tris(hydroxymethyl) groups to which redox active polyoxometalates (POMs), of formula [P₂V₃W₁₅O₆₂]⁹⁻, are bound via an esterification reaction. The resulting poly-POM arborol, {[P₂V₃W₁₅O₅₉(O-CH₂)₃CNHCO]₂CH(CH₂)₁₂CH[(CO-NHC(CH₂O)₃P₂V₃W₁₅O₅₉]₂]²⁴⁻, catalyzes the rapid oxidation of HD simulants such as tetrahydrothiophene (THT) by peroxides and, by virtue of its nature, can be readily recovered and reused.

- Johnson, R. P.; Hill, C. L. "CW-Agent Detecting Barrier Creams" Proceedings of the 1997 U.S. Army Edgewood Research, Development and Engineering Center Scientific Conference on Chemical and Biological Defense Research, US Army Armament, Munitions & Chemical Command, 1998, pp 393-399.

Abstract: The goal of this research is to develop an HD detecting cream. Conceptually, a polyoxometalate (POM, e.g., H₅PV₂Mo₁₀O₄₀) would be suspended in a perfluoropolyether (PFPE, CF₃O[-CF(CF₃)CF₂O-]_x(-CF₂O-)_yCF₃) barrier cream, where it would oxidize the highly toxic bis(2-chloroethyl) sulfide (or mustard, HD) upon contact with a concurrent color change in the POM, in this case, from orange to blue, warning the wearer that HD was present.

In a typical reaction, approximately 10% by weight of each of five finely crushed, strongly oxidizing POMs is suspended in the cream, and a stoichiometric amount of a sulfide analog of HD is layered on top of the cream-POM mixture. The time for the reaction (time for the POM to turn a different color) is recorded. Results

from representative systems indicate that these reactions are thermodynamically favorable. In order to elucidate the mechanism of the system, we have used a PFPE oil analog of the barrier cream, in a solution with the sulfide, POM, perfluorinated surfactant, and ethanol co-surfactant.

- Johnson, R. P.; Hill, C. L. " Polyoxometalate Oxidation of CW Agent Simulants in Fluorinated Media" Proceedings of the 1999 U.S. Army Edgewood Research, Development and Engineering Center Scientific Conference on Chemical and Biological Defense Research, US Army Armament, Munitions & Chemical Command, in press.

Abstract: The aim of this research is to determine if appropriate polyoxometalates (POMs) could be added to perfluoropolyether topical skin protectants (TSPs) currently available or under development to give these TSPs the additional capability of detecting and in some cases catalytically decontaminating HD and perhaps other chemical warfare (CW) agents at ambient temperatures. Detection would be based on significant color changes in the POM upon reduction by the CW agent, while catalytic decontamination would be based on the ability of some families of POMs to catalyze O₂-based oxidations by more than one mechanism. Five POMs (10-25% by weight) were each suspended in ~5g of the perfluoropolyether (PFPE, CF₃O[-CF(CF₃)CF₂O-]_x(-CF₂O-)_yCF₃) "barrier" cream. A stoichiometric amount of HD sulfide simulant was layered on top of each POM-cream mixture. The short reaction times were recorded for each system. Mechanistic studies were conducted using a PFPE oil analog of the barrier cream in a microemulsion with the sulfide simulant, POM, PFPE surfactant, and 2,2,2-trifluoroethanol co-surfactant.

List of all participating scientific personnel:

Qin Chen, Ph.D	(18 months; 1995 & 1996)
Dean Duncan	(19 months; 1995 & 1996)
Robin Gall	(6 months; 1995 & 1996)
Rhoma Johnson	(12 months; 1996-1997 and 1997-1998)
Ling Xu	(8 months; 1997 & 1998)
Xuan Zhang	(5 months; 1996)
Zhanmiao Zheng	(18 months; 1995-1997)

Report of inventions:

No patents filed. One patent is in the process of being filed and will be assigned to the subsequent grant. See section below—collaborations and technology transfer.

The principal investigator's collaborations and technology transfer:

- He has an ongoing research collaboration on several fronts (catalytic decontamination of HD and VX analogs and the design, fabrication and characterization of materials with catalytic decontamination activity) with Dr. John E. Walker and others at the U. S. Army Natick RD & E Center, Natick, Massachusetts.
- He also has a collaboration started in 1997 with Maj. Erich Lehnert and Dr. Ernie Braue of the USAMRICD (Aberdeen Proving Ground) on the design, preparation and characterization of cream formulations that detect and decontaminate HD and VX like compounds. Promising results in this area have lead to an SBIR grant in collaboration with Nantek, Inc., of Manhattan, Kansas.
- A third collaboration involves the development of catalytically decontaminating fabrics with a TDA Research in Wheat Ridge, Colorado and a fabric supplier, Malden Mills, In Massachusetts. Dr. John E. Walker at the U. S. Army Natick RD & E Center is also involved.
- A fourth collaboration involves the development of a device for combating vesicant injury of human tissues extracellularly and intracellularly with Dr. David A. DuBose of the U. S. Army Natick RD & E Center.