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13. ABSTRACT (Maximum 200 words)  This grant has been quite successful in that many of the targeted issues (basic reactivity, mechanistic and structure-reactivity features) for catalyzed O <sub>2</sub> -based oxidations, and in particular O <sub>2</sub> -based decontamination reactions, were established. In addition, several new and effective catalysts for oxidative decontamination were discovered and/or developed. The new catalytic systems include Au(III)-based homogeneous systems, coinage metal salts of polyoxometalates (POMs), POMs electrostatically bound to cationic silica nanoparticles, POMs catenated with redox active counterions, and multi-iron-containing POMs. Nearly all the publications address the relationships between the physical and electronic structures of the catalysts in varying environments and their reactivity and mechanisms of oxidative decontamination. The most reactive catalysts developed under this program, including some multi-iron-containing POMs, are forming the basis of intellectual property and collaborative efforts with companies (Gentex Corporation and TDA Research).				
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Enclosure 1

## FINAL PROGRESS REPORT

**Project/Proposal Title:** New Catalytic Molecules and Materials for Decontamination

**Source of Support:** US Army

**Agency Grant Number:** DAAD19-01-1-0593

**Contact:** Stephen Lee, POB 12211, Research Triangle Park, NC 27709-2211

**Total Award Amount:** \$225,000

**Total Award Period Covered:** 5/15/01-2/14/04

### Statement of problem

To understand the basic reactivity, mechanistic and structure-reactivity features of homogeneous catalytic air/O<sub>2</sub>-based oxidations of organic substrates with an emphasis on the chemical warfare agents and their simulants. To develop new metal complexes and materials that catalyze oxidative decontamination, with a focus on mustard (HD) analogues and thiols (the hydrolysis product of VX).

### Summary of the most important results

This grant has been quite successful in that many of the targeted issues (basic reactivity, mechanistic and structure-reactivity features) for catalyzed O<sub>2</sub>-based oxidations, and in particular O<sub>2</sub>-based decontamination reactions, were established. The many fundamental structural and reactivity findings are addressed in the abstracts of our publications listed below. In addition, several new and effective catalysts for oxidative decontamination were discovered and/or developed. The new catalytic systems include Au(III)-based homogeneous systems (addressed in publications 1, 2 and 11 below), coinage metal salts of polyoxometalates (POMs) (addressed in publication 3), POMs electrostatically bound to cationic silica nanoparticles (addressed in publications 6 and 9), POMs catenated with redox active counterions (addressed in publication 8), and multi-iron-containing POMs. Nearly all the publications address the relationships between the physical and electronic structures of the catalysts in varying environments and their reactivity and mechanisms of oxidative decontamination. One of many noteworthy findings is that both Au(III) and several POM systems involve oxidation of the target (HD simulant or other substrate) in the slow step; O<sub>2</sub> is only involved in reoxidation of the reduced form of the catalyst. The rates for decon in these systems are consequently independent of the O<sub>2</sub> pressure. The oxidative decontamination rates in some systems do depend on O<sub>2</sub> pressure. Another noteworthy point is that the most active catalysts for decontamination of mustard contain multiple d-electron-containing centers proximal to one another in the surface of the POM clusters. Thus cooperativity between these centers may be involved in the chemistry. The most reactive catalysts developed under this program, including some multi-iron-containing POMs, are forming the basis of intellectual property and collaborative efforts with companies (Gentex Corporation and TDA Research). The research on these multi-metal POMs has not yet been published in part because they are hard to characterize and very complicated.

## Listing of all publications

For each publication, the abstract is given along with the usual requested information (authors, article title, journal, year, volume, page numbers) because our abstracts are usually detailed and quite informative with respect to the requested points (goals, experiments, findings, conclusions). In a few cases where the abstract is not clear on this point, the importance of the publication is stated.

### Papers published in peer-reviewed journals.

**1. Boring, E.; Gueletii, Y.; Hill, C. L. "A Homogeneous Catalyst for Selective O<sub>2</sub> Oxidation at Ambient Temperature. Diversity-Based Discovery and Mechanistic Investigation of Thioether Oxidation by the Au(III)Cl<sub>2</sub>NO<sub>3</sub>(thioether) / O<sub>2</sub> System." *J. Am. Chem. Soc.* **2001**, *123*, 1625-1635.**

(This article was written up in March 5 issue of *Chemical and Engineering News*, **2001**, *79*, 5) It was also cited by the editors of *Chemical and Engineering News* in their year-end summary of "the most significant scientific achievements of 2001" (cover story by S. Borman, December 10, 2001 issue of *Chemical and Engineering News*, **2001**, *79*, 45-55).

**Abstract:** A library of inorganic complexes with reversible redox chemistry and/or the ability to catalyze homogeneous oxidations by peroxides, including but not limited to combinations of polyoxometalate anions and redox-active cations, was constructed. Evaluation of library members for the ability to catalyze aerobic sulfoxidation (O<sub>2</sub> oxidation of the thioether, 2-chloroethyl ethyl sulfide, CEES) led to the discovery that a combination of HAuCl<sub>4</sub> and AgNO<sub>3</sub> forms a catalyst that is orders of magnitude faster than the previously most reactive such catalysts (Ru(II) and Ce(IV) complexes) and one effective at ambient temperature and 1 atm air or O<sub>2</sub>. If no O<sub>2</sub> but high concentrations of thioether are present, the catalyst is inactivated by an irreversible formation of colloidal Au(0). However, this inactivation is minimal in the presence of O<sub>2</sub>. The stoichiometry is R<sub>2</sub>S + 1/2 O<sub>2</sub> → R<sub>2</sub>S(O), a 100% atom efficient oxygenation, and not oxidative dehydrogenation. However, isotope labeling studies with H<sub>2</sub><sup>18</sup>O indicate that H<sub>2</sub>O and not O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> is the source of oxygen in the sulfoxide product; H<sub>2</sub>O is consumed and subsequently regenerated in the mechanism. The rate law evaluated for every species present in solution, including the products, and other kinetics data, indicate that the dominant active catalyst is Au(III)Cl<sub>2</sub>NO<sub>3</sub>(thioether) (**1**); the rate-limiting step involves oxidation of the substrate thioether (CEES) by Au(III); reoxidation of the resulting Au(I) to Au(III) by O<sub>2</sub> is a fast subsequent step. The rate of sulfoxidation as Cl is replaced by Br, the solvent kinetic isotope effect (*k*<sub>H<sub>2</sub>O</sub>/*k*<sub>D<sub>2</sub>O</sub>) of 1.0), and multiparameter fitting of the kinetic data establish that the mechanism of the rate-limiting step involves a bimolecular attack of CEES on a Au(III)-bound halide and it does not involve H<sub>2</sub>O. The reaction is mildly inhibited by H<sub>2</sub>O and the CEESO product because these molecules compete with those needed for turnover (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>) as ligands for the active Au(III). Kinetic studies using DMSO as a model for CEESO enabled inhibition by CEESO to be assessed.

**2. Boring, E.; Gueletii, Y.; Hill, C. L. "Catalytic aerobic oxidation of 2-chloroethyl ethyl sulfide (CEES), an HD simulant, under ambient conditions. Effect of**

**solvents, ligands, and transition metals on reactivity" *J Mol. Cat. A., Chem.* 2001, 176, 49-63.**

The complexes  $\text{Au(III)(Hal)}_2(\text{NO}_x)(\text{L})$ ,  $\text{Hal} = \text{Cl}^-$  or  $\text{Br}^-$ ,  $\text{NO}_x = \text{NO}_3^-$  or  $\text{NO}_2^-$ ,  $\text{L} =$  thioether, catalyze the selective aerobic sulfoxidation of thioethers, including the mustard simulant 2-chloroethyl ethyl sulfide (CEES), by dioxygen (stoichiometry:  $\text{CEES} + 0.5 \text{O}_2 \rightarrow \text{CEESO}$ ) under ambient conditions (25 °C, 1 atm  $\text{O}_2$ ) in both homogeneous solution (acetonitrile, trifluoroethanol, nitromethane, 1,2-dichloroethane) or non-toxic perfluoropolyether (PFPE) suspensions. The reaction rate, induction period, and the extent of product inhibition are dependent on the Au(III) ligands, the solvent, and the presence of additional redox active metals. Catalytic aerobic CEES oxidation is 1.8 times faster when  $\text{NO}_3^-$  is replaced by  $\text{NO}_2^-$  and 3.3 times faster when  $\text{Cl}^-$  is replaced by  $\text{Br}^-$  in acetonitrile. This reaction in trifluoroethanol exhibits no induction period and is 2.8 times faster than in acetonitrile. Addition of 2 equiv. of Cu(II) per Au(III) to the system increases the rate by a factor of 2.7. The  $\text{Au(III)/(Br)}_2/\text{NO}_3^-/\text{Cu(II)}$  system exhibits high rates for the selective aerobic oxidation of CEES to CEESO under ambient conditions (~68 turnovers per hour), with little if any inhibition by the CEESO product. At low concentrations, sulfoxides reduce the induction period and increase the rate of CEES oxidation in acetonitrile, but at high concentrations they inhibit the reaction. These Au(III) catalysts are extremely efficient for aerobic CEES sulfoxidation when suspended in the PFPE Fomblin® MF-300 (up to 200 turnovers in 10 min). This is a significant improvement from the Au system described in the first study,  $\text{Au(III)(Cl)}_2(\text{NO}_3)(\text{CEES})$  in acetonitrile, which yielded approximately 5 turnovers of CEESO after 10 min. The catalytic reactivity of the  $\text{Au(III)(Cl)}_2(\text{NO}_3)(\text{L})$  in Fomblin® MF-300 for aerobic CEES oxidation was evaluated in the presence of the common amino acids to assess the extent to which the various functional groups in human skin (epidermal polypeptides) might inhibit the catalysis. Some amino acids inhibit the reaction, but the reaction still proceeds even in the presence of 7.5 equiv. of the most inhibitory functional group, indole (tryptophan).

**3. Rhule, J. T.; Neiwert, W. A.; Hardcastle, K. I.; Do, B. T.; Hill, C. L. "Ag<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub>, a Heterogeneous Catalyst for Air-Based Selective Oxidation at Ambient Temperature" *J. Am. Chem. Soc.* 2001, 123, 12101-12102.**

This ms acknowledged the previous 3-yr ARO grant but was also funded in part by and finished during this ARO grant (DAAD19-01-1-0593)

**Abstract.** The preparation, structure and properties of a new material that catalyzes the heterogeneous and selective  $\text{O}_2$  oxidation of the representative thioether, 2-chloroethyl ethyl sulfide (CEES) to its corresponding far less toxic sulfoxide (CEESO) under ambient conditions (room temperature and 1.0 atm of air) is reported. The catalyst,  $\text{Ag}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  ( $\text{Ag}_5\mathbf{1}$ ) is a salt of a redox active polyoxometalate (POM),  $\text{PV}_2\text{Mo}_{10}\text{O}_{40}^{5-}$  ( $\mathbf{1}$ ) and a redox active d-block cation, Ag(I). X-ray crystallography reveals that the dominant structural feature of the complex crystallized from MeCN and  $\text{Et}_2\text{O}$  involves two  $\text{PV}_2\text{Mo}_{10}\text{O}_{40}^{5-}$  units bridged by two Ag(I) ions, each of which bonds to both bridging and terminal oxygens of the POM units. In addition, each POM has two non-bridging Ag(I) ions. All the Ag(I) centers are 4 coordinate, with terminally coordinated acetonitrile molecules (one each for the POM-bridging Ag centers and two each for the non-bridging Ag centers). The catalyst achieves ~2300 turnovers (moles of sulfoxide product per mole of surface accessible  $\text{Ag}_5\mathbf{1}$  in the powder) in 7.1 days. The catalytic action of  $\text{Ag}_5\mathbf{1}$  is inhibited by the binding of the sulfoxide product. Two lines of evidence, spectroscopy

(UV-Vis and  $^{51}\text{V}$  NMR) and a reaction-filtration-reaction sequence methodology confirm that the actual solid  $\text{Ag}_5\mathbf{1}$ , and not a small quantity of dissolved  $\text{Ag}_5\mathbf{1}$ , is responsible for the observed catalysis.

**4. Cowan, J. J.; Hill, C. L.; Reiner, R. S.; Weinstock, I. A. "Dodecatungstoaluminic Acid and its Mono-Lacunary and Mixed Addendum Derivatives" *Inorganic Syntheses* Coucouvanis, D., Ed. **2002**, 33, 18-26.**

The work in this peer reviewed publication was checked by peers in another laboratory. These articles have no abstract as such but give detailed reproducible preparations of the title compounds. These polyoxometalates underlie various families of catalysts central to our Army-funded catalytic and decontamination research.

**5. Kim, G.-S.; Zeng, H.; Neiwert, W. A.; Weinstock, I. A.; Cowan, J. J.; VanDerveer, D.; Hill, C. L. "Dimerization of  $\text{A-}\alpha\text{-}[\text{SiNb}_3\text{W}_9\text{O}_{40}]^{7-}$  by pH-Controlled Formation of Individual Nb- $\mu\text{-O}$ -Nb Bonds" *Inorg. Chem.* **2003**, 42, 5537-5544.**

This work addressed fundamental reactivities and stability of Keggin-type POMs in solution or in contact with liquids, work of clear importance to the ultimate goal of formulating optimally active and stable decontamination catalysts.

**Abstract.** Although undetected by traditional pH or conductometric titration curves, quantitative  $^{183}\text{W}$  NMR spectroscopy reveals that cleavage of the tri- $\mu\text{-oxo}$  dimer  $\text{A-}\alpha\text{-}[\text{Si}_2\text{Nb}_6\text{W}_{18}\text{O}_{77}]^{8-}$  (or, alternatively,  $\text{A-}\alpha\text{-}[(\text{SiNb}_3\text{W}_9\text{O}_{37})_2(\mu\text{-O})_3]^{8-}$ ) ( $\text{A-}\alpha\text{-}\mathbf{1}$ ) to 2 equiv of  $\text{A-}\alpha\text{-}[\text{SiNb}_3\text{W}_9\text{O}_{40}]^{7-}$  ( $\text{A-}\alpha\text{-}\mathbf{4}$ ) and reformation of  $\text{A-}\alpha\text{-}\mathbf{1}$  from 2 equiv of  $\text{A-}\alpha\text{-}\mathbf{4}$  in water both occur by reversible step-wise hydrolysis or acid condensation reactions of individual Nb- $\mu\text{-O}$ -Nb linkages. The *syn* isomer of di- $\mu\text{-oxo}$   $\text{A-}\alpha\text{-}[\text{Si}_2\text{Nb}_6\text{W}_{18}\text{O}_{78}]^{10-}$  (*syn-A-}\alpha\text{-}\mathbf{2}; a product of arrested hydrolysis in which only one of the three Nb- $\mu\text{-O}$ -Nb linkages in  $\text{A-}\alpha\text{-}\mathbf{1}$  has been cleaved) was characterized by X-ray crystallography (hydrated mixed  $\text{H}^+$  and  $\text{Cs}^+$  salt; orthorhombic, space group  $\text{Cmcm}$  with  $a = 40.847(2)$  Å,  $b = 13.2130(7)$  Å and  $c = 16.8179(9)$  Å at 173K with  $Z = 4$ ; final  $R_1 = 0.0685$ ). Pure samples of water-soluble  $\text{A-}\alpha\text{-}\text{Cs}_7\text{H}\mathbf{1}$ ,  $\text{A-}\alpha\text{-}\text{K}_{10}\mathbf{2}$  (*syn* and *anti*) and  $\text{Cs}_7\text{A-}\alpha\text{-}\mathbf{4}$  in  $\text{D}_2\text{O}$  solution were characterized by  $^{183}\text{W}$  NMR spectroscopy and the results used to identify the  $^{183}\text{W}$  NMR spectrum of mono- $\mu\text{-oxo}$  bridged  $\text{A-}\alpha\text{-}[\text{Si}_2\text{Nb}_6\text{W}_{18}\text{O}_{79}]^{12-}$  ( $\text{A-}\alpha\text{-}\mathbf{3}$ ). Quantitative  $^{183}\text{W}$  NMR spectroscopy was then used to document the step-wise hydrolysis of  $\text{A-}\alpha\text{-}\mathbf{1}$  to  $\text{A-}\alpha\text{-}\mathbf{4}$  and subsequent step-wise condensation of  $\text{A-}\alpha\text{-}\mathbf{4}$  to  $\text{A-}\alpha\text{-}\mathbf{1}$  as a function of  $[\text{D}^+]$  in  $\text{D}_2\text{O}$ . At specific pD values ranging between  $-0.08$  and  $3.0$ , spectra acquired after incremental additions of  $\text{LiOH}$  to  $\text{D}_2\text{O}$  solutions of  $\text{A-}\alpha\text{-}\mathbf{1}$  (11 pD values in all) were identical to those observed after additions of  $\text{DCl}$  to  $\text{A-}\alpha\text{-}\mathbf{4}$ . Effectively identical  $^{183}\text{W}$  NMR spectra were observed after aging each solution for several weeks at room temperature. The combined results were used to construct a speciation diagram showing the relative concentrations of all 5 POMs as a function of pD value.*

**6. Okun, N. M.; Anderson, T. M.; Hill, C. L. "Polyoxometalates on Cationic Silica. Highly Selective and Efficient  $\text{O}_2$ /Air-Based Oxidation of 2-Chloroethyl Ethyl Sulfide at Ambient Temperature, *J. Mol. Catal. A. Chem.* **2003**, 197, 283-290.**

**Abstract.** Binary cupric nitrate and triflate systems catalyze the homogeneous air

oxidation of the mustard (HD) simulant 2-chloroethyl ethyl sulfide (CEES) to the corresponding desired sulfoxide (CEESO) with effectively quantitative selectivity in acetonitrile under ambient conditions. This activity is enhanced when cationic silica nanoparticles coated with the anionic multi-iron polyoxometalates (POMs) are also present. The POM-coated nanoparticles are prepared by treatment of aqueous suspensions of Akzo Nobel BindzilCAT® cationic silica nanoparticles with aqueous solutions of the POMs,  $K_9[(Fe^{III}(OH_2)_2)_3(PW_9O_{34})_2]$  (**K<sub>9</sub>4**) or  $Na_{12}[(FeOH_2)_2Fe_2(P_2W_{15}O_{56})_2]$  (**Na<sub>12</sub>5**).

**7. Kim, Gyu-Shik,; Zeng, Huadong; Hill, C. L. “X-Ray Structure of Keggin-type Peroxo Polyoxometalate A- $\alpha$ -[Si(NbO<sub>2</sub>)<sub>3</sub>W<sub>9</sub>O<sub>37</sub>]<sup>7-</sup>” *Bull. Korean Chem. Soc.* **2003**, *24*, 1005-1008.**

This paper had no abstract. It was done in collaboration with my former Korean postdoctoral research associate, Dr. Gyu-Shik Kim, a talented synthetic inorganic chemist. It provided characterization of peroxo polyoxometalates of relevance to peroxide-based organic oxidations catalyzed by some families of polyoxometalates.

Sadly, Dr. Kim passed away in 2003.

**8. Okun, N. M.; Anderson, T. M.; Hardcastle, K. I.; Hill, C. L. “Cupric Decamolybdodivanadophosphate. A Coordination Polymer Heterogeneous Catalyst for Rapid, High Conversion, High Selectivity Sulfoxidation Using the Ambient Environment.” *Inorg. Chem.* **2003**, *42*, 6610-6612.**

**Abstract.** A new type of coordination network polymer involving the redox active polyanion,  $PV_2Mo_{10}O_{40}^{5-}$ , and bridging  $-Cu^{II}(OH_2)_4-$  units,  $\{[(Cu^{II}(OH_2)_4)_3(OH)]PV_2Mo_{10}O_{40}\}_n$  (**1**) has been characterized by X-ray crystallography and several other methods. It is the first efficient heterogeneous (insoluble) catalyst for selective and rapid sulfoxidation using only the ambient environment (air at room temperature). Catalytic activity is enhanced by soluble nitrate in nontoxic perfluoropolyether (PFPE) media.

**9. Okun, N. M.; Ritorto, M. D.; Anderson, T. M.; Apkarian, R. P.; Hill, C. L. “Polyoxometalates on Cationic Silica Nanoparticles. Physicochemical Properties of an Electrostatically Bound Multi-Iron Catalyst” *Chem. Mater.* **2004**, in press.**

This paper will be published very shortly.

**Abstract.** Reaction of a solution of the multi-iron polyoxometalate (POM)  $K_9[(Fe^{III}(OH_2)_2)_3(A-\alpha-PW_9O_{34})_2]$  (**K<sub>9</sub>1**) with a colloidal suspension of cationic silica nanoparticles ((Si/AlO<sub>2</sub>)Cl) results in the production of a new heterogeneous oxidation catalyst (**K<sub>8</sub>1**/(Si/AlO<sub>2</sub>)). Dynamic light scattering data, coupled with elemental analysis and streaming potentials, suggests that there are 58 molecules of POM electrostatically bound to the surface of each silica particle on average. Transmission electron microscopy (TEM) confirms the presence of the POM on the surface of the cationic silica and shows the diameter of the (Si/AlO<sub>2</sub>)Cl and of the **K<sub>8</sub>1**/(Si/AlO<sub>2</sub>) nanoparticles to be ~12 nm and ~17 nm, respectively. Significantly, cryo-high resolution scanning electron microscopy (cryo-HRSEM) shows that the POM retards the natural gelation process

colloidal silica is known to undergo upon aging. EPR and catalytic data collectively suggest that the exchange of the cationic silica for one of the nine  $K^+$  cations associated with each POM is responsible for subtle structural changes in the POM which result in its activation as a catalyst.

**10. Gelettii, Y. V.; Musaev, D. G.; Khavrutskii, L.; Hill, C. L. "Peroxynitrite Reactions with Dimethylsulfide and Dimethylselenide. An Experimental Study." *J. Phys. Chem.* **2004**, *108*, 289-294.**

**Abstract.** The kinetics of the peroxynitrite ( $ONOO^-$  and  $HOONO$ , PN for both) reaction with  $(Me)_2X$  ( $X = S$  and  $Se$ , dimethylsulfide (DMS) and dimethylselenide (DMSe)) was studied. The reaction is a first order with respect to both PN and  $(Me)_2X$  concentrations.  $(Me)_2X=O$  and  $NO_2^-$  were formed with 100% yield based on PN in all cases except in the DMS reaction with  $HOONO$ , where the yield was  $\sim 80\%$ . DMSe is much more reactive than DMS towards both  $ONOO^-$  and  $HOONO$ , while  $HOONO$  reacts much faster than  $ONOO^-$  with both  $(Me)_2X$ . The activation entropies (in  $cal. deg^{-1} mol^{-1}$ ) and enthalpies (given in parentheses, in  $kcal/mol$ ) for the reactions of DMS and DMSe with  $HOONO$  were determined to be:  $-23 \pm 3$  ( $5.9 \pm 0.5$ ) and  $-20.5 \pm 3$  ( $4.6 \pm 0.5$ ), respectively. The corresponding values for the reaction with  $ONOO^-$  were  $-29 \pm 3$  ( $9.7 \pm 0.6$ ) and  $-28 \pm 3$  ( $7.2 \pm 0.5$ ). A partial replacement of water with an organic co-solvent resulted in a decrease in the rate of reaction of  $ONOO^-$  with both DMS and DMSe, while it had no effect on the rates of reaction with  $HOONO$ . The experimental data were analyzed using the reaction mechanism based on our previous computational studies (D.G. Musaev, Y.V. Gelettii, and C.L. Hill, *J. Phys. Chem. A*, 2003, in press). This mechanism includes the formation of a pre-reaction complex followed by O-O bond cleavage in a rate-limiting step. Strong hydration of  $ONOO^-$  decreases the O-O bond cleavage barrier in a transition state, resulting in a lower reaction rate in mixed aqueous-organic solvents. In general, a fairly quantitative agreement between experimental and theoretical data was obtained.

### Papers published in non-peer-reviewed journals.

This was actually a book (an invited sizable review)

**11. Boring, E.; Gelettii, Y.; Hill, C. L. "Catalysts for Selective Aerobic Oxidation under Ambient Conditions. Thioether Sulfoxidation Catalyzed by Gold Complexes" In "Advances in Catalytic Activation of Dioxygen by Metal Complexes" Simandi, L. I., Ed.; Kluwer: Dordrecht, The Netherlands, 2003, pp 227-264.**

Diversity-based methods for catalyst discovery coupled with the knowledge of lead systems for the catalysis of  $O_2$ -based organic oxidation reactions has led to the development of new species that actually catalyze rapid and selective (non-radical-chain), reductant-free,  $O_2$  oxidation under ambient conditions (room temperature and 1.0 atmosphere of air). The first process of focus is selective sulfoxidation of thioethers (organic sulfides). The principal work reviewed here involves homogeneous catalysis, but highly reactive heterogeneous formulations have already been identified. The stoichiometry is that characteristic of dioxygenase enzymes:  $R_2S$  (thioether) +  $1/2 O_2 \rightarrow$

R<sub>2</sub>S(O) (sulfoxide). Oxidative dehydrogenation, a less desirable net process, is not seen. Studies have primarily been conducted with 2-chloroethyl ethyl sulfide (CEES), which is both notoriously unreactive and a useful simulant for mustard. Extensive kinetics and product studies have identified the active catalyst, at least in acetonitrile solution, to be Au(III)Cl<sub>2</sub>NO<sub>3</sub>(thioether) (**1**), and the rate limiting step to be reaction of **1** with another molecule of the thioether substrate. Reoxidation of the resulting Au(I) to Au(III) by O<sub>2</sub> is a fast subsequent step. The solvent kinetic isotope effect ( $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.0$ ), rate of sulfoxidation when Cl is replaced by Br, and multiparameter fitting of the kinetic data establish that the mechanism of the rate-limiting step itself involves a bimolecular attack of CEES on a Au(III)-bound halide and it does not involve H<sub>2</sub>O. Isotope labeling studies with H<sub>2</sub><sup>18</sup>O indicate that H<sub>2</sub>O and not O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> is the source of oxygen in the sulfoxide product. Interestingly, H<sub>2</sub>O is consumed and subsequently regenerated in the mechanism. Despite the impressive (unique) reactivity attributes above, these recently developed catalytic systems have some limitations that include an induction period and inhibition by sulfoxide product. However, these two difficulties are eliminated in other solvents or in nontoxic developmentally attractive perfluoropolyether (PFPE) media. Another potential problem, is catalyst inactivation by precipitation of the Au as colloidal Au(0), but this can be largely avoided by use of appropriate reaction conditions. Finally, these Au-catalyzed aerobic sulfoxidation reactions can be co-catalyzed by some d-block ions. Cu(II) is particularly effective in this context resulting in substantial increases in reaction rate at low Cu(II) concentrations. Co-catalysis by the d-block ions also results in elimination of the induction period in some cases.

### **Papers presented at meetings, but not published in conference proceedings.**

No papers, other than my various PowerPoint presentations at conferences, have been presented but not published. I have already made PowerPoint presentations available to several colleagues and will be happy to make them available to other appropriate colleagues.

### **Manuscripts submitted but not yet published.**

None. However other manuscripts will be submitted shortly including one that has been invited by the editors of *Science* on catalytically decontaminating multi-cluster nanoarrays.

### **Miscellaneous**

The following is a massive and definitive review (80 pages and 600 references) on the title subject, which underlies all my ARO funded efforts:

**Hill, C. L. "Polyoxometalates: Reactivity" Comprehensive Coordination Chemistry II: From Biology to Nanotechnology, Elsevier: Amsterdam; December 2004; pp. 679-759.**

I would be happy to forward a pdf file of this to anyone who requests it. The reviews in this compendium were not allowed to acknowledge support, but ARO should get credit in part for making this useful review possible.

**List of all participants employed on the project.**

Yurii Geletii (Ph.D. Research Associate)  
Jane Gonzales (Master's level researcher)  
Lyuba Khavrutskii (Ph.D. student)  
Wade Neiwert (Ph.D. student; will obtain his degree in 2 months)  
Nelya Okun (Ph.D. Research Associate)  
Michelle Ritorto -- just obtained her Ph.D.  
Chris Tarr (undergraduate)  
Lei Zhang -- just obtained her Master's degree)

**Report of inventions.**

None, but the patent filed at the end of the preceding 3-year grant (ending in 2001) is now in national and international (PCT) phases. Additional patents will be filed shortly.