Division of Mathematics and Science

CAPT William C. Ostendorff, USN
Director

Chemistry Department

Professor Boyd A. Waite
Chair

This past year was very successful in terms of external recognition of research accomplishments within the Chemistry Department. Associate Professor Judith Harrison continues to develop an international reputation in the emerging field of tribology, and has supported again a post-doctoral associate within the Department. In addition, she was awarded the Academy-wide Research Excellence Award for 2000. Associate Professor Mark L. Campbell completed his three years of funding through the prestigious Henry Dreyfus Teacher/Scholar Award (one of five nation-wide), providing funding for his own research and for the Department. Professor Graham Cheek and Associate Professor William Heuer were awarded the Kinnear Fellowship at the Naval Academy in support of their work in analytical and inorganic chemistry.

The Chemistry Department faculty and midshipmen chemistry majors are supported by a diverse array of state-of-the-art instrumentation and computational facilities. Ten different midshipmen participated in directed research courses. Several of the midshipmen attended national scientific meetings and presented results of their work during the year.

The Chemistry Department faculty have continued to pursue collaborative research efforts with Navy laboratories and other government and private institutions. This year faculty collaborated with projects at the Naval Research Laboratory, the National Aeronautics and Space Administration, and the Johns Hopkins University. Faculty members were supported by grants from the Air Force Office of Scientific Research, NASA, the Office of Naval Research, the Petroleum Research Fund, the National Science Foundation, and the Research Corporation.

Other research interests of the faculty include: organic synthesis of species for methanol fuel cells, radio-isotope studies in connection to specialized medical scanning technology, detonation simulations, electrochemical studies of fused salts, development of analytical methods based on electrophoretic techniques, synthesis and characterization of organic and organometallic species, and the effects of chemical agents in atmospheric chemistry, among others. The active involvement of both civilian and military faculty in research provides strength to the curriculum and helps prepare our chemistry graduates for the technical challenges awaiting them in the fleet.

Sponsored Research

Kinetics of Gas Phase Oxidation Reactions of Transition Metal Atoms with Oxygen Containing Oxidants

RESEARCHER: Associate Professor Mark L. Campbell
SPONSOR: The Camille and Henry Dreyfus Foundation

The objective of this research was to determine the rate constants for reactions of ground state and low-lying excited state transition metal atoms in the gas phase with oxygen-containing oxidants as a function of temperature and pressure. In particular, three projects are in varying stages of completion: (1) reactions of transition metals with N_2O, (2) reactions of ground state and low-lying excited states of niobium and tantalum with several oxidants, and (3) reactions of zirconium and hafnium with water. By obtaining Arrhenius parameters for these reactions, geometric factors and energy barrier effects were determined. The experimentally measured rate constants and barriers were analyzed to determine if a relationship exists between these values and the physical properties of the transition metals and reactants. Results for the reactions with N_2O were compared to the calculated values from a theoretical model developed by Fontijn and co-workers. The reactions of niobium and tantalum indicated the importance electronic effects have on the reaction rate. The reactions of zirconium and hafnium with water yielded a better understanding of chemical reactions that may occur during accidents in nuclear reactors. Completion of this research greatly enhanced our understanding of transition metal chemical reactions.

Niobium Electrodeposition from Low-Valent Niobium Species

RESEARCHER: Professor Graham T. Cheek
SPONSOR: Air Force Office of Scientific Research (AFOSR)

Continuing studies of niobium electrodeposition involved reduction of low-valent niobium species in the aluminum chloride: EMIC melt. It had been determined earlier that reduction of Nb(V) species did not result in co-deposition of significant amounts of niobium in aluminum films deposited from the acidic melt. Addition of aluminum powder to Nb(V) solutions enabled deposition of slightly more niobium; however, aluminum is capable of reducing niobium to the zero-valent state and proved unreliable in forming consistent amounts of low-valent niobium species. A similar approach using niobium powder proved successful in forming Nb(III) species, the reduction of which resulted in niobium contents of 10 - 12 % in the co-deposited niobium/aluminum films.

Evaluation of Lewis Acidity in Chloroaluminate Systems

RESEARCHER: Professor Graham T. Cheek
SPONSOR: 1999 Kinnear Fellowship

The Lewis acidities of several solvent systems in the Fries rearrangement (aromatic esters to ketones) has been assessed. The solvent systems studied were sulfolane / aluminum chloride, acetonitrile / aluminum chloride, and the room-temperature molten salt system composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride (EMIC). The substrate molecule was phenyl benzoate, chosen because its electrochemical properties (relative ease of reduction) allow it to be monitored in solution by voltammetric techniques. Although the reduction of phenyl benzoate could be observed in all of the solvent systems mentioned, the most promising results were obtained in the $AlCl_3$:EMIC molten salt system. This system allowed voltammetric observation of all components of the reaction, including the ester substrate, the ketone product, and the melt acidity. Melt compositions are given as mole ratios of $AlCl_3$ to EMIC; for example, a 0.8:1.0 melt composition is basic, a 1.0:1.0 melt is neutral, and a 1.2 : 1.0 melt is acidic.

The reduction of phenyl benzoate appears as a reduction peak at - 1.86 V. As $AlCl_3$ is added to the system to give only a slight molar excess of $AlCl_3$, a shift in the reduction process to -0.78 V occurs. This shift is due to complexation of the substrate by $AlCl_3$. Heating the solution to 85^{0}C resulted in a decrease of the reduction peak at -0.78 V (complexed ester peak), and the appearance of another peak at -1.20 V (rearrangement product). After 2-3 days, the voltammetric scan appeared to undergo no further change. The reaction mixture was found to contain both the rearrangement product (hydroxybenzophenone) and some phenyl benzoate starting material by GC/MS. These results demonstrate the feasibility of using voltammetric studies, coupled with the usual compound characterization techniques, to study Lewis-acid catalyzed reactions in the chosen system. Studies have begun in the neutral buffered melt, in which addition of sodium chloride produces relatively constant acidity levels. Good yields of 4-hydroxybenzophenone (with 3 isomer as minor product) have been obtained.

Investigations into Electrodeposition Processes in Room-Temperature Molten Salts

RESEARCHERS: Dr. John Mitchell (ASEE Post-Doctoral fellow)
Major Paul C. Trulove, USAF (AFOSR), Co-PI
Major Hugh C. De Long, USAF (Assistant Professor at USNA and Co-PI)
Dr. Patrick Hagans (NRL/Carderock)
Professor Graham T. Cheek (USNA)
Dr. Gery Stafford (NIST)
SPONSOR: Air Force Office of Scientific Research (AFOSR)

Aluminum alloys with enhanced resistance to chloride-induced pitting corrosion have been produced using solute elements such as Ti, Cr, Mn, Cu, Zr, Nb, Mo, Ta, and W. These “stainless” aluminum alloys are of interest both for use as bulk deposits and as coatings over existing structural aluminum alloys. Producing improved corrosion resistance in the aluminum alloys often requires solute concentrations (up to 50 atom percent, a/o) that are far in excess of the equilibrium solubility limit (ca. 1 a/o). Consequently, nonequilibrium methods such as sputter deposition, melt spinning, and ion implantation have been employed to prepare these metastable single-phase aluminum alloys. Unfortunately, these techniques are of limited commercial

utility because of their high inherent cost and the difficulty associated with their application to large structures. Electrochemical deposition is an alternative method for producing nonequilibrium aluminum alloys that generally does not suffer from the cost and applicability disadvantages of the above methods.

Room-temperature molten salts provide some unique properties which make them ideal for studying the deposition of aluminum and aluminum alloys. Aluminum can be reversibly electrodeposited from acidic melt compositions. The molten salts readily solubilize both ionic and molecular species, they possess a wide electrochemical window, they have high intrinsic conductivities, and they are thermally stable over a very wide temperature range.

We have demonstrated the deposition of Al-Mn, Al-Co, Al-Ni, Al-Nb, and Al-Cr from the molten salts. Characterization of these deposits shows them to be non-equilibrium alloys with solute concentrations up to 80 a/o. Aqueous corrosion studies indicate significant improvement in the chloride pitting potential over unalloyed aluminum.

Investigations of Ionic Liquid-Polymer Gel Electrolytes

RESEARCHERS: Dr. Thomas E. Sutto (ASEE Post-Doctoral Fellow)
Major Hugh C. De Long, USAF (Assistant Professor at USNA and Co-PI)
Major Paul C. Trulove, USAF (AFOSR)
Professor Graham T. Cheek (USNA), Co-PI
SPONSOR: Air Force Office of Scientific Research (AFOSR)

Room-temperature ionic liquids composed of perfluoroanions and 1,3- dialkylimidazolium and 1,2,3-trialkylimidazolium cations possess a number of unique properties that make them ideal electrolytes for compact power sources. In particular, they are nonflammable, nonvolatile, and chemically inert, and they display wide electrochemical windows, high inherent conductivities, and wide thermal operating ranges. Also, unlike room temperature ionic liquids based on chloroaluminate anions, these perfluoro anion electrolytes are not moisture sensitive.

For manufacturing and design optimization, solid-state electrolytes with high ionic conductivities are preferred to liquid electrolytes. In this research program we investigated the generation of solid-state electrolytes that incorporate perfluoro anion ionic liquids into a poly(vinylidene fluoride)-hexafluoropropylene copolymer. These free-standing rubbery electrolytes appear to retain much of the desirable properties of the perfluoro anion ionic liquids. We also investigated the physical and electrochemical properties of these gel electrolytes using thermal mechanical analysis, differential scanning calorimetry, imbedded microelectrode techniques, AC-impedance, and luminescent probe molecules. In addition, we evaluated graphite intercalation anodes and cathodes with the ionic liquid-polymer gel electrolytes in solid-state cells employing the dual intercalating molten electrolyte (DIME) concept.

Molecular Dynamics Simulations of Shock-Induced Chemistry in Acetylene

RESEARCHER: Professor Mark L. Elert
SPONSOR: Naval Research Laboratory (NRL), Code 6189

Workers in Russia and the United States first proposed in the 1960's that oligomers and perhaps polymers could result from shocked olefins.The noted astronomer Carl Sagan has also suggested that the orange color of Jupiter's atmosphere might be due to shock-induced production of polycyclic aromatic hydrocarbons from acetylene due to meteor impact. To investigate these hypotheses, two-dimensional molecular dynamics (MD) simulations of shock-induced chemistry in solid acetylene were carried out, using a reactive empirical bond order potential for hydrocarbons. These are the first MD simulations ever performed of shock-induced chemistry in hydrocarbons. Flyer plate impact speeds of less than twelve km/sec produced no chemical reactions, but above that threshold significant polymerization occurred in the vicinity of the impact site. The major products were oligomers of *trans*-polyacetylene.

Studies of the Mechanism of Anomalous Low Temperature Crystallization on Laboratory Analogs of Interstellar Grains

RESEARCHER: Associate Professor Robert F. Ferrante
SPONSOR: NASA/Goddard Space Flight Center

Comets and other interstellar objects are believed to have formed by the accretion of silicate dust grains upon which volatile molecules have condensed as ices; the particles may have undergone various types of processing both before and after accretion. Laboratory studies have been used to model such condensation processes, and their results employed in the interpretation of the thermal- and radiation-processing history of the natural systems. Such models have always assumed the formation of amorphous ice at low temperatures. However, our work over the last few years, utilizing silicate grain analogs as a substrate for simple ices of astrophysical interest (H_2O, CH_3OH, etc.), have indicated that the nature of the dust particle surface may have an effect on the crystallization behavior of the ice coating. The ices are observed to form in the crystalline phase, even during deposition at temperatures near 10 K; in contrast, similar studies performed in the absence of the silicate lead only to amorphous ices on low temperature deposition. If these laboratory studies represent good models for the natural process, then a re-evaluation of the amorphous ice assumption is warranted. The work performed here is designed to explore the mechanism of the observed anomalous low-temperature crystallization (LTC). The goal is to provide a better understanding of the significance of these observations towards interpretation of astrophysical data.

Our evidence suggests that the LTC effect is associated with the degree of oxidation of the silicate grains, and with the surface area and pore size distribution of the material. We are using thermal and chemical treatments to vary the surface properties. Silicate "smoke" substrates are baked at varied temperatures and durations, in vacuum, hydrogen and oxygen. Some samples are exposed to chemical oxidation by ozone. Samples are also being processed by electron, proton, and argon ion irradiation in and attempt to alter pore characteristics. Treated samples are analyzed for surface area and pore size distribution, and tested for efficacy in the LTC effect by low temperature FTIR spectroscopy of condensed adsorbate ices. Current evidence suggests that the LTC may be an extreme example of the lowering of phase transition temperatures for materials confined to small pores, or result from an anomaly in surface diffusion rates that places the sample below the theoretical "critical flux" for amorphous ice formation. Additional ices, and other model grain models with different (e.g., Fe and Mg silicates) or sharp (silica aerogels; molecular sieves) pore size distributions will also be utilized.

Explorations of Laboratory Models for the Catalytic Formation of Methane by Silicate Interstellar Dust Grains

RESEARCHER: Associate Professor Robert F. Ferrante
SPONSOR: NASA/Goddard Space Flight Center

In the molecular cloud from which the solar system condensed, CO was the most abundant carbon-bearing molecule. However, gas-phase reactions converting CO to methane are quite slow, and are thought to be insufficient to account for the large amount of organic material observed. Catalysis by dust grains, especially those bearing transition metal atoms, may offer an alternative route to methane and other organics. The Fischer-Tropsch synthesis of methane

$$3\,H_2 + CO \xrightarrow{\text{grain}} CH_4 + H_2O$$

catalyzed by Fe or Ni surfaces, has been considered theoretically, and appears to provide reasonable yields of organics under some appropriate conditions.

Preliminary studies indicate that the conversion of H_2/CO mixtures into simple hydrocarbons is quite facile on our silicate smoke grain analogs, which have been doped to 10-50% (by mass) with iron. Methane, ethane, and ethene all formed in amounts totaling a few percent conversion in a period of only 3 hours, at relatively low temperatures (300°C). Isotopic substitution proves that the organics are mostly formed from the added gas, and not from impurities in the silicates. Some characteristics of the catalysts have been explored. While this work continues, the possible formation of NH_3 by catalysis of a H_2/N_2 mix has also been pursued. This has very important implications from the point of view of the origin of biochemical precursors, a process also of great interest. It has not yet been observed. Additionally, the analysis of some used catalysts suggests the formation of new <u>non</u>-volatile compounds formed in the matrix. Work on these interesting findings is continuing.

Molecular Dynamics Investigations of the Tribology of Diamond Surfaces

RESEARCHERS: Dr. Paul T. Mikulski, Dr. Alan B. Tutien,
Dr. Steven J. Stuart (Post-Doctoral Fellows)
and Associate Professor Judith A. Harrison
SPONSOR: Office of Naval Research (ONR)

Friction and the related phenomenon of wear are two of the more costly problems facing industry today. Understanding and ultimately controlling friction and wear have long been recognized as being central to many areas of technology. For instance, combustion engines break down and cutting tools become dull usually because of friction induced wear. Despite the obvious importance of friction and the induced wear, much of the atomic-scale dynamics responsible for these phenomena remain elusive. If the atomic-scale origins of friction and wear were understood, this might ultimately lead to the design of materials with specific friction and wear properties.

Molecular dynamics (MD) simulations have been used to investigate the atomic-scale origins of friction and wear in hydrocarbon systems. Previously, the atomic-scale friction that resulted when two diamond (111) surfaces are placed in sliding contact was examined. Using MD simulations has proven useful in examining atomic-scale friction and relating the results to experimental data. For example, tribochemical reactions and their atomic-scale mechanisms were cataloged. These reactions and their products were consistent with inferences drawn from macroscopic friction experiments on diamond.

More recently, we have re-fit the potential energy function needed to carry out these simulations. We have adapted this potential so that, in addition to solid and gas phase hydrocarbons, liquids can also be simulated. This will allow us to examine the break down of liquid lubricants and self-assembled monolayer systems. This new potential energy function has been documented and has appeared in *The Journal of Chemical Physics*.

Atomic force microscope measurements show that the friction of alkylsilane chains bound to silicon surfaces decreases as the length of the alkyl portion of the chain increases. This phenomenon was recently examined using C_8, C_{13}, and C_{22} alkane monolayers bound to diamond surfaces. The simulations showed that friction is intimately linked to the formation of gauche defects, or disorder, within the monolayers. In addition, the simulations showed that the contact area of the tip used in the simulations affects the observed friction. For large contact areas, friction is higher the shorter the alkane chain in agreement with experimental results. These results have been published in *Langmuir* and *The Journal of Physical Chemistry B*.

Investigation of the Physical Properties of Carbon Nanotubes

RESEARCHERS: Dr. Carter T. White (NRL),
Dr. Daniel H. Robertson (IUPUI), and Associate Professor Judith A. Harrison (USNA)
SPONSORS: Office of Naval Research (ONR) and Naval Research Laboratory (NRL)

It has been recently proposed that carbon nanotubes might constitute well-defined tips for scanning probe microscopies (SPM). Multiwalled nanotubes have been shown to perform well as SPM tips when used in tapping mode, due to their desirable combination of stiffness and flexibility. We have been using molecular dynamics simulations to examine the physical properties of hemispherically-capped carbon nanotubes. These simulations provided insight into the utility of these tubes as scanning force microscope tips. Simulations demonstrate that the capped nanotubes, although undergoing complex deformations, have the remarkable ability to recover reversibly when pushed into a hard substrate, such as diamond.

The lateral and transverse motions of [n,n] single-walled nanotubes have been investigated. These results show that single-walled nanotubes vibrate in both the transverse and the lateral directions. Examination of [10,10] nanotubes of various lengths revealed that the frequency of the vibrations was linear with the square of the nanotube length. The frequency of lateral vibrations of nanotubes with different radii was shown to be linear with radius. These results were presented at the 1998 Fall Meeting of the *Materials Research Society* in Boston.

More recently, we have examined the usefulness of double-wall nanotubes as SPM tips compared to single-wall nanotubes.

Molecular Dynamics Investigations of the Tribology of Diamond Surfaces and Films

RESEARCHERS: Dr. Alan B. Tutien (Post-Doctoral Fellow)
and Associate Professor Judith A. Harrison
SPONSOR: Air Force Office of Scientific Research (AFOSR)

Microelectromechanical systems (MEMS) represent an emerging technology. These systems have generated a great deal of interest because of their potential use as sensors and actuators. The devices are on the order of microns in size and it is possible to fabricate thousands of devices at one time for a cost of a few cents per device. Consequently, any system with MEMS-based technologies will be lighter, smaller, and less expensive than a system utilizing non-MEMS-based technologies. Workers at Sandia National Labs predict that these devices will play a significant role in future technologies with a broad range of commercial and military applications. Possible future applications of MEMS-based devices include accelerometers for use in military systems such as stability control, attitude heading reference, and short-time flight navigation. The use of silicon-based MEMS devices in nanosatellites to form an interconnected aerospace surveillance system has been proposed by The Aerospace Corporation. Workers at Hughes Aircraft Company and collaborators have proposed a MEMS-based system to replace current rocket, missile, and space vehicle navigational systems.

Silicon-based MEMS devices suffer from two major problems. First, because these devices are so small, the fabrication process can leave critical components adhered to one another. The phenomenon, call stiction, renders the MEMS device inoperable. Second, the wear rate of silicon is such that MEMS composed of silicon cannot be used in applications were parts are in relative motion for extended periods of time.

To overcome these problems researchers at the University of California have suggested coating the silicon-based MEMS with carbon coatings. Researchers at the Raytheon Corporation have suggested constructing MEMS devices from diamond because it posesses superior friction and wear properties compared to silicon.

We have extensive experience investigating the friction and wear of diamond, which should lend insight into the construction of diamond-based MEMS. In addition, we are currently debugging a molecular dynamics code that will be capable of examining the friction and wear properties of silicon-based MEMS devices coated with carbon films.

Funding was recently increased for this project so that a full-time postdoctoral associate could be hired to conduct the research. This postdoctoral associate is scheduled to be appointed at the end of July 2000.

DoD Reactive Atomic-Scale Potential Molecular Dynamics (RASP-MD) for Computation and Prediction of Materials Properties

RESEARCHERS: Dr. John W. Mintmire and Dr. Carter T. White (NRL),
Dr. Brad L. Holian (Los Alamos National Laboratories),
Dr. Daniel H. Robertson (IUPUI), Professor Mark L. Elert (USNA),
Dr. Steven J. Stuart, and Associate Professor Judith A. Harrison
SPONSOR: Common HPC Software Support Initiatives

The overall goal of this project is to develop a scalable and portable suite of programs for MD simulations of materials of critical DoD interest using chemically realistic potentials. The planned software suite was developed as a main set of MD programs that interface with the empirical potential routines via a custom application programming interface (API). A set of auxiliary routines will be constructed that implement the NRL-developed REBO and ES+EAM potentials and the USNA developed AIREBO potential using API.

Investigations into the Effects of Tripodal Ligands on Transition Metal Environments

RESEARCHERS: Assistant Professor J.R. Hartman and Midshipman 1/C R. Jeremy Wheat, USN
SPONSORS: Naval Academy Research Council (NARC) and Office of Naval Research (ONR)

Crown and cryptand ligands are useful for binding metal ions because the constrained nature of crown and cryptand ligands allows them to form metal-complexes in which the metal has unusual steric and electronic properties. Unfortunately, crowns and cryptands are difficult to prepare and purify, and hence expensive.

Podands ("many-armed" ligands) can act as either constrained ligands that form cryptand-like metal complexes or as unconstrained ligands that form cross-linked polymeric metal complexes. In the proposed research, the chemistry of a novel series of TREN-based tripodal ligands have been synthesized and are being studied to characterize their method of binding and to determine where they fit in the scale of preorganization that ranges from linear ligands to cryptands.

We have begun to study the binding properties of TREN-based podand ligands by comparing the properties of the metal complexes with a series of podands to those with the analogous linear ligands. We have chosen to focus initially on a series of aminopyridyl ligands. We have prepared the ligands and are currently studying the steric, electronic, and gas-phase-reactivity properties of copper(II) and nickel(II) complexes to determine if the tripod cavity is constraining the conformation of the metal ions.

Synthesis and Characterization of Amphiphilic Ruthenium-based MLCT Complexes

RESEARCHER: Associate Professor William B. Heuer
SPONSOR: 1999 Kinnear Fellowship

Metal complexes exhibiting strong metal-to-ligand charge-transfer (MLCT) absorptions have been studied as potential non-linear optical (NLO) materials, as components of solar energy conversion systems, and as environmentally-sensitive probes for study of membrane structure. The goal of this project is to prepare new types of LMCT complexes bearing non-polar hydrocarbon "tails". The most important class of MLCT complexes are based on Ruthenium(II) complexed with various substituted pyridine or polypyridine ligands. Our initial efforts have focused on the preparation of a series of $[Ru(NH_3)_5L]^{n+}$ complexes, where L represents a series of alkylated 4,4'-bipyridine derivatives. A series of mono-alkylated 4,4'-bipyridinium salts bearing C_8, C_{12} and C_{16} "tails" have been synthesized and characterized using ^1H NMR spectroscopy. Efforts are currently underway to prepare coordination complexes of these ligands by ligand substitution onto $[Ru(NH_3)_5(H_2O)]^{2+}$. Since the proposed complexes contain both a charged, polar "head" group (the Ru(II) center) with a nonpolar hydrocarbon tail, it is expected that they will exhibit interesting amphiphilic properties. For example, depending upon the length of the hydrocarbon "tail" they may show interesting aggregation properties and perhaps micelle formation in aqueous solution. We also anticipate that these amphiphilic $[Ru(NH_3)_5L]^{n+}$ complexes will form supramolecular "host-guest" complexes with helical amylose as host. Ultimately, we plan to study the effect of supramolecular inclusion upon the photophysical properties of the MLCT chromophore. Besides providing a new approach for study of fundamental aspects of MLCT photochemistry, such complexes may exhibit improved NLO properties.

Synthesis of [C-11]L-159,884: A Radiolabeled, Nonpeptide Angiotensin II Antagonist for Angiotensin II, AT_1 receptor Imaging

RESEARCHERS: Assistant Professor Christopher M. Kinter and Midshipman 2/C John T. Hendrix, USN
SPONSORS: Naval Academy Research Council (NARC) and Division of Nuclear Medicine and Radiation Health Sciences, The Johns Hopkins University Medical Institutions

Angiotensin II (Ang II) plays a key role in the regulation of cardiovascular function. The octapeptide angiotensin II is produced from angiotensin I by reaction involving the enzyme angiotensin converting enzyme (ACE). Ang II, through interaction with membrane receptors in various tissues, controls the constriction of vascular smooth muscle, modulation of glomerular filtration rates, and sodium retention. Through these effects Ang II plays a critical role in the regulation of blood pressure. In fact, antihypertensin drugs such as captopril, enalopril, and lisinopril function by preventing the formation of Ang II by inhibiting ACE. Despite the clinical usefulness of the ACE inhibitors they do suffer from problems such as poor oral availability and their short duration of action. Additionally, these drugs suffer from common side effects such as a dry cough and angioneurotic edema. Pharmaceutical companies have begun to pursue a more direct method of regulating blood pressure by developing Ang

II antagonist. Studies have shown that there are at least two distinct Ang II receptor subtypes, AT_1 and AT_2. The first, AT_1, is thought to be responsible for all the known physiological function of Ang II. The functional role of the AT_2 receptors has yet to be clearly demonstrated. Research effort has been directed towards the synthesis of [C-11]L-159,884 a radiolabeled, nonpeptide angiotensin II antagonist that is useful in imaging the angiotensin II, AT_1, receptor using positron emission tomography (PET). L-162,914 serves as the precursor to [C-11]L-159,884 and was prepared by a convergent route in 11 steps with an overall yield of 34.4%. [C-11]L-159,884 was produced by methylation of the phenolic group of the precursor by cyclotron produced [C-11] methyl iodide. Studies of the angiotensin II AT_1 are currently underway using [C-11]L-159,884.

Hydrogen peroxide, methylhydroperoxide, and formaldehyde: Their Relationship to Tropospheric Oxidant Chemistry and Transport over the Equatorial South Pacific

RESEARCHERS: Assistant Professor Daniel W. O'Sullivan (Co-PI)
and Associate Professor Brian G. Heikes (PI; University of Rhode Island)
SPONSOR: National Aeronautics and Space Administration (NASA)

We completed measurements of gas-phase hydrogen peroxide, methylhydroperoxide, and formaldehyde on board both the NASA DC-8 and P3-B aircraft as part of the NASA/GTE PEM-Tropics B mission. Atmospheric concentrations of the above species were observed in the Pacific troposphere at altitudes from 0.5 to 13 km and from 130°E to 115°W and from 40°N to 38°S. The target species are directly coupled to tropospheric oxidants as sources of odd-hydrogen and odd-oxygen radicals, as reservoirs of these species, and as conductors in their loss. The net production of ozone or odd-oxygen in the troposphere is largely predicted on the basis of photochemical point model simulations based upon measured concentrations of hydrocarbons, nitric oxide, water, carbon monoxide, ozone, and sunlight; and both measured and model diagnosed concentrations of nitrogen dioxide, perhydroxyl, methylperoxyl, and hydroxyl radicals. The peroxide compounds and formaldehyde measured during the field program provided mechanistic insight and chemical constraints to the purely chemical model simulations and provided an additional measure of confidence in the model results. Multi-dimensional space-time models suggest that atmospheric motions, the vertical transport and mechanical redistribution of the hydroperoxides, may have a profound effect on odd-O and odd-H chemistry in the upper troposphere. Results from this project have demonstrated that photolysis of the peroxides in the upper troposphere are significant sources of odd-H, particularly at high latitudes. These observations and examinations of their impact on our understanding of tropospheric gas phase chemistry have resulted in three papers in the Journal of Geophysical Research Atmospheres.

Impact of Superoxide Redox Cycling on the Chemical and Optical Properties of Chromophoric Dissolved Organic Matter

RESEARCHER: Assistant Professor Daniel W. O'Sullivan
SPONSORS: Naval Academy Research Council (NARC) and Office of Naval Research (ONR)

Interest in reactive oxygen species in the environment has been stimulated by atmospheric chemical problems such as smog formation, stratospheric ozone depletion, and acid rain. Because of the need to understand these chemical problems, atmospheric gas-phase reactions of oxidants and the related primary photochemical processes have been intensely studied. As a result atmospheric photochemistry has become a highly developed subdiscipline. Aquatic photochemistry is less well developed, largely because of the complex chemical composition of most natural waters. Recent studies indicate that photo reactions producing reactive oxygen species ($O_2G^1O_2$, singlet dioxygen; OH, hydroxyl radical, and RO_2, organic peroxy radicals) can significantly influence the cycling of carbon, oxygen, sulfur, and biologically important trace metals. As in the atmosphere, reactive oxygen species can act to cleanse the aquatic environment of bioactive pollutants or in some cases, convert wastes into more toxic substances. Superoxide has the highest steady state concentration of reactive oxygen species in natural waters, and is the first intermediate in most oxygen mediated oxidations. Recently photo induced redox reaction involving superoxide have been shown to significantly alter chromophoric dissolved organic matters optical properties in surface waters. In spite of the central role of superoxide in natural water photochemistry, the kinetics and mechanisms of its formation and destruction are poorly understood. We have demonstrated that superoxide can be qualitatively determined in aqueous solutions using luminol-based chemiluminescence. This method has the sensitivity, selectivity, and samplig resolution required to perform detailed kinetic studies of superoxide and chromophoric dissolved organic materials at levels near those found in natural waters.

Segmental Relaxation of Polystyrene-co-vinylphenol

RESEARCHER: Assistant Professor Maria J. Schroeder
SPONSOR: Office of Naval Research (ONR)

The segmental dynamics of polymers underlie to some extent motions at all longer times; thus, investigation of the structural relaxation associated with the glass transition has obvious appeal. Copolymers allow structure/property relationships to be probed via systematic changes in chemical composition. In this work, dielectric and mechanical measurements on polystyrene copolymerized with varying levels of vinylphenol are obtained. The presence of the hydroxyl groups on the vinylphenol substantially increases both the glass transition temperature and the segmental relaxation times of the copolymer. However, the shape of the relaxation function, as well as the temperature dependence of the relaxation times, is invariant to copolymer composition. This indicates that there is no variation among these copolymers in the degree of intermolecular cooperativity associated with their segmental relaxation and enhanced interactions arising from polar modification of the polystyrene are short-lived on the time scale of the segmental dynamics. Although fragility was found to be independent of copolymer composition, the heat capacity change at T_g increases with increasing vinylphenol content. The absence of a correlation between these two quantities is contrary to an energy landscape interpretation of fragility.

Assembly-Phobic Behavior of *p*-MethylStyrene Rodcoil Molecules

RESEARCHER: Assistant Professor Craig M. Whitaker
SPONSORS: Petroleum Research Foundation (PRF-ACS) and
Naval Academy Research Council (NARC)

The goal of this research project was the continued study of how changes in the length and cross-sectino of the coil segment affect the self-assembly of rodcoils. Recently, several rodcoil derivatives have been synthesized with a variety of functional group and only a handful of these compounds self-assembled into nanostructured materials with a polar-stacked architecture. We are still not sure of the dominant force(s) that lead to self-assembly of rodcoils. It is a great scientific challenge to learn how to encode in the structure of simple molecules the factors that will lead to their programmed assembly into identical, supramolecular structures. Learning to control the macroscopic self-assembly of materials into functional devices is a fascinating prospect for technology.

The creation of a family of rodcoil materials will probe the role the coil segment of the rodcoil molecules play in the ability to spontaneously form regular shaped units when cast from a solution. Rodcoil contains one block of a bulky *p*-methylstyrene oligomer, a second block of a flexible isoprene oligomer, and the third block of a mesogenic (liquid crystalline) unit containing multiple biphenyl groups. By systematically changing the length of the *p*-methylstyrene and isoprene segments we will probe how the self-assembly of the system is changed. The following rodcoil derivatives have been synthesized and are currently being studied for their mesogenic behavior: (9,9), (9,15), and (15,15), *p*-methylstyrene and isoprene, respectively.

Synthesis of Molecules for Liquid Crystalline Displays

RESEARCHER: Assistant Professor Craig M. Whitaker
SPONSORS: Dr. R. Shashidhar, Naval Research Laboratory (NRL)
and Office of Naval Research (ONR)

We are continuing to study novel molecules to demonstrate a new alignment process that does not require mechanical rubbing and is suitable for flat panel displays. The new process, which involves a combination of chemisorption and photo polymerization, creates an anisotropic surface that guides the orientation of the liquid crystal molecules. The process is a room temperature process, easy to scale-up for manufacturing, applicable to different types of surfaces and capable of fine-control of the pre-tilt needed for active-matrix display devices. The research is aimed at demonstrating the feasibility of the process for attaining stable and varying pre-tilt angles with out compromising the quality of the alignment and show the applicability of the process for active matrix and passive matrix displays.

The following molecules have been synthesized to achieve pre-tilt angle in the range of 1 - 5° with an accuracy of +/- 0.2^o.

Previously, a series of ester and ether derivatives were synthesized with different alkyl chain lengths. During these studies we became interested in a new family of materials, coumarin derivatives. The coumarins have the unique ability to form cross-linked structures upon photolysis which is important for the alignment of the liquid crystals. Several different coumarin derivatives were prepared with alkyl groups ranging from 4 to 10 methylene units.

Mesogenic Properties of Laterally Substituted Terphenyls

RESEARCHER: Midshipman 1/C Garrett Burkholder, USN (SC495 and SC496 Projects)
ADVISER: Assistant Professor Craig M. Whitaker
SPONSORS: Naval Research Laboratory (NRL) and Office of Naval Research (ONR)

In recent years, the synthesis of new mesogenic materials has increased dramatically in an attempt to satisfy the growing range of applications. Mr. Burkholder attempted to synthesize several homologues of dialkylterphenyls then evaluate their mesogenic properties. Palladium-catalyzed cross-coupling reactions and Friedel-Crafts acylations were used in the synthesis of the novel compounds. These materials were prepared in order to understand the steric effects of lateral alkyl-substituents on mesomorphic properties. The mesomorphic behavior and hence the suitability for applications of compounds has been shown to depend strongly on the relative positions and types of the lateral substitutents incorporated into the materials. However, the chemistry involving the addition of the lateral side-chains has proven to be extremely difficult. We were only able to synthesize the parent compound in good yield.

Synthesis of Liquid Crystalline Materials with Hexadecyl Side Chains

RESEARCHER: Midshipman 2/C Sandra Smith, USN (SC496 Project)
ADVISER: Assistant Professor Craig M. Whitaker
SPONSORS: Naval Research Laboratory (NRL) and Office of Naval Research (ONR)

The synthesis and characterization of an organic liquid crystalline material with multiple hexadecyl side chains were pursued. The compound was based on an (alkoxybenzoyloxy)hydroquinone backbone laterally substituted with the hexadecyl side-chains. In recent years, the synthesis of new mesogenic materials has increased dramatically in an attempt to satisfy the growing range of industrial applications. Much interest surrounds the family of hydroquinone compounds due to their ability to form interesting mesophases. These materials may also find widespread applications as host materials for display devices, in nonlinear optics, information storage, and twisted nematic electro-optic systems.

Ms. Smith began the project in the second half of the semester and nearly completed the entire synthesis. She was only unable to get the final step in the reaction to proceed in good yield.

^{1}H NMR Studies of Coordination Environments for Nickel(II) Complexes

RESEARCHER: Midshipman 2/C Sandra Smith, USN (SC496 Project)
ADVISER: Assistant Professor Craig M. Whitaker
SPONSORS: Petroleum Research Foundation (PRF-ACS) and Office of Naval Research (ONR)

The solution state study of coordination environments for Nickel(II) complexes containing three aminopyridine ligands is reported. The molecular geometries in the solid and gas phases of various aminopyridine-nickel(II) complexes have recently been reported. The ^{1}H NMR evalution of the nickel complexes will give valuable evidence the solvation affects on the coordination chemistry and the binding preferences of the ligands toward square planar or octahedral geometries. The three complexes that were studied are *Ni(AM-pyr)$_2$*, *Ni(DIEN-pyr)*, and *Ni(TRIEN-pyr)*. Nickel occurs in the active site of many classes of metalloenzymes. By itself, nickel(II) does not have a strong preference for a specific geometry in solution chemistry. Therefore, biological ligands determine nickel's structure and affect its catalytic activity. The aminopyridine ligands are highly-constrained and can be thought of as a rigid cage around the nickel center. Because of the ligand's rigidity, the complexes can be stable, even in unusual oxidation states. Ms. Smith was initially trained on the NMR. The ^{1}H NMR studies in acetonitrile-d$_3$ solvent revealed that all three nickel complexes prefer to adopt an octahedral geometry, despite the variation in the number of coordination sites, which ranged from three to seven donor atoms per ligand.

Independent Research

Synthesis of Phosphorus Analogs of Amino Acids

RESEARCHER: Associate Professor Debra K. Dillner

In this project, the synthesis of various alpha-aminophosphonate esters, analogs of amino acids, are being synthesized. These types of compounds are of great interest as potential therapeutic agents and the specific targets may be potential agonists of botulism toxin. Alpha-aminophosphonate esters are considered to be transition state mimics of natural polypeptide substrates of a variety of enzymes. The inherent geometry of the phosphonate group makes these compounds competitive inhibitors for the active site.

The targets of this project are a selection of alpha-aminophosphonates with two key features. The first feature is the ability to vary alkyl and aryl groups at the alpha position, including analogs of several amino acids, such as arginine. The other unique feature is the inclusion of specific groups on the nitrogen. The desired groups are either an acetate or a carboxybenzoyl (CBz) group. The acetate group would allow these compounds to be placed at the N-terminus of a polypeptide chain with the nitrogen remaining protected in the therapeutic agents. The inclusion of a CBz would allow these compounds to be incorporated in the interior of a polypeptide chain. Solid state peptide synthesis can incorporate appropriate phosphonates and the CBz group can then be removed from the nitrogen and additional amino acids added to the N-terminus.

The synthetic pathways being investigated involve condensation of aldehydes with various amine and phosphorus reagents. The goal of the pathways being investigated is to produce the desired products with a minimum of protection/deprotection steps. One pathway that has been successful requires seven synthetic steps. Shorter syntheses of the same compounds are greatly desirable. For example, benzaldehyde can be condensed with benzyl carbamate to form the CBz protected imine. This agent can then be reacted with the anion of diethyl phosphite to yield the CBz protected alpha-aminophosphonate. Manipulation of the groups on the phosphonate is then required to produce a substrate suitable for peptide synthesis. In another pathway, aldehydes are condensed with phosphites directly to produce the alpha-hydroxy phosphonates. Methods for conversion of the alcohol to the acetamide or CBz protected amine are possible. Successful completion of either of these routes would be three steps shorter than previous syntheses of similar compounds.

Octa(hydroxymethyl)tetraazaporphyrin: A New Water Soluble Tetraazaporphyrin Macrocycle

RESEARCHER: Associate Professor Jeffrey P. Fitzgerald

Tetraazaporphyrins bearing peripheral functional groups capable of acting as ligands have recently been reported. The classic example of such a complex is Hoffman's nickel(II) *star*- porphyrazine in which eight thiolate groups on the macrocycle periphery bind four tin(IV) ions (in addition to the nickel(II) ion bound in the center of the tetraazaporphyrin ring). Synthetic routes to macrocycles possessing thiols, amines, ethers and alcohols have also been described.

Our interest in these macrocycles stems not from their ability to coordinate additional metal ions but from how these peripheral functional groups might cause the macrocycles to aggregate. Such molecular assemblies may have novel optical and/or magnetic properties. In this work, we synthesized a novel tetraazaporphyrin macrocycle, octa(hydroxymethyl)tetraazaporphyrin. Our strategy has been to convert 1,4-dihydroxy-2-butyne to a maleonitrile bearing two protected hydroxymethyl groups. Cyclization of this pecursor followed by deprotection gives octa(hydroxymethyl)tetraazaporphyrin, albeit in low yield. We are presently working on improving the yield in the cyclization reaction.

Vanadium Dicyanoperfluorostilbene: A Charge-Transfer Magnet with Tc ~ 210 K

RESEARCHER: Associate Professor Jeffrey P. Fitzgerald

In 1991, Miller and coworkers reported the reaction of V(benzene)$_2$ and tetracyanoethylene (TCNE) to yield a solid which is magnetic at room temperature. In the intervening years, other metals have been found to react similarly, however no other organic receptor has been reported to replace TCNE. We have synthesized the novel one-electron acceptor, dicyanoperfluorostilbene (DCPFS), and discovered that it reacts with V(CO)6 or V(benzene)2 in THF to give a solid, characterized as V(DCPFS)2, that appears to order ferrimagnetically with Tc ~ 210 K. This second example of magnetic ordering in a molecule-based magnet may provide needed insight into the mechanism of magnetic ordering in these poorly understood systems.

Electrochemistry of D-*p*-D and D-π-A Chromophores Incorporating Dithienothiophene (DTT) as π-Center

RESEARCHER: Associate Professor William B. Heuer

This project involves studies of potential Electroluminescent (EL) materials being conducted in collaboration with Dr. Oh-Kil Kim at the Naval Research Laboratory. Up to now, organic light-emitting diodes (OLED's) have typically been constructed by sandwiching multiple polymer layers with different structures/functions (hole transport, electron transport, emitter) between a transparent indium tin oxide (ITO) anode and a metallic (Ca, Al or Mg-Ag alloy) cathode. High device efficiency requires balanced injection of electrons and holes (through their respective transport layers) into the emitting layer, where they recombine, forming singlet exitons whose radiative decay produces visible light. An alternative approach involves the use of a single layer comprised of a "hybrid" material which incorporates all three functions into the same molecule. Specifically, we have been studying a series of D-π-A chromophores containing weak donor (hole transporting) and acceptor (electron tranporting) substituents appended to a fused terthiophene (dithienothiophene, DTT) "π-center" as the emitter. Analogous D-π-D systems have also been studied for comparison. Cyclic voltammetry of these molecules (in DMF) indicates a unique role of DTT in the redox processes, such that conjugation through the DTT center facilitates *both* the oxidation of the donor groups and reduction of the acceptor groups. HOMO/LUMO gap energies obtained from electrochemical potentials are in good agreement with those obtained by spectroscopic means, and suggest that these materials may be well-suited for OLED applications. A communication describing the results of the electrochemical studies has been submitted for publication.

Depletion Kinetics of Chromium Atoms by Sulfur Dioxide

RESEARCHER: Associate Professor Roy E. McClean

This work is part of a project (initially funded by the Research Corporation) to determine the reactivity of transition metal atoms toward sulfur dioxide in the gas phase. The focus of this part of the project is on the interaction of chromium and sulfur dioxide. This work was started during the 1998 - 1999 academic year and is now complete. The manuscript has been submitted to *The Journal of Physical Chemistry* for publication.

Ground state and excited states of atomic chromium interact with sulfur dioxide at exceptional rates. Ground state Cr forms a 1:1 adduct with SO_2 with an estimated bond energy of 53 kcal mol^{-1}. The bond energy was estimated by combining the kinetic results with unimolecular rate theory and density functional theory. A charge-transfer intermediate is indicated for $CrSO_2$ formation. In the presence of SO_2, the excited states deplete at or greater than the gas collision rate. For the state depleting at greater than the collision rate, long range interactions based on molecular polarizabilities and ionization potentials of the interacting particles are indicated.

A comparison of this system with the other group 6 (Mo and W) + SO_2 systems indicates that charge-transfer, long range attractions, and transition metal orbital occupancy play major roles in the depletion kinetics of transition metals by SO_2.

Crystal Structure Determinations of Pentadentate and Hexadentate Nickel and Copper Compounds

RESEARCHERS: Associate Professor Wayne Pearson and Assistant Professor J.R. Hartman

This study is a continuation of the previous work which Midshipman 1/C Jeremy Wheat performed in his second class year. These comounds have proven to be difficult to refine structurally yet we have made considerable progess in obtaining final structures for future publication. Only one of the structures is well behaved, Ni-TRIEN at R(F) = 2.6 % while the other four structures suffer from either disorder in the counter anion or ambiguities in the space group determination. At this stage of the project we have three final structures for publication, one structure which still holds promise for a final structure solution, and one structure which appears to need another data set collected. In spite of the difficulties, Mr. Wheat presented a paper on this work during the Eastern College Science Conference in April 2000.

Photochemical Study of Cyano-Isocyanide-Phosphine Complexes of Iron and Ruthenium

RESEARCHER: Professor J. E. Shade

The chemistry of carbonyl-cyano-phosphine complexes of iron has been studied extensively for the last ten years. In general, reflux or photolytic reaction conditions have been employed to initiate the loss of a carbonyl (CO) group from cyclopentadienyl-iron-carbonyl starting materials with a subsequent inclusion of a phosphine or phosphite ligand on the metal center. The resulting complexes obtained in these studies, however, all contain at least one carbonyl group. The purpose of this research was to prepare a series of anionic, neutral and cationic cyano, mono- and bisisocyanide complexes for reaction with phosphine or phosphite groups under photolytic conditions. Photolysis of the monoisocyanide complex, (η^5-C_5H_5)Fe(CO)(CN)($CNCH_3$), in the presence of a slight excess of triphenylphosphine at room temperature gave the desired product [(η^5-C_5H_5)Fe(CN)($CNCH_3$(PPh_3)] with loss of one equivalent of carbon monoxide. Two additional products have been obtained, however: (η^5-C_5H_5)Fe($CNCH_3$)$_2$(CN) and (η^5-C_5H_5)Fe(CN)(PPh_3)$_2$. Similar results were obtained with a variety of phosphine, phosphite, arsine and antimony ligands. Several of the reaction products have been isolated from the fairly clean reaction mixtures and a variety of spectral data have been obtained to verify their identity. Further purification and characterization of these compounds is continuing. In addition, trends of reaction product yields with bulk and basicity of ligand are being studied. Effect of ligand identity (both on the metal prior to photolysis and as an incoming group), wavelength of the photolysis lamp and temperature of the reaction mixture are being studied as they affect the reaction products obtained. Anionic and cationic starting materials are being investigated under a variety of reaction conditions in order to analyze the system for any trend which might develop as a function of complex charge. A collaborative effort was established with Professor Antony Rest at The University in Southampton in an effort to conclusively identify the reaction intermediate(s). The results of this work have been very promising and the identity of the reaction intermediate has been postulated, as a result of low-temperature matrix isolation studies conducted by Prof. Rest. Work on the project is continuing with a shift in focus to the analogous ruthenium species. Manuscripts on the synthetic portions of the project as well as the spectroscopic matrix work are being prepared and final spectral data are being obtained for inclusion in the papers.

Conformational Analysis of Acetylcholine and Related Compounds

RESEARCHER: Associate Professor Joseph J. Urban

Acetylcholine is a major neurotransmitter in both the central and peripheral nervous systems. The cholinergic nerve transmission system is of particular importance to the military because this system is the target of the organophosphorous G nerve agents. The mechanism of action of these agents is to block nerve transmission by inhibition of the enzyme acetylcholinesterase, an essential component of the nerve transmission process. Upon binding to its receptor acetylcholine undergoes a conformational change and NMR studies that have been reported in the literature provide a hypothesized “bound conformation” (to the nicotinic acetylcholine receptor). The energy cost associated with this conformational change, however, is not known and is extremely difficult to estimate experimentally. In this work a combination of molecular modeling techniques have been employed to determine the difference in energy between the bound and unbound conformations of acetylcholine. The results indicate that the bound conformation reported in the previous NMR work lies significantly above the ground state in energy. This suggests that further experimental work is needed to establish the bioactive conformation of acetylcholine when bound to its receptor. In addition, this work established the effects of substituents (N-methyls) and the surrounding environment on the conformational preferences of acetylcholine and similar systems.

Research Course Projects

Synthesis and Study of a Series of Amine Functionalized Silica Gels Made Via the Sol Gel Process

RESEARCHERS: Midshipman 2/C Wesley Campbell, USN
Midshipman 2/C Ian Hudson, USN and Midshipman 2/C James Valentine, USN
ADVISER: Assistant Professor J.R. Hartman

Copper contamination in JP-5 jet fuel is a source of great concern to the Navy. Copper catalyzes auto-oxidative degradation reactions at high temperatures that result in the formation of insoluble gums and sediments. This process, also called coking, results in a decrease in the performance of engines even at copper concentrations of less than 15 ppb. Currently, chelants are added to jet fuel to address this problem. These chelants form soluble complexes with the copper cations that render the copper catalytically inactive. However, studies have shown these complexes break down at high temperatures, freeing the copper to act as a catalyst for the auto-oxidative degradation. Therefore, if engines are to be operated at higher temperatures, it is necessary to find a better way to inactivate the copper. The Naval Research Laboratory has been studying the feasibility of removing the copper ions entirely by adsorbing them to functionallized solid materials such as polymeric resins or silica gels. They have concluded that silica gel appears to be the most suitable matrix although they do not currently have a silica gel that meets all of their criteria.

The silica gels that were studied by the Naval Research Laboratory were prepared by chemically modifying the surface of preformed silica gels. We have decided to prepare and study amine-functionallized silica gels made via the sol gel process to determine if it is possible to further optimize the performance of the silica gels. This semester, we have prepared silica gels with the following amine groups: propyl amine, propylethylenediamine, and propyl diethylene triamine. For each amine group we prepared silica gels with ratios of TEOS:amine silane ranging from 9.74:0.25 to 60:40. (TEOS is tetraethoxysilane.) and studied the copper adsorption properties of the resulting silica gel. Preliminary results suggest that the identity and amount of the amine group has no effect at amine levels above 20% (mole percent of amine-substituted silica). At levels lower than 20%, the copper adsorption increased with the number of chelating rings in the amine functional group.

Future plans include running the sol-gel reactions in the presence and absence of metal ions to determine if these metal ions will serve as a template to form “custom” silica gels that will selectively bind the desired metal ion with a high capacity. Then, we will use adsorption isotherms and spectroscopy to study the mechanisms of adsorption and the types of surface metal complexes formed.

Studies Directed Toward the Total Synthesis of Dolabelladiene

RESEARCHER: Midshipman 1/C Eugina Hopson, USN
ADVISER: Associate Professor Debra K. Dillner

Dolabelladiene is the parent compound in a class of molecules isolated from marine mollusks. Its interesting structure includes a cyclopentane ring with three asymmetric centers and a medium-size ring. Synthetic studies are being carried out into the formation of the cyclopentane ring with complete control of the stereochemistry. The template for introduction of the required stereocenters is a oxabicyclo[3.3.0]octane. This bicyclic system is rigid and the various substituents required can be added stereospecifically to this molecule. Once the stereocenters are in place, the lactone ring can be reduced, leaving the cyclopentane system intact.

Synthesis of the bicyclic lactone was optimized in this project. This compound had previously been synthesized in six steps. Two of these steps were difficult, using either hazardous starting materials or giving poor yields. Alternative routes to avoid these two steps were investigated.

The original step involved a Diels-Alder reaction with 1,3-butadiene and methyl acrylate. To avoid use of the gaseous, hazardous 1,3-butadiene, equivalent reagents were investigated. Butadiene sulfone was found to be an excellent alternative. Using this solid, relatively non-hazardous material, the reaction could be carried out easily on scales of up to 50 grams. The ester

was then converted to the dimethyl alcohol by addition of methyl lithium. This reaction is also amenable to scale up. The next difficult step had been an ozonolysis followed by oxidation with 30% hydrogen peroxide. An acceptable alternative has been found. Ruthenium tetraoxide oxidation achieves both steps simultaneously, with both a higher yield and a shorter reaction time. Previously optimized procedures were used to convert the product of this reaction into the bicyclic system.

As a result of this investigation, it is now possible to produce the bicyclic lactone in 10-20 gram quantities. The synthesis requires five steps, two fewer than previously possible. The overall yield now approaches 40%. Again this is a significant improvement. With the synthesis of this crucial substrate now optimized, studies on introduction of the remaining portions of dolabelladiene are underway.

Development of an Advanced Laboratory Experiment: Synthesis and Characterization of Polydiacetylene Polymers

RESEARCHER: Midshipman 1/C Luan Lam, USN
ADVISER: Assistant Professor Maria J. Schroeder

This project focuses on the development of a new, integrated laboratory experiment intended for advanced chemistry majors. The experiment incorporates aspects of traditional chemistry disciplines such as organic, physical, analytical and biochemistry, into a multi-week experience where students synthesize and characterize a material not generally encountered in undergraduate laboratories, a polymeric system. The laboratory procedure begins with students synthesizing hydrazide derivatives of single-chain diacetylene lipids using typical organic synthesis techniques (extraction, recrystallization, separation, rotoevaporation). Only when the material is in a highly ordered state can polymerization of the diacetylene occur upon thermal annealing or exposure to UV radiation. Characterization of the synthesized polymer involves UV/Vis, FTIR, and NMR spectroscopies for confirmation of structure as well as thermal and optical measurements for determining the extent of polymerization. Because of the highly conjugated backbone, polydiacetylenes exhibit interesting colorimetric order-disorder transitions in response to external stresses of heat, radiation, pH change, and surface pressure. For example, in the oriented, unstressed state, the polymer is blue however if the effective conjugation length is reduced by strain or torsion imposed onto the backbone, the polymer changes to a bright red color. From a student perspective, the optical transitions of polydiacetylenes are dramatic and generate interest in potential applications as molecule-based sensory materials. Investigations of the polymer's behavior in response to various applied stresses lead students to an understanding of the conformational changes and chemical reactions occurring in this system.

Synthesis and Characterization of Polyurethane-Maleamides for Cardiovascular Applications

RESEARCHER: Midshipman 1/C Jeremy P. Moore, USN
ADVISER: Assistant Professor Maria J. Schroeder

A great demand for tissue substitutes exists due to an increasing number of burn injuries and cases involving arterial repair. This project investigates the synthesis and characterization of segmented polyurethanes which have been recently employed in the construction of cardiovascular devices. Polyurethane-maleamides (PUMA) containing polyether soft segments and aliphatic hard segments were synthesized by solution and bulk polymerization using maleic acid as the chain extender. Through this process, grafting between the activated double bonds introduced into the polymer and the base polyurethanes may improve the tissue compatibility of the final product. By varying the composition of the polyurethane hard and soft segments and the chain extender, polyurethane films with different mechanical properties can be produced. Characterization studies involving FTIR, SEM, DSC, and tensile strength were conducted Fourier transform infrared spectroscopy (FTIR) confirmed the presence of amide and conjugated double bonds. Scanning electron microscopy (SEM) on solution polymerized PUMA indicated general surface homogeneity with further magnification revealing surface pores. High melting temperatures as evidenced by differential scanning calorimetry (DSC) data corroborate literature values. All PUMA samples exhibited high tensile strength with the bulk polymerized sample subject to heat stress displaying the highest tensile properties. To effectively model natural tissue, PUMA films must be strong, elastic, biocompatible, and semi-permeable to water yet prevent bacterial and viral passage. Future studies involve investigating these permeability and biocompatibility issues.

Synthesis and Characterization of Hybrid Electron Donors Containing Fused Ferrocene and Tetrathiafulvalene Units

RESEARCHER: Midshipman 2/C Cameron E. Shaver, USN
ADVISER: Associate Professor William B. Heuer

This project continues our ongoing efforts to prepare novel, unsymmetrical tetrathiafulvalene (TTF) derivatives via cross-coupling reactions of the novel precursor 1,3-dithia[3]ferrocenophane-2-thione, (DFT), first reported by Sato and Akabori (*Bull. Chem. Soc. Jpn*. 1985, 58, 1615). These authors also reported the triphenylphosphine-mediated self-coupling of DFT to form insoluble 2,2'-bi(1,3-dithia[3]ferrocenophane-2-ylidene) in 68% yield. We have been attempting to use similar methodology to prepare unsymmetrical derivatives by cross-coupling reaction between DFT and 4,5-Bis(2'-cyanoethylthio)-1,3-dithiole-2-thione (BDT). Reaction of DFT and BDT in a 1:2 molar ratio with a 5-fold molar excess of PPh_3 in refluxing tolune for 24 hr gives the desired mixed coupling product in ca. 10% yield. The product has been fully characterized by MS, $^1H/^{13}C$ NMR, and IR. A pronounced decrease in yield with increasing solvent volume was noted, and the workup is complicated by the difficult chromatographic separation of the product from unreacted BDT which always seems to be present in the toluene/PPH_3 reaction mixtures. If the reaction is conducted in molten PPh_3 at 80-100°C, no unreacted BDT is found, however the yield is lowered presumably due to increased decomposition of starting materials and/or products. Use of more reactive phosphite ($P(OEt)_3$, $P(OME)_3$) coupling agents in refluxing toluene was also explored as a means of decreasing the reaction time, but this also resulted in extensive decomposition. Reactions using these coupling agents at lower temperatures are currently being investigated. As part of this study, we also prepared the heretofore unknown dithiocarbonate analogue of DFT, namely 1,3-dithia[3]ferrocenophane-2-one (DFO), via the reaction of ferrocene-1,1'-dithiol with triphosgene in THF at -78°C. This compound proved to be less reactive than DFT in phosphine-mediated coupling reactions. However, we did confirm our hunch that this molecule might exhibit interesting photochemical reactivity, presumably by loss of CO to give a transient diradical species, which subsequently polymerizes. Solid-state photopolymerization of DFO films will be investigated as a means of producing electroactive poly(ferrocenyldisulfide) coatings on electrode surfaces. Photoreactions of DFO with appropriate radical-trapping agents in solution are also currently being explored.

Publications

Bitterwolf, T.E., Saygh, Abdel, SHADE, Joyce E., Rheingold, Arnold L., Yap, Glenn P.A., and Liable-Sands, Louise, "Photochemistry of Ring-Coupled Group VI Bimetallic Compounds I: Phosphine Substitution Without Disproportionation. The Molecular Structures of $Mo_2(CO)_5[P(C_6H_5)_3](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ and $Mo_2(CO)_4[P(CH_3)_3]_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$," *Journal of Organometallic Chemistry*, 562 (1998) 89-96.

Solution photolysis of ring-coupled bimetallic compounds of the formula $M_2(CO)_6(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CR_2C_5H_4)$, where M = Mo or W and R = H or CH_3, in the presence of triphenylphosphine or trimethylphosphine yields simple substitution derivatives $M_2(CO)_5L(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ or $M_2(CO)_4L_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$. The compounds have been fully characterized by IR and NMR spectroscopy and elemental analysis. Phosphine ligands are found to occupy positions *trans* to the M-M bond. No evidence was found for disproportionation processes such as those found for similar reactions to the non-ring-coupled species. The molecular structures of two compounds have been determined.

Bitterwolf, T.E., Saygh, A. A., Bays, J.T., Scallorn, B., Weiss, C., Rheingold, A. L., Liable-Sands, L., and SHADE, Joyce E., "Synthesis, Nujol Matrix and Solution Photochemistry of $M(CO)_2$ $[\eta^5, \eta^3\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_6]$, where M = Cr or Mo. Molecular Structures of $Cr(CO)_2[\eta^5, \eta^3\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_6]$, $Mo(CO)_2[\eta^5, \eta^3\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_6]$, and $Mo(CO)[P(C_6H_5)_3][\eta^5, \eta^3\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_6]$," *Journal of Organometallic Chemistry*, 563 (1999) 152-161.

Reaction of chromium or molybdenum carbonyl with 2,2-bis(cyclopentadienyl)propane yields mixtures of products including $M_2(CO)_6[\eta^5, \eta^5\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_4]$. $M_2(CO)_6[\eta^5\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_4]_2$, and the title compound, $M(CO)_2[\eta^5, \eta^3\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_6]$, in which an η^3-pentenyl group is tethered to the η^5-cyclopentadienyl (Cp) group by a 2,2-propyl linkage. Although several isomers are possible for the cyclopentenyl groups, chromium and molybdenum appear to form only single, but unique isomers. Photolysis of $M(CO)_2[\eta^5, \eta^3\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_6]$, M = Cr or Mo, in

Nujol glass at ca. 77 K has been found to be wavelength-dependent with low energy photolyses resulting in η^3 to η^1 transformations while higher energy photolyses result in loss of carbon monoxide. Solution photolysis of the molybdenum derivative with triphenylphosphine yields as a first product $Mo(CO)_2[P(C_6H_5)_3][\eta^5, \eta^1\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_6]$, which undergoes decomposition upon work-up to yield both starting material, and $Mo(CO)[P(C_6H_5)_3][\eta^5, \eta^3\text{-}C_5H_4\text{-}C(CH_3)_2\text{-}C_5H_6]$. The molecular structures of three compounds have been determined.

CAMPBELL, Mark L., Associate Professor, "Temperature Dependent Rate Constants for the Reactions of Gas Phase Lanthanides with N_2O," *J. Chem. Phys.* 111 (1999), 562-566.

The reactivity of gas phase lanthanide atoms Ln (Ln = La - Yb with the exception of Pm) with N_2O from 298 to 623 K is reported. Lanthanide atoms were produced by the photodissociation of $Ln(TMHD)_3$ (TMHD = 2,2,6,6-tetramethyl-3,5-heptanato ion) and detected by laser induced fluorescence. Large variations in the reaction rate constants are observed.

The bimolecular rate constants are described in Arrhenius form by: $k[Ce(^1G_4)] = (1.90.5) \times 10^{10} \exp(-0.80.8\ kJ\cdot mol^{-1}/RT)$; $Pr(^4I_{9/2})$, $(3.61.2) \times 10^{10} \exp(-8.01.2\ kJ\cdot mol^{-1}/RT)$; $Nd(^5I_4)$, $(3.40.4) \times 10^{10} \exp(-8.80.5\ kJ\cdot mol^{-1}/RT)$; $Sm(^7F_0)$, $(3.21.1) \times 10^{10} \exp(-11.21.2\ kJ\cdot mol^{-1}/RT)$; $Eu(^8S_{7/2})$, $(2.70.4) \times 10^{10} \exp(-12.70.5\ kJ\cdot mol^{-1}/RT)$; $Gd(^9D_2)$, $(2.00.3) \times 10^{10} \exp(-6.40.5\ kJ\cdot mol^{-1}/RT)$; $Tb(^6H_{15/2})$, $(2.90.5) \times 10^{10} \exp(-10.90.6\ kJ\cdot mol^{-1}/RT)$; $Dy(^5I_8)$, $(3.40.8) \times 10^{10} \exp(-16.20.8\ kJ\cdot mol^{-1}/RT)$; $Ho(^4I_{15/2})$, $(2.90.5) \times 10^{10} \exp(-17.10.6\ kJ\cdot mol^{-1}/RT)$; $Er(^3H_6)$, $(3.31.2) \times 10^{10} \exp(-18.41.2\ kJ\cdot mol^{-1}/RT)$; $Tm(^2F_{7/2})$, $(3.50.6) \times 10^{10} \exp(-19.50.6\ kJ\cdot mol^{-1}/RT)$; $Yb(^1S_0)$, $(2.50.2) \times 10^{10} \exp(-20.20.3\ kJ\cdot mol^{-1}/RT)$ where the uncertainties represent 2 σ. The reaction barriers are found to correlate to the energy required to promote an electron out of the 6s subshell.

CAMPBELL, Mark L., Associate Professor, "Temperature-Dependent Rate Constants for the Reactions of Gas-Phase Lanthanides with O_2," *Journal of Physical Chemistry* A," 103 (1999), 7274-7279.

The reactivity of the gas phase lanthanide atoms Ln (Ln = La - Yb with the exception of Pm) with O_2 is reported. Lanthanide atoms were produced by the photodissociation of $[Ln(TMHD)_3]$ and detected by laser induced fluorescence. For all the lanthanides studied with the exception of Yb, the reaction mechanism is bimolecular abstraction of an oxygen atom.

The bimolecular rate constants are described in Arrhenius form by: $k[Ce(^1G_4)] = (3.00.4) \times 10^{10} \exp(-3.41.3\ kJ\cdot mol^{-1}/RT)$; $Pr(^4I_{9/2})$, $(3.10.7) \times 10^{10} \exp(-5.31.5\ kJ\cdot mol^{-1}/RT)$; $Nd(^5I_4)$, $(3.60.3) \times 10^{10} \exp(-6.20.4\ kJ\cdot mol^{-1}/RT)$; $Sm(^7F_0)$, $(2.40.4) \times 10^{10} \exp(-6.21.5\ kJ\cdot mol^{-1}/RT)$; $Eu(^8S_{7/2})$, $(1.70.3) \times 10^{10} \exp(-9.60.7 kJ\cdot mol^{-1}/RT)$; $Gd(^9D_2)$, $(2.70.3) \times 10^{10} \exp(-5.20.8\ kJ\cdot mol^{-1}/RT)$; $Tb(^6H_{15/2})$, $(3.50.6) \times 10^{10} \exp(-7.20.8\ kJ\cdot mol^{-1}/RT)$; $Dy(^5I_8)$, $(2.80.6) \times 10^{10} \exp(-9.10.9\ kJ\cdot mol^{-1}/RT)$; $Ho(^4I_{15/2})$, $(2.40.4) \times 10^{10} \exp(-9.40.8\ kJ\cdot mol^{-1}/RT)$; $Er(^3H_6)$, $(3.00.8) \times 10^{10} \exp(-10.61.1\ kJ\cdot mol^{-1}/RT)$; $Tm(^2F_{7/2})$, $(2.90.2) \times 10^{10} \exp(-11.10.4 kJ\cdot mol^{-1}/RT)$ where the uncertainties represent 2 σ. The reaction barriers are found to correlate to the energy required to promote an electron out of the 6s subshell. The reaction of $Yb(^1S_0)$ with O_2 reacts through a termolecular mechanism. The limiting low-pressure third-order rate constants are described in Arrhenius form by: $k_o[Yb(^1S_0)] = (2.01.3) \times 10^{-28} \exp(-9.52.8\ kJ\cdot mol^{-1}/RT)\ molecule^{-2}cm^6s^{-1}$.

CAMPBELL, Mark L., Associate Professor, "Temperature Dependent Rate Constants for the Reactions of Gas Phase Lanthanides with CO_2," *Physical Chemistry Chemical Physics*, 14 (1999), 3731-3735.

The reactivity of the gas phase lanthanide atoms Ln (Ln = La - Yb with the exception of Pm) with CO_2 is reported. Lanthanide atoms were produced by the photodissociation of $[Ln(TMHD)_3]$ and detected by laser induced fluorescence. For all the lanthanides studied with the exception of Yb, the reaction mechanism is bimolecular abstraction of an oxygen atom.

The bimolecular rate constants are described in Arrhenius form by: $k[Ce(^1G_4)] = (3.41.0) \times 10^{10} \exp(-3.51.0\ kJ\cdot mol^{-1}/RT)$; $Pr(^4I_{9/2})$, $(2.50.4) \times 10^{10} \exp(-7.90.7\ kJ\cdot mol^{-1}/RT)$; $Nd(^5I_4)$, $(3.30.6) \times 10^{10} \exp(-12.00.8\ kJ\cdot mol^{-1}/RT)$; $Sm(^7F_0)$, $(1.70.8) \times 10^{10} \exp(-15.81.8\ kJ\cdot mol^{-1}/RT)$; $Eu(^8S_{7/2})$, $(6.62.3) \times 10^{10} \exp(-39.21.6\ kJ\cdot mol^{-1}/RT)$; $Gd(^9D_2)$, $(1.10.3) \times 10^{10} \exp(-5.80.9\ kJ\cdot mol^{-1}/RT)$; $Tb(^6H_{15/2})$, $(1.10.3) \times 10^{10} \exp(-10.81.2\ kJ\cdot mol^{-1}/RT)$; $Dy(^5I_8)$, $(4.00.7) \times 10^{10} \exp(-30.30.7\ kJ\cdot mol^{-1}/RT)$; $Ho(^4I_{15/2})$, $(3.71.1) \times 10^{10} \exp(-33.11.3\ kJ\cdot mol^{-1}/RT)$; $Er(^3H_6)$, $(5.82.5) \times 10^{10} \exp(-36.92.0\ kJ\cdot mol^{-1}/RT)$; $Tm(^2F_{7/2})$, $(1.10.5) \times 10^{10} \exp(-45.42.3\ kJ\cdot mol^{-1}/RT)$ where the uncertainties represent 2 σ. $Yb(^1S_0)$ is unreactive with CO_2 below 623 K. The reaction barriers are found to correlate to the energy required to promote an electron out of the 6s subshell.

CHEEK, Graham T., Professor, "Electrodeposition of Niobium and Tantalum from a Room-Temperature Molten Salt System", P.C. Trulove, H.C. De Long, G. Stafford, and S. Deki, eds., Electrochemical Society Proceedings Volume PV-99-41, (1999), pp. 527-534.

The electrochemical behavior of $NbCl_5$ and, to some extent, $TaCl_5$, has been investigated in the aluminum chloride : 1-ethyl-3-methylimidazolium chloride ambient temperature molten salt system. Reduction of $NbCl_5$ occurs in a series of one-electron steps in the acidic melt and apparently does not produce Nb^o at potentials approaching the aluminum deposition potential. Electrodeposition of Nb / Al films has been found to be feasible only when Nb(V) is reduced to the trivalent state in a preceding chemical reduction. Niobium powder was observed to be the most effective reducing agent for this purpose. The voltammetric characteristics of various other niobium complexes, such as $NbCl_4(thf)_2$ and $NbCl_3dme$, have also been briefly investigated.

COPPER, C.L., Assistant Professor and KOUBEK, E., Professor, "An Experiment Designed to Demonstrate How a Catalyst Affects the Rate of Reaction," *J. Chem. Educ.*, 1999, *76*, 1714.

Most chemistry students know that a catalyst is a substance that causes the rate of a reaction to increase and is regenerated at the end of the reaction, but they are not always certain how or why a catalyst works. We believe that this is because many beginning texts simply state that a catalyst provides a new pathway for the reaction, one with a lower activation energy. This, of course, need not be the case, since *any* additional pathway will lead to an increase in rate even if it has a higher activation energy. This is because two reactions running simultaneously will always have a combined rate that is faster than one alone. Too often, authors fail to emphasize that the original reaction is still taking place and that, depending upon conditions, it is possible for this original reaction to proceed at a faster rate than the catalyzed reaction. This situation is purposefully created by the conditions chosen for this experiment.

COPPER, C.L., Assistant Professor and KOUBEK, E., Professor, "Kinetics of the Molybdate and Tungstate Catalyzed Oxidation of Iodide by Hydrogen Peroxide," *Inorg. Chim. Acta*., 1999, *288*, 229.

Several studies of the Mo(VI) and W(VI) catalyzed reaction of H_2O_2 with various substrates have been documented previously. The experiments described herein attempt to settle some apparent contradictions in these reports. Specifically, the oxidation of I^- with H_2O_2 in the presence of molybdate or tungstate ion in an acid solution was studied. The rate law for this system was found to be $rate_i = k_{cat}[MoO_4^{2-}][I^-] + k_{uncat}[H_2O_2][I^-]$ with values of $k_{cat} = 3.87\ M^{-1}\ s^{-1}$ and k_{uncat} of $9.5 \times 10^{-3}\ M^{-1} s^{-1}$ (at 22.8ºC). The values of $\Delta H^{\#}$ for the molybdate catalyzed and uncatalyzed reactions were found to be 39.4 and 56.8 kJ mol^{-1}, respectively. Similarly, the value of k_{cat} was found to be $32.7 M^{-1}\ s^{-1}$ and $\Delta H^{\#}$ was found to be 41.1 kJ mol^{-1} (at 21.8ºC) for the same system catalyzed with tungstate rather than molybdate.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, editor, *Proceedings of the Twelfth International Symposium on Molten Salts*, Vol. 99-41, The Electrochemical Society: Pennington NJ, 2000.

The Twelfth International Symposium on Molten Salts was held during the Joint International Meeting of the Electrochemical Society and the Physical Society of Japan in Honolulu, Hawaii, Oct, 1999. Over 90 papers were presented on topics ranging from theoretical studies to technological applications of molten salts. Authors were from over fifteen different countries with well over half from outside North America. Funding for this meeting was provided by the Physical Electrochemistry, the High Temperature Materials, the Electrodeposition divisions of the Electrochemical Society, and the Electrochemistry Society of Japan. Further funding was provided by the Air Force Office of Scientific Research.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Ionic Liquid, Graphite and Gel Polymer Electrolytes and Electrodes Using 1,2-Dimethyl-3-propyl-imidazolium Tetrafluoroborate," in *Proceedings of the 12th International Symposium on Molten Salts*, Paul C. Trulove, Hugh C. De Long, Gery R. Stafford, and Shigehito Deki, Eds.; Vol. 99-41, The Electrochemical Society: Pennington NJ, 2000, pp. 32-42.

The effect of the molten salt in these gels can be seen when considered along with the results observed for the graphite-polymer composite electrodes . For these composites, samples with less than 66% graphite or more than 33% polymer

failed to exhibit any charge discharge behavior. In these materials, peak efficiencies were observed when there was less than 40% graphite, and nearly 50% polymer in some cases. Clearly, the incorporation of the molten salt most likely facilitates the ease with which it can intercalate graphite, regardless of the presence of nearly 50% polymer in some cases. In fact, for samples with too little polymer, low efficiencies were observed. This is easily attributable to the fact that with too little polymer, charging of the gel results in a breakdown in the electrical connectivity between graphite particles as they swell upon intercalation of the $DMPI^+$. The presence of a significant amount of polymer results in improved efficiencies by prevent this loss of connectivity, even though the polymer itself is non-conductive.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Electrochemical Studies of Metal Dichalcogenide-Polymer Composite Electrodes in 1,2-dimethyl-3-propyl-imidazolium Tetrafluoroborate and 1-ethyl-3-methyl-imidazolium Tetrafluoroborate," in *Proceedings of the 12th International Symposium on Molten Salts*, Paul C. Trulove, Hugh C. De Long, Gery R. Stafford, and Shigehito Deki, Eds.; Vol. 99-41, The Electrochemical Society: Pennington NJ, 2000, pp. 43-53.

Cyclic Voltammetry of the metal sulfides indicated improving conductivity of the electrodes as the amount of metal sulfide increased from the 1:2 ratio up to the 4:1 ratio. Further increasing of the metal sulfide did not seem to significantly alter the observed internal resistance. For both TiS_2 and TaS_2, the cyclic voltammetry showed a singe strong reductive peak, and a large broad oxidative peak. For MoS_2, no real reductive or oxidative behavior was observed. Similarly, as was expected, only minimal surface charging effects were seen for all of the MoS_2 composite materials, and no charge/ discharge efficiencies were noticeable for both cation and anion charging in either molten salt. For TiS_2 and TaS_2, exfoliation proved to be an even greater problem than for graphite, and more so for the TaS_2 than for TiS_2. For samples of composition over 5:1, the polymer strips clearly began to disintegrate in both molten salts. However, for TiS_2 a peak cation charging efficiency of 79% was observed in $DMPIBF_4$ for the 6:1 sample. In $EMIBF_4$, the peak efficiency was only 45%, for the 4:1 sample. For TaS_2, it was observed that only those samples with a high polymer content could resist exfoliation, and peak cation charge/discharge efficiencies did not reach above 40% in either molten salt.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Electrochemical Intercalation Studies of 1,2-Dimethyl-3-propyl-imidazolium Tetrafluoroborate and 1-Ethyl-3-methyl-imidazolium Tetrafluoroborate in Graphite and Graphite-Polymer Composite Electrodes," in *Proceedings of the 12th International Symposium on Molten Salts*, Paul C. Trulove, Hugh C. De Long, Gery R. Stafford, and Shigehito Deki, Eds.; Vol. 99-41, The Electrochemical Society: Pennington NJ, 2000, pp. 54-64.

In order to study the overall stability of the charged graphite species, a series of time-delayed charge/ discharge experiments were run, where the time between charging and discharging ranged from 5 minutes to 9 hours. These time-delayed experiments indicated many significant details of both of these molten salts. First, it was observed that over time, peak efficiencies fell off much faster when done in air, as opposed to being run in an inert nitrogen atmosphere. In fact, for the $DMPI^+$, efficiencies dropped from near 90% in air, to below 20% after 9 hours, and from near 80% for the EMI^+, to 0% efficiency in less than 6 hours, also when run in air. However, when performed in a dry box, the $DMPI^+$ showed a drop of less than 5% when the discharging was delayed by 9 hours. For EMI^+, a similar improvement was observed when the charge/discharge cycling was run in a dry box, but its efficiency still fell below 20% after a 9-hour delay in discharging. This is a clear indication that the EMI+ cation is not as stable in a charged environment as the DMPI+, as was originally proposed. For BF_4^-, the time delayed charge/discharge experiments indicated that after 9 hours, the efficiencies dropped below 10% for BF_4^- in both molten salts, even when run in the dry box. This lack of stability in a charged environment is most likely related to its stability as a graphite intercalate. Intercalation studies have indicated that under certain conditions, the BF_4^- anions will breakdown, generating F^- and BF_3. This most likely results in the low efficiencies observed.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Studies of Cation Transport in Molten Salts and Molten Salt-Polymer Gels by Pulsed-Field-Gradient Spin-Echo NMR," in *Proceedings of the 12th International Symposium on Molten Salts*, Paul C. Trulove, Hugh C. De Long, Gery R. Stafford, and Shigehito Deki, Eds.; Vol. 99-41, The Electrochemical Society: Pennington NJ, 2000, pp. 169-176.

Studies of the transport properties of the ambient-temperature molten salt, 1-ethyl-3-methylimidazolim chloride:aluminum chloride ($EMIC:AlCl_3$), found that the internal transport number of the cation, EMI^+, was 1.00 over a wide range of melt compositions. This indicates that the cation predominates charge transport in these molten salts. Efforts to measure the

diffusion coefficient of the EMI^+ cation in these melts have met with limited success. Carlin and Osteryoung (2) used microelectrode techniques to obtain a value of $D = 1.0 \times 10^{-7}$ cm^2/s in an N = 0.44 melt. Unfortunately, due to the limitations of the technique, this value is at best an estimate of the true diffusion coefficient.Self-diffusion coefficients of the EMI^+ cation for EMIC:$AlCl_3$ melts have been measured as a function of composition and temperature. These data correlate strongly with corresponding changes in melt viscosity. The temperature dependence of the diffusion coefficient data has been used to determine activation energies for diffusion in these melts. We have also measured the self-diffusion coefficients of the EMI^+ cation in LiCl and NaCl buffered neutral melts, and in molten salt-polymer gels.

DE LONG Hugh C., Major (USAF) and Assistant Professor, co-author, "Electrodeposition and Pitting Corrosion Behavior of Aluminum-Manganese Alloys deposited from Room Temperature Chloroaluminate Molten Salts," in *Proceedings of the 12th International Symposium on Molten Salts*, Paul C. Trulove, Hugh C. De Long, Gery R. Stafford, and Shigehito Deki, Eds., Vol. 99-41, The Electrochemical Society: Pennington NJ, 2000, pp. 517-526.

Electrochemical deposition has proved to be an excellent alternative method for producing nonequilibrium alloys. It generally does not suffer from the cost and applicability disadvantages of the more common methods. The key to application of electrodeposition, however, is finding a system from which the alloys can be deposited. The excellent Al-Mn deposits obtained by Stafford and Moffat in acidic $AlCl_3$:NaCl molten salts prompted our attempts to electrodeposit an amorphous aluminum-manganese alloy from the acidic room temperature $AlCl_3$:EMIC chloroaluminates. Additionally, the successful deposition of Al-Mn, Al-Co, and Al-Ni alloys from room-temperature ionic liquids has recently been reported. The room temperature Al-Mn deposits are of sufficient quality to allow corrosion cell testing to determine their pitting potential. The pitting potential for all samples was within 0.3 V of each other with pitting starting at or very near the open circuit potential. In all cases the deposit almost completely delaminated. This delamination suggests a lack of adhesion, possibly due to the deposits' porosity, and may not represent the true corrosion resistance.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Electrodeposition of Niobium and Tantalum from a Room-Temperature Molten Salt System," in *Proceedings of the 12th International Symposium on Molten Salts*, Paul C. Trulove, Hugh C. De Long, Gery R. Stafford, and Shigehito Deki, Eds.; Vol. 99-41, The Electrochemical Society: Pennington NJ, 2000, pp. 527-534.

We have undertaken a study of the electrochemical properties of niobium and tantalum in the aluminum chloride: 1-ethyl-3-methylimidazolium chloride (EMIC) room temperature molten salt system in order to understand the processes occurring during electrodeposition of these metals from acidic (molar excess of $AlCl_3$) melt. Such conditions allow the co-deposition of these metals with aluminum, conferring anti-corrosion properties on the resulting films. Depositions have been carried out in high-temperature fluoride molten salts (1), but it is hoped that the present system will allow milder, more convenient conditions to be employed.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Investigations of the Electrodeposition of Aluminum-Manganese Alloys from Room Temperature Chloroaluminate Molten Salts," in Advances in Molten Salts: From Structural Aspects to Waste Processing, Marcelle Gaune-Escard, Ed.; Begell House,Inc., 1999, pp.137-148.

The electrochemical reduction of manganese (II) in acidic $AlCl_3$:EMIC (aluminum chloride:1-ethyl-3-methylimidazolium chloride) room temperature molten salt results in co-deposition of aluminum and manganese. Constant potential deposition in the region of the reduction peak results in the deposition of manganese rich amorphous manganese-aluminum alloys. We have employed an Electrochemical Quartz Crystal Microbalance (EQCM) to investigate, in situ, the deposition and stripping behavior of Al and Al-Mx in acidic $AlCl_3$:EMIC molten salts. The EQCM provides both mass and charge data during electrodeposition and stripping processes. This information can be used to determine co-deposited metal composition and to model deposition nad/or stripping processes.

ELERT, Mark L., Professor, co-author, "Molecular Dynamics Simulation of Shock-Induced Chemistry in Acetylene," in *Shock Compression of Condensed Matter - 1999*, M. D. Furnish, L. C. Chhabildas, and R. S. Hixson, eds., New York: American Institute of Physics Press, 2000, pp. 283-286.

Many experimental studies have demonstrated the existence of shock-induced chemical reactions in organic materials. Some of this work was motivated by the possible cosmochemical significance of shock-induced synthesis resulting from meteor bombardment of planetary atmospheres. In most cases, fundamental reaction mechanisms and kinetics, and threshold conditions for reaction initiation, remain poorly understood. Using a recently developed reactive empirical bond order (REBO) potential for hydrocarbons, we have carried out molecular dynamics simulations of shocked condensed-phase acetylene to investigate the resulting shock-induced chemistry at an atomistic level.

ELERT, Mark L., Professor, co-author, "Critical Widths in Molecular Dynamics Simulations of Detonations," in Shock Compression of Condensed Matter - 1999, M. D. Furnish, L. C. Chhabildas, and R. S. Hixson, eds., New York: American Institute of Physics Press, 2000, pp. 377-380.

Previously, we have developed several models for molecular dynamics simulations of shock-induced chemistry in detonating materials. A series of earlier simulations established that our original AB model can support a detonation with properties consistent with the continuum theory of compressive reactive flows. These studies also showed that this model has an extremely short reaction zone length, suggesting a critical width for detonation small enough to be directly determined from molecular dynamics simulations of 2-D strips. Herein, we report results that show that the AB model does exhibit a critical width for detonation that can be found using molecular dynamics simulations. These results also suggest the possibility of observing detonations in highly reactive strips only ten's of nanometers wide.

ELERT, Mark L., Professor, co-author, "Detonation Hugoniots Produced by Piston-Driven Simulations," in *Shock Compression of Condensed Matter - 1999*, M. D. Furnish, L. C. Chhabildas, and R. S. Hixson, eds., New York: American Institute of Physics Press, 2000, pp. 385-388.

We have previously introduced a model of an energetic diatomic molecular solid based on reactive empirical bond order (REBO) potentials. This model is capable of supporting a detonation in two and three dimensions. When the range of the REBO potential is varied, a wide variety of properties ais exhibited, including a split shock wave and a dissociative phase transition. We present simulations with the boundary conditions behind the detonation front maintained by a constant-velocity piston. Detonation Hugoniots are derived from these calculations and analyzed using continuum theory.

FERRANTE, Robert F., Professor, coauthor, "Laboratory Studies of Catalysis of CO to Organics on Grain Analogs," *Icarus*, 145, #1 (May 2000), 297-300.

Experiments simulating heterogeneous conversion of H_2 and CO into simple hydrocarbons in astrophysical environments have been performed, utilizing realistic cosmic grain analogs of Fe-doped silicates as Fischer-Tropsch-Type catalysts. Catalysis was studied for temperatures from 460-670 K and reactant gas mixtures of H_2/CO with a ratio of 2-100. The total gas pressure was near 0.5 bar. Maximum conversion rates of a few percentage points were achieved over a 3-h time period. Major products were methane, ethane, ethylene, carbon dioxide and water. Products were identified by IR spectroscopy.

FITZGERALD, Jeffrey P., Associate Professor, "Synthesis of Substituted 1-Methyl-2-cyanopyrroles via Unprecedented Addition of N,N-Dimethylformamide to Electron-Deficient Alkenes in the Presence of Copper(I) Cyanide," *Journal of Organic Chemistry*, 65 (April 2000), 2222-2224.

Attempts to prepare 1,2-bis(trifluoromethyl)-1,2-dicyanoethylene by reaction of copper(I) cyanide with 1,2-bis(trifluoromethyl)-1,2-dibromoethylene in N,N-dimethyl- formamide (DMF) were unsuccessful, instead producing 1-methyl-2-cyano-3,4-bis-(trifluoromethyl)pyrrole and 1-methyl-2,5-dicyano-3,4-bis(trifluoromethyl)pyrrole. Analogous products were formed on treating dimethyl 2,3-dibromo-2-butenedioate with CuCN in DMF. Labelling studies show that a DMF molecule adds to the alkene to form the pyrrole ring. A mechanism involving a dipolar cycloaddition between an azomethine ylid and the alkene is proposed.

FITZGERALD, Jeffrey P., Associate Professor, "Vanadium [dicyanoperfluorostilbene]$_2$·THF: a molecule-based magnet with T_c ~ 205 K," *Chemical Communications*, (January 2000), 49-50.

A new radical anionic bridging ligand, derived from the *in-situ* reduction of α, α' - dicyanoperfluorostilbene, is reported to support ferrimagnetic ordering below 205 K in a three-dimensional vanadium-based coordination polymer.

HARRISON, Judith. A., Associate Professor, "Role of Defects in Compression and Friction of Anchored Hydrocarbon Chains on Diamond," *Langmuir*, 16 (2000) 291-296.

The classical molecular dynamics simulations presented in this work examine the compression and friction of monolayers composed of linear hydrocarbon chains with 8, 13, or 22 carbon atoms that are chemically bound (or anchored) to a diamond (111) substrate. The roles structural defects and their formation play in compression, friction, and energy dissipation processes are examined. The number of defects increases under increasing load, reaching a plateau at a specified load. Defects are also clearly implicated in the energy dissipation associated with sliding friction. The friction is found to be highest in shorter chains and disordered surfaces, in agreement with previous atomic force microscopy studies.

HARRISON, Judith A., Associate Professor, "A Reactive Potential for Hydrocarbons with Intermolecular Interactions," *J. Chem. Phys*., 112 (2000) 6472-6486.

A potential function is presented that can be used to model both chemical reactions and intermolecular interactions in condensed-phase hydrocarbon systems such as liquids, graphite, and polymers. This potential is derived from a well-known dissociable hydrocarbon force field, the reactive empirical bond-order potential. The extensions include an adaptive treatment of the non-bonded and dihedral-angle interactions, which still allows for covalent bonding interactions. Torsional potentials are introduced via a novel interaction potential that does not require a fixed hybridization state. The resulting model is intended as a first step towards a transferable, empirical potential capable of simulating chemical reactions in a variety of environments. The current implementation has been validated against structural and energetic properties of both gaseous and liquid hydrocarbons, and is expected to prove useful in simulations of hydrocarbon liquids, thin films, and other saturated hydrocarbon systems.

HARRISON, Judith A., Associate Professor, "Indentation Analysis of Linear-Chain Hydrocarbon Monolayers Anchored to Diamond," *J. Phys. Chem. B*, 103 (1999) 11357-11365.

Classical molecular dynamics simulations were used to examine the indentation of monolayers composed of linear hydrocarbon chains with 8, 13, or 22 carbon atoms that are chemically bound (or anchored) to a diamond (111) substrate. Indentation is accomplished using both a flexible and rigid single-wall, capped [10,10] nanotube as the tip. Regardless of the nanotube used, the simulations show that indentation of the hydrocarbon monolayers causes a disruption of the original ordering of the monolayer, pinning of selected hydrocarbon chains beneath the tube, and the formation of *gauche* defects within the monolayer. Because nanotubes are stiff along their axial direction, the flexible nanotube is distorted only slightly by its interaction with the softer monolayers. However, interaction with the hard diamond substrate causes the tube to buckle. Severe indents with a rigid nanotube tip result in rupture of chemical bonds within the hydrocarbon monolayer.

HARTMAN, J.R., Assistant Professor, Vachet, R.W.; and Callahan, J.H., "Gas, Solution, and Solid State Coordination Environments for the Nickel(II) Complexes of a Series of Aminopyridine Ligands of Varying Coordination Number," *Inorg. Chem. Acta*, 2000, 297(1-2), 79-87.

The synthesis and characterization of the nickel(II) complexes from a series of aminopyridine ligands that range from tri- to heptadentate is described. The ligands include the tripod ligand tris(2-((2-pyridylmethyl)amino)ethyl)amine, TREN-pyr, and the following linear ligands: (2-pyridylmethyl)(2-((2-((2-((2-pyridylmethyl)amino)ethyl)amino)ethyl)amine, TRIEN-pyr: bis(2-((2-pyridylmethyl)amino)ethyl)amine, DIEN-pyr; (2-pyridylmethyl)(2-((2-pyridylmethyl)amino)ethyl)amine, EN-pyr; bis(2-pyridylmethyl)amine, AM-pyr; and methyl(2-((-pyridylmethyl)amino)ethyl)amine, MeEN-pyr. The following methods were used to determine the binding geometries of the nickel(II) complexes in the solid, solution, and gas phases: magnetic susceptibility measurements, absorption spectroscopy, electrochemistry, and analyzing the gas phase ion-molecule reactions in a mass spectrometer. The linked 5-membered chelate character of the linear ligands appear to

have imposed high-spin, octahedral geometry on the complexes in the condensed phases. The tripod ligand TREN-pyr and the two tridentate ligands, AM-pyr and MeEN-pyr, form 6-coordinate complexes in the gas phase. In contrast, the rest of the complexes (TRIEN-pyr, DIEN-pyr, and EN-pyr) were found to have lower coordination numbers in the gas phase (5-, 5-, and 4-coordinate respectively). The potentially heptadentate tripod ligand TREN-pyr does not appear to confer any unusual properties on the Ni(II) ion in the solution or solid phases, but does appear to be more effective than the hexadentate ligand TRIEN-pyr at maintaining the 6-coordinate geometry in the gas phase.

HARTMAN, J.R., Assistant Professor, "An In-Class Experiment to Illustrate the Importance of Sampling Techniques and Statistical Analysis of Data to Quantitative Analysis Students," *J. Chem. Education*, 77(8), 1017-1018 (2000).

A simple in-class experiment designed to show the importance of sampling protocol and the use of statistics in data analyses is described. Two samples are presented to the class, an unmixed core sample and a mixed core sample. Both samples contain equal amounts of two colors of otherwise identical candies. The candies in the unmixed sample are in two separate layers in a tall opaque cup and the candies in the mixed sample are in a paper bag. The class is divided into two groups, each of which repeatedly analyzes one of the samples by each person drawing out one candy. The results from each analysis (as a percentage of one of the colors) are tabulated on the blackboard. These results are used to discuss what constitutes a good sampling protocol and a good sample. In addition, these results are used throughout the entire unit on statistics to demonstrate many calculations such as pooling data, comparison of means, confidence limits, and the use of student's t-tests. This demonstration has proved to be useful for engaging the interest of most students in sampling and statistics, and is a particularly effective means of teaching active learners the very formalistic subject of statistics.

KINTER, Christopher M., Associate Professor, (co-author), "Synthesis of N1'-([F-18]Fluoroethyl)naltrindole. A Radioligand for Positron Emission Tomographic Studies of the Delta Opioid Receptors," *Journal of Labelled Compounds and Radiopharmaceuticals*, (1999), 42, 43-54.

N1'-([F-18]Fluoroethyl)naltrindole ([F-18]FEtNTI) a novel analog of the delta opioid receptor antagonist naltrindole (NTI), has been prepared for evaluation as a radioligand for use in positron emission tomography. The precursor for radiolabeling was obtained in four steps from naltrexone hydrochloride with an overall yield of 47%. Nucleophilic displacement of a tosylate leaving group by [F-18]fluoride, followed by hydrogenolysis (H_2, 10% Pd/C) of the benzyl protecting group on the phenolic moiety, gave [F-18]FEtNTI. The average time for radiosynthesis, HPLC purification, and formulation was 77 minutes from the end of bombardment. [F-18]FEtNTI of high radiochemical purity was obtained with an average specific activity of 846 mCi/micromole at the end of synthesis, and an average radiochemical yield of 10% (not corrected for decay).

KINTER, Christopher M., Associate Professor, (co-author), "Quantification of the Delta Opioid Receptor in Human Brain With N1'-([C-11]methyl)naltrindole and Positron Emission Tomography," *Journal of Cerebral Blood Flow and Metabolism* (1999), 19, 956 - 966.

The title compound N1'-([C-11]methyl)naltrindole [C-11]MeNTI, a selective delta opioid antagonist, was synthesized and study in health human subjects using positron emission tomography (PET). After intravenous administration of high specific activity N1'-([C-11]methyl)naltrindole, PET was performed over 90 minutes and the data was analysed. This tracer showed irreversible binding characteristics during the scanning period. The results of the analysis also were compared with the distribution of the delta opioid receptor in the human brain *in vitro* and found to be consistent with selective bonding to the delta receptor. Additionally, computer simulations were performed to assess the effects of changes in receptor binding parameters obtained with the model. A constrained three-compartment kinetic model was demonstrated to be superior to other quantification models for the description of MeNTI kinetics and quantification of delta receptor binding in the human brain with C-11 labeled MeNTI.

SCHROEDER, Maria J., Assistant Professor, (co-author), "Segmental Relaxation of Poly(styrene-co-vinylphenol)," *Macromolecules*, 32(19), 6249-6253.

Dielectric and mechanical measurements of the α-relaxation for polystyrenes of varying vinylphenol content are reported. The presence of the polar moiety substantially increases both the glass transition temperature and the segmental relaxation times of the copolymer. However, the shape of the relaxation function, as well as the temperature dependence of the relaxation times, is invariant to copolymer composition. This indicates that the enhanced interactions arising from polar modification of the polystyrene are short-lived on the time scale of the segmental dynamics. Although fragility was found to be independent of copolymer composition, the heat capacity change at T_g increases with increasing vinylphenol content. The absence of a correlation between these two quantities is contrary to an energy landscape interpretation of fragility.

WHITAKER, Craig M., Assistant Professor, "Molecular Variables in the Self-Assembly of Supramolecular Nanostructures," *Macromolecules*, 2000, 33, 3550-3556.

Supramolecular structures have the potential to provide macromolecular behavior using relatively low molar mass building blocks. We present here data on the self-assembly of triblock rodcoil molecules which contain a rigid biphenyl ester segment covalently linked to structurally diverse oligomeric segments. These molecules form supramolecular aggregates with molar masses in the rang of 105 - 106 Da, and our experiments probe how supramolecular structure can be manipulated by varying the volume fraction of the coil-like flexible segments with respect to that of rod segments. Small-angle X-ray scattering scans revealed layer spacing corresponding to monolayers that increase in size as the coil's molar mass increases. We observed that an increase in coil rod segment length can counteract this effect. Finally, the self-organized nanostructures seem to pack into a superlattice based on evidence obtained by X-ray scattering and transmission electron microscopy.

Presentations

Bitterwolf, T. E. and SHADE, J. E., Professor, "Photochemical Reactions of Cyclopentadienyl Metal Carbonyl Dimers with Hydrogen. Evidence for a CO-loss Intermediate in the Formation of Metal Hydrides," 220th National Meeting of the American Chemical Society, Washington D.C., 20-25 August 2000.

CAMPBELL, W, Midn 1/C; HUDSON, I, Midn 1/C; VALENTINE, J, Midn 1/C; and HARTMAN, J.R., Assistant Professor, "Synthesis and Study of a Series of Amine Functionalized Silica Gels Made Via the Sol Gel Process," Eastern Colleges Science Conference, 1 April 2000.

CAMPBELL, Mark L., Associate Professor, "Temperature Dependent Rate Constants for the Reactions of Gas Phase Lanthanides with N_2O," XVIIth Conference on the Dynamics of Molecular Collisions, Lake Harmony, PA, 20 July 1999.

CHEEK, Graham T., Professor, "Electrodeposition of Niobium and Tantalum from a Room-Temperature Molten Salt System," 196th Electrochemical Society Meeting, Honolulu, HI, 20 October 1999.

CHEEK, Graham T., Professor, "Electrochemical Studies the Fries Rearrangement in Room-Temperature Molten Salts," Gordon Conference on Electrochemistry, Ventura, CA, 19 January 2000.

CHEEK, Graham T., Professor, "Investigations of the Fries Rearrangement of Phenyl Benzoate in a Room-Temperature Molten Salt," 33rd Middle Atlantic Regional Meeting of the American Chemical Society, Newark, DE, 16 May 2000.

COPPER, C.L., Assistant Professor, Boyd, T.J., and Callahan, J. "Isolation and Characterization of Metabolic Intermediates from Polycyclic Aromatic Hydrocarbon Biodegradation," Southeast Regional Meeting of the American Chemical Society, Knoxville, TN, October 1999.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Ionic Liquid, Graphite and Gel Polymer Electrolytes and Electrodes Using 1,2-Dimethyl-3-propyl-imidazolium Tetrafluoroborate," The Twelfth International Symposium on Molten Salts was held during the Joint International Meeting of the Electrochemical Society and the Physical Society of Japan in Honolulu, Hawaii, October 1999.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Electrochemical Studies of Metal Dichalcogenide-Polymer Composite Electrodes in 1,2-Dimethyl-3-propyl-imidazolium Tetrafluoroborate and 1-Ethyl-3-methyl-imidazolium Tetrafluoroborate," The Twelfth International Symposium on Molten Salts was held during the Joint International Meeting of the Electrochemical Society and the Physical Society of Japan in Honolulu, Hawaii, October 1999.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Electrochemical Intercalation Studies of 1,2-Dimethyl-3-propyl-imidazolium Tetrafluoroborate and 1-Ethyl-3-methyl-imidazolium Tetrafluoroborate in Graphite and Graphite-Polymer Composite Electrodes," The Twelfth International Symposium on Molten Salts was held during the Joint International Meeting of the Electrochemical Society and the Physical Society of Japan in Honolulu, Hawaii, October 1999.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Studies of Cation Transport in Molten Salts and Molten Salt-Polymer Gels by Pulsed-Field-Gradient Spin-Echo NMR," The Twelfth International Symposium on Molten Salts was held during the Joint International Meeting of the Electrochemical Society and the Physical Society of Japan in Honolulu, Hawaii, October 1999.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Electrodeposition and Pitting Corrosion behavior of Aluminum-Manganese Alloys deposited from Room Temperature Chloroaluminate Molten Salts," The Twelfth International Symposium on Molten Salts was held during the Joint International Meeting of the Electrochemical Society and the Physical Society of Japan in Honolulu, Hawaii, October 1999.

DE LONG, Hugh C., Major (USAF) and Assistant Professor, co-author, "Electrodeposition of Niobium and Tantalum from a Room-Temperature Molten Salt System," The Twelfth International Symposium on Molten Salts was held during the Joint International Meeting of the Electrochemical Society and the Physical Society of Japan in Honolulu, Hawaii, October 1999.

ELERT, Mark L., Professor, "Molecular Dynamics Simulation of Shock-Induced Chemistry in Acetylene," Conference of the American Physical Society Topical Group on Shock Compression of Condensed Matter, Snowbird, Utah, 27 June - 2 July 1999.

ELERT, Mark L., Professor, "Critical Widths in Molecular Dynamics Simulations of Detonations," Conference of the American Physical Society Topical Group on Shock Compression of Condensed Matter, Snowbird, Utah, 27 June - 2 July 1999.

ELERT, Mark L., Professor, "Detonation Hugoniots Produced by Piston-Driven Simulations," Conference of the American Physical Society Topical Group on Shock Compression of Condensed Matter, Snowbird, Utah, 27 June - 2 July 1999.

FITZGERALD, Jeffrey P., Professor, co-author, "Molecule-based Ferromagnets, Ferrimagnets, Metamagnets and Spin-Glasses," 219th ACS National Meeting, San Francisco, CA, 26 March 2000.

HARRISON, Judith A., Associate Professor, "Mechanical and Tribological Properties of Anchored Alkane Chains on Diamond," American Physical Society March Meeting, Minneapolis, MN, March 20-24, 2000.

HARRISON, Judith A., Associate Professor, "Atomic-Scale Tribology of Alkane Monolayers," National Institute of Standards and Technology Workshop on *Nanotribology Critical Assessment and Research Needs*, Gaithersburg, MD, March 13-15, 2000.

HARRISON, Judith A., Associate Professor, "The Tribology of Hydrocarbon-Containing Lubricants: The Role of Defects," Adhesion Society 23rd Annual Meeting, Myrtle Beach, SC, February 20-21, 2000.

HARRISON, Judith A., Associate Professor, "A New, Reactive Potential Energy Function to Study the Tribology of Hydrocarbon Systems," University of Maryland, College Park, MD, December 9, 1999.

HARRISON, Judith A., Associate Professor, "Mechanical and Tribological Properties of Anchored Hydrocarbon Chains on Diamond," University of Nebraska, Lincoln, NB, November 5, 1999.

HARRISON, Judith A., Associate Professor, "Atomistic-Scale Modeling and Molecular Dynamics for Nano- and Microstructures," National Science Foundation Workshop on *Nano- and Micromechanics of Solids for Emerging Science and Technology*, Palo Alto, CA, October 7-8, 1999.

HARRISON, Judith A., Associate Professor, "A Molecular Dynamics Investigation of the Atomic-Scale Friction of Hydrocarbon Self-Assembled Monolayers," 218th American Chemical Society National Meeting, New Orleans, LA, August 22-26, 1999.

HARRISON, Judith A., Associate Professor, "Using Molecular Dynamics Simulations to examine Adhesion and Tribology," National Science Foundation Workshop on *Model Based Simulation*, Washington, DC, June 24-25, 1999.

HARRISON, Judith A., Associate Professor, "Friction and Wear of Hydrocarbon Chains Anchored to Diamond Surfaces," Materials Research Society Workshop on *Tribology on the 300th Anniversary of Amontons' Law*, San Jose, CA, June 20-22, 1999.

HARRISON, Judith A., Associate Professor, "Molecular Dynamics Investigations of the Tribology of Hydrocarbon containing Systems," AFOSR/ONR/NSF Tribology Program Review, Islamorada, FL, June 13-18, 1999.

HEUER, William B., Associate Professor, co-author, "Supramolecularly Functionalized Hemicyanine Dye by Confinement in Helical Amylose," 4th International Symposium on Functional Dyes, Osaka, Japan, 31 May - 04 June, 1999.

HEUER, William B., Associate Professor, co-author,"Electronic/Photonic Property Modulations of D-*p*-D and D-π-A Chromophores by DTT as π-Center," 219th American Chemical Society National Meeting, San Francisco, CA, 26-30 March, 2000.

KINTER, Christopher M., Associate Professor and HENDRIX, John T., Midshipman 2/C (Poster), "Synthesis of [C-11]L-159,884: A Radiolabeled, Nonpeptide Angiotensin II Antagonist that is Useful for Angiotensin II, AT_1, Receptor Imaging," Eastern College Science Conference, Wagner College, New York, 1 April 2000.

LOMAX, Joseph F., Associate Professor, DILLNER, Debra K, Associate Professor, and STREIB, M. Andrew, Midshipman 3/C, "Midshipman Online Laboratory System: A web-published laboratory with CGI-based feedback of analysis," 218th American Chemical Society National Meeting, August 22-26, 1999, New Orleans, Louisiana, Abstract 183.

LOMAX, Joseph F., Associate Professor, DILLNER, Debra K, Associate Professor, and STREIB, M. Andrew, Midshipman 3/C, "Construction of the Midshipman Online Laboratory System: Web-based analysis and feedback structure," 218th American Chemical Society National Meeting, August 22-26, 1999, New Orleans, Louisiana, Abstract 118.

MCCLEAN, Roy E., Associate Professor, "Depletion Kinetics of Chromium Atoms by Sulfur Dioxide," presented at the 219th American Chemical Society National Meeting, San Francisco, California, 29 March 2000.

O'SULLIVAN, Daniel W., Assistant Professor, (Poster) "Hydroperoxide observations from the P3-B aircraft during PEM TROPICS B", NASA Science Team Meeting, Hampton VA, May 15, 2000.

SCHROEDER, Maria J., Assistant Professor, "Relaxation Processes in Polymer Blends and Copolymer Systems," *Gordon Research Conference on Elastomers, Networks, and Gels*, New London, New Hampshire, 20 July 1999.

SCHROEDER, Maria J., Assistant Professor, "Segmental Relaxation of Poly(styrene-co-vinylphenol) Copolymers," *155th Rubber Division (of the American Chemical Society) National Meeting*, Dallas, Texas, 5 April 2000.

SHADE, J. E., Professor, and Rest, A., "Synthesis and Matrix Isolation Studies of Isocyanide Iron Complexes," 220th National Meeting of the American Chemical Society, Washington D.C., 20-25 August 2000. Invited speaker: *Synthetic and Mechanistic Organometallic Chemistry* symposium in honor or Dr. Andrew Wojcicki.

URBAN, Joseph J., Assistant Professor, "Use of 3-D Molecular Models in Instructional Chemistry Web Pages" Curriculum Development Presentation, United States Naval Academy, Oct, 1999.

WHEAT, R.J., Midshipman 1/C, HARTMAN, J.R., Assistant Professor, PEARSON, W.H., Associate Professor, and Callahan, J.H. "Comparison of Gas and Solid Phase Structures for a Series of Ni(II) and Cu(II) Aminopyridine Complexes," Eastern Colleges Science Conference, 1 April 2000.