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24th AFOSR Chemistry

Program Review

FY-79

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FRONT COVER

The Air Force Office of Scientific Research and the Air Force Materials Laboratory are conducting a corporate research program to attain self-reinforced or molecular composites. The objective is the attainment of mechanical properties from polymers which are comparable with those now being obtained from fiber-reinforced composites, but without the use of fiber reinforcement. Differing from other known efforts to achieve superior properties through molecular orientation, this goal is being achieved with extended chain para-polymers possessing significantly higher thermal stability and greater environmental resistance than that exhibited by current structural composites. The high degree of order in terms of structure has been accomplished with para-configured polybenzobisthiazole (PBT) synthesized by Dr. James Wolfe of SRI International. A fractured PBT film, exhibiting a high degree of fibrillar structure in the direction of shear, is shown in the cover electron micrograph. In addition to excellent thermal stability and environmental resistance, the mechanical properties of PBT compare favorably with those of high performance steel and graphite fibers. For a detailed account of this research see "Highlights - Air Force Structural Chemistry" on page 23. Dr. Donald R. Ulrich, AFOSR, and Dr. Thaddeus E. Helminiak, AFML, are the focal points for this program.

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<p>This review provides a record of research in progress, along with illustrative achievements resulting from the basic research program of the Directorate of Chemical and Atmospheric Sciences, Air Force Office of Scientific Research (AFSC). The first section of the document contains articles written by each of the Chemistry Program managers at AFOSR plus a report on a typical in-house research project conducted at an AF lab and a survey of chemistry research in Europe. The second section contains program statistics. The third section lists research efforts completed in FY-79.</p>		

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24TH AFOSR
CHEMISTRY PROGRAM REVIEW
FY79



LORELEI A. KREBS, EDITOR

MARCH 1980

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)
DIRECTORATE OF CHEMICAL AND ATMOSPHERIC SCIENCES
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MISSION

The Directorate of Chemical and Atmospheric Sciences of the Air Force Office of Scientific Research has the mission to encourage and support fundamental research designed to increase knowledge and understanding to stimulate the recognition of new concepts, and to provide for early exploitation of their military implications.

The Directorate obtains and maintains for the Air Force a diversified program of research at in-house laboratories as well as extramurally at university and industrial laboratories. The Directorate also functions as a dynamic interface between the Air Force and the scientific community, ensuring the free, full, and constant interchange of ideas from each to the other through publications, personal contacts, meeting attendance, and sponsored symposia. In these ways, the Directorate helps the Air Force maintain technological superiority.

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March 1980

TO: FRIENDS OF AFOSR

Once again we are pleased at this opportunity to summarize program goals and accomplishments of the past year within the Directorate of Chemical and Atmospheric Sciences. Notably, during this period the name of the Directorate was changed to reflect the broadened responsibilities we announced with the previous edition of our annual review.

As always, time brings its changes in personnel assigned to the Directorate. Captain Lorelei Krebs, you will note, has assumed responsibility as editor with the 24th Review as well as the program manager for surface chemistry. Major Ted S. Cress has replaced Lieutenant Colonel William J. McKechney as directorate program manager for atmospheric sciences. Captain Russell A. Armstrong has now left military service and joined the Air Force Geophysics Laboratory as a civilian research scientist. Soon his duties will be assumed by Captain William G. Thorpe from the Frank J. Seiler Research Laboratory. Two major changes also occurred in our secretarial staff. Mrs. Iris Worley went on to another position outside AFOSR after some ten years of loyal, efficient, and valuable service. Fortunately, we have found an able replacement with the reassignment of Mrs. Eugenia Woodman from the Directorate of Aerospace Sciences. Mrs. Martha Bloom has joined our staff to replace Mrs. Annette Jones, who moved from the area.

Effective management of an agency research program requires, of course, two kinds of available resource - able staff and adequate funds. Fortunately I can be confident about both aspects. The recent and forecast trends in funding for the Air Force research program are favorable - "real" growth is expected (beyond the rate of inflation). If the research we support continues to be as successful as it has been in the past - and if we can effectively convince others of this fact - we can be optimistic about the future.

Sincerely,

A handwritten signature in cursive script that reads "Donald L. Ball".

DONALD L. BALL
Director of Chemical and
Atmospheric Sciences

A STATUS REPORT FROM ABROAD

Lt Colonel Charles J. LaBlonde*

During the past year the international chemistry program remained healthy in magnitude and scope. New contacts were established throughout Europe and the Middle East, some new projects were started, several symposia were supported, and a number of Window-on-Science travelers were sent to Air Force laboratories in the USA. The latter three items will be briefly discussed here; information pertaining to contacts made can be found in the "EOARD Quarterly Highlights."

NEW PROJECTS

An exciting new project in the field of multi-component glasses for optical fibers was begun with Professor Renata Reisfeld at the Hebrew University of Jerusalem. Purpose of the study is to develop multi-component glass which will have a high transparency in the 0.8 to 1.5 μm region of the spectrum. Combinations of oxides such as SiO_2 , B_2O_3 , P_2O_5 , GeO_2 and TeO_2 with alkali metals and alkaline earths will be prepared and doped with ions of Yb, Ga, In, Tl, Sb, Pb and Ce. The glasses will be irradiated using various sources; spectroscopic measurements (absorption and fluorescence) will be made before and after irradiation. Valence states of the dopants and the redox conditions in the glass melt which control the valence states will be controlled and systematically evaluated. Theories will be developed for the mechanism by which the various dopants affect glass transmissivity after exposure to ionizing radiation.

The interactions of hydrazine and hydrazine derivatives with soils is the subject of a new project with Dr. Michael Hayes, University of Birmingham, UK. Purpose of the study is to allow predictions about the types of interactions which should be expected when hydrazine, monomethylhydrazine or dimethylhydrazine enter the soil environment. To make such predictions would require a certain knowledge of soil composition and properties. In the event of accidental spills large concentrations of hydrazine would enter soils which might range in water content from saturated to nearly dry. The vaporized products could also be expected to interact with the soils. Hence it is necessary to study interactions between the adsorbate gaseous and solution phases and soils. Hayes assumes that interactions will take place principally with the soil colloidal constituents. For that reason, in order to measure the capacity of different soil colloidal constituents for the hydrazine products, to measure the strengths of binding, and to

investigate the adsorption mechanisms, initial work will concentrate on well characterized clays, oxides and hydrous oxides, and with fractions of humic substances. Desorption measurements will be made in all cases. When extending this work to actual soils, measurements of the uptake of hydrazine derivatives by different soils and by the colloidal isolates from these soils will be made. It must be borne in mind that clays, hydrous oxides, and humic substances can exist independently in soils, but they can also be intimately associated. For instance, hydrous oxides bound to clays can carry adsorbed humic materials. Thus Hayes proposes to make adsorption-desorption measurements on the total soil colloids, on the soil colloids minus humic substances, and on these colloids minus humic substances and oxides and hydrous oxides. Comparisons between the amounts taken up by the total colloid and by the residual materials after the different removals will allow predictions to be made about the components of that colloid which are most active in the binding processes. This will also focus attention on the importance of the "exposed surface" in so far as the binding is concerned.

A mini-grant at Oxford University with Dr. Tony Cheetham is concerned with magnetic ordering in solid oxide solutions. This phenomenon has been extensively studied by susceptibility and neutron diffraction, and the nature of the magnetic interactions in systems containing one type of paramagnetic ion is well understood. The current study will focus on the magnetic ordering characteristics of some simple oxide solutions in which two paramagnetic ions have competing anisotropies. Specific solid solutions to be investigated are the first transition series monoxides MnO, CoO and NiO. A systematic investigation of the NiO-CoO system will be carried out by powder neutron diffraction; parameters are temperature and composition. The result will be a complete magnetic phase diagram for the NiO-CoO system. Preliminary measurements will also be carried out on the MnO-CoO and MnO-NiO systems.

At the H. H. Wills Physics Laboratory, University of Bristol (UK), Professor A. Keller and Dr. E.D.T. Atkins are beginning a study of the orientability of rigid macromolecules. Hydrodynamically characterized elongational flow fields as developed and hitherto applied to flexible synthetic polymers will be used to study the chain alignment of these molecules. Materials will be supplied by AFML. The investigation of the solution behavior of these polymers, and in particular the scrutinization of the development and onset of nematic mesophases, using the above methods will supplement previous rheological examinations of these polymers in both dilute and concentrated solutions. Specifically the investigation should provide information on chain rigidity and chain association leading to long range nematic type liquid crystalline orientational order, and beyond that to the structure, texture and morphology of the resulting product as a function of the above orientation conditions. Further, the influence of all these factors on the mechanical properties will be assessed and optimized as far as possible.

SYMPOSIA

As pointed out in last year's "Chemistry Program Review," conference support is a very cost effective tool for meeting the top European names in a given field. Each year EOARD receives a large number of requests for support of meetings. The requests are carefully scrutinized to insure that the subject matter is relevant to Air Force interests, that the top names in the field will be at the meeting and that the meeting appears well organized. During the past year the following symposia were supported with EOARD mini-grants:

EUCHEM Conference on Molecular Spectroscopy, Cirencester, UK,
9-13 July 1979

VIIth Conference, International Association for the Advancement
of High Pressure Science and Technology, Le Creusot, France,
30 July - 3 August 1979

Sixth International Conference on Molecular Energy Transfer,
Rodez, France, 16-20 July 1979

WINDOW-ON-SCIENCE

One of the most powerful tools available to EOARD for use in transferring European technology to Air Force laboratories is the Window-on-Science program. Within the framework of this program top European scientists are invited to visit one or more labs where they present a seminar on their work and hold discussions with Air Force scientists active in their field. Window-on-Science visits are generally the first step towards long-lasting technical and personal friendships from which both the Europeans and the USAF benefit. During the past year the following Window-on-Science visitors were sent to AFSC labs:

Professor Alan Carrington	Southampton University, UK
Dr. Kurt Banholzer	Swiss Federal Testing Laboratories
Dr. Michael Dove	Nottingham University, UK
Dr. Malcolm Ingram	Aberdeen University, UK
Dr. David Husain	Cambridge University, UK
Dr. Roger Parsons	CNRS, France
Dr. Jehuda Yinon	Weizmann Institute, Israel
Professor Horst Czichos	BAM, Berlin
Dr. Joel Schamps	University of Lille, France

Laboratories benefiting from the visits of these scientists include AFGL, AFML, AFAPL, AFWL, AFRPL and FJSRL.

*Lt Colonel Charles J. LaBlonde is presently the Chief, Chemistry, for the European Office of Aerospace Research and Development (EOARD). EOARD is a detachment of the AFOSR located in London and, among other things, provides liaison with members of the scientific and engineering community in Europe, the Near East, India and Africa.

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AFOSR RESEARCH IN MOLECULAR DYNAMICS

CAPTAIN RUSSELL A. ARMSTRONG

The objective of the molecular dynamics program remains to enhance the fundamental understanding of the dynamic interaction of optical radiation, atoms and small molecules. Both experimental and theoretical efforts are involved; indeed we encourage cooperative theory/experiment approaches. As in the past, the program is divided into four general categories; chemical lasers, atmospheric chemistry, plume and wake chemistry and interactive dynamics. The last category has been renamed to more adequately reflect its content.

The chemical laser category is, perhaps, misnamed in that the intent of the program is not necessarily to make a laser. It is, rather to develop the fundamental understanding of chemical interactions that give rise to excited state populations which might be of interest as laser candidates. Of course, if in this process, one of our projects results in laser action, we are more than just dutifully excited about it. It is quite interesting that even though the HF chemical laser has been around for some time, there are still some outstanding fundamental questions, one of which is rotational non-equilibrium and the resulting relaxation phenomena. Drs. Jack Hinchey and Bob Hobbs at United Technologies Research Center are performing some excellent probe experiments and using the results to model the relaxation process. In related work, Dr. Lee Sentman at the University of Illinois is including the rotational non-equilibrium in investigating the coupling of the flow dynamics with the optical cavity for cw operation. Some very interesting time dependent oscillations have resulted. The concept of rotational non-equilibrium for the pulsed case is being investigated by Dr. Ron Kerber at Michigan State University in collaboration with a related experiment at the Air Force Weapons Laboratory. The agreement between theory and experiment is good to date. This particular interest in HF lasers notwithstanding, we are continuing our emphasis on new concepts in electronic transition lasers, specifically in metastable reservoir states and new excimer systems (exclusive of rare gas-halogen systems).

We are now continuing to place increased emphasis on the atmospheric related investigations. This is being driven to a large extent by the increased capabilities of the Air Force Geophysics Laboratory in optical detection and atmospheric sampling techniques. One of the very interesting efforts in this area is that of Dr. Bill Klemperer at Harvard University. His research group is looking at the structure of van der Waals molecules and their effect on macroscopic spectroscopy. A very recent and rather exciting discovery is that despite prior expectations

based on the similarity of N_2O and CO_2 , and despite the fact that the structures of $Ar-N_2O$ and $Ar-CO_2$ are nearly identical, the $HF-N_2O$ structure is clearly quite different from the $HF-CO_2$ structure. This has implications for other polar donors to complexes of atmospheric importance.

The area involving plume and wake chemistry continues to receive our attention. After several years of intensive investigation, a combination of experimental efforts at Yale University under direction of Dr. John Fenn (see 23rd AFOSR Chemistry Program Review) and Dr. Al Rahbee at AFGL along with a theoretical approach by Dr. Dudley Herschbach at Harvard and Dr. Mike Faist at Aerodyne are showing a pattern of $T \rightarrow V$ cross section for excitation versus relative velocity in explainable terms. Dr. Mike Redmon at Battelle Laboratory is looking at the problem in a more fundamental ab initio investigation and the marriage of the efforts should result in a highly useful predictive understanding of the phenomena.

The interactive dynamics area is so named as it has broad application to all of the above mentioned more directed areas. It is both experimental and theoretical in nature aimed at the fundamental interaction of optical radiation with atoms and molecules. One particular aspect of this problem is "At what point does molecular behavior become ergodic upon absorption of photons?" Dr. Simon Bauer at Cornell has begun a program to determine if one can apply some fundamental concepts to generalize an answer to this question or, if one cannot generalize, what molecular parameters must be specified in order to answer the question.

This year a contractors meeting was held at the Air Force Academy in Colorado Springs at which nearly all present Molecular Dynamics grantees and contractors presented their research. The meeting was a total success and the feedback has indicated that it was one of the better scientific meetings of the year. This is not so much a credit to AFOSR as it is a tribute to the principal investigators (and their students) that we support. No research program is a success without the total dedication to excellence of its investigators. I continue to believe that we have the best there is.

CHEMICAL TECHNIQUES

DENTON W. ELLIOTT

The Chemical Techniques program includes in its bailiwick the fields of electrochemistry and detection. The electrochemistry is obvious in its connotation, while that of detection is rather broadly described. It is concerned with new and improved analytical tools, new ideas, and the attainment of fundamental data that will assist in characterizing and testing various types of materials. It focuses on detection and measurement of trace quantities of matter and various chemical species. It is concerned with the identification of atomic and molecular structural effects, along with the attainment of basic information involved in energy distribution.

Some indications of recent research accomplishments in the Chemical Techniques area are here noted:

The field of flame diagnostics has made some significant strides with the advances in instrumentation and novel techniques, especially in the local sensing of chemical and physical phenomena and the parameters of flames. This should lead to improvements of experimental conditions in all types of atomic flame spectrometry and a better understanding of combustion processes, so important in the operation of jet engines and in energy production.

Professor J. D. Winefordner at the University of Florida has spent the major part of his scientific career in the study of flame chemistry. His contributions are too numerous to elaborate, but we shall dwell on his study of flames by at least one of his inventive techniques.

A flame is a free flow of principally gaseous matter of rather high temperature. The temperature is attained through conversion of chemical energy of the initial components into mostly thermal energy of the products. In order to recognize the limitation of the concept of temperature in a flame, it is necessary to compare the actual state of the gases with the state of thermodynamic equilibrium. A volume of gas is said to be in thermodynamic equilibrium at a temperature, T , when this temperature, T , describes:

- (i) the radiation density in the volume according to the Planck's radiation formula;
- (ii) the distribution of energy in the internal and external degrees of freedom of the gas according to the Maxwell-Boltzmann formula;
- (iii) the degrees of ionization and dissociation according to the Saha formula and mass action law, respectively.

Only when all of these requirements have been fulfilled, has the temperature, T , a unique meaning. To avoid confusion, "temperatures" are named after the processes to which they apply, e.g., translational temperature, T_{trans} , excitation temperature, T_{exc} (excitation can involve electronic states, $T_{exc,e}$, vibrational states, $T_{exc,vib}$, and rotational states, $T_{exc,rot}$), ionization temperature, T_{ion} , dissociation temperature, T_{dis} , and the radiational temperature, T_{rad} . The translational temperature, deduced from Maxwell's formula for the velocity distribution of particles is considered the most true temperature from which others deviate, because kinetic energy is established after the fewest number of collisions, say 10 collisions (at standard pressure). On the other hand, excitation temperatures (electronic, vibrational, or rotational) may be slightly too significantly different for every type of particle.

Temperatures of flames can be measured by a variety of techniques including line reversal, two-line emission, two-line absorption, Raman scatter, and two-line fluorescence. Of these, only Raman scatter and the two-line fluorescence techniques give temperature information for small flame volumes without the need to deconvolute the line of sight measurements taken at various flame positions. The two-line fluorescence technique has the advantage of increased signal level and signal-to-noise ratio over the Raman scatter methods, while also maintaining immunity from scatter.

Winefordner and his group developed the two-line atomic fluorescence method for the measurements of local flame temperatures of analytical flames and have applied it successfully to a variety of flames. Furthermore they have demonstrated that the technique is very useful for the measurement of temperature profiles and atomic intensity profiles in the flames. The advantages of the optical alignment and detection system in atomic fluorescence spectrometry have been proved and utilized in these works. It should be stressed here that the benefits, which make it possible to measure local flame temperatures and local atomic intensity profiles, are important and desirable for the study of flame diagnostics and also for local sensing of chemical and physical phenomena or parameters in the analytical flames.

The two-line fluorescence method involves excitation of an atomic probe, e.g., Pb, In, Tl, Ga, etc. which have low metastable electronic levels (3-level systems) in the flame. First excitation is at λ_{02} corresponding to excitation of the uppermost, 2, state via the ground, 0, state and measurement of the fluorescence occurring λ_{21} . Also, excitation is at λ_{12} corresponding to excitation of the upper most, 2, state via the metastable state, 1, and measurement of the fluorescence occurring at λ_{20} .

In a paper published in Applied Spectroscopy, Volume 31, Number 4, 1977, Winefordner et al, extended the two-line atomic fluorescence method to the measurement of full temperature profiles of air-hydrogen flames.

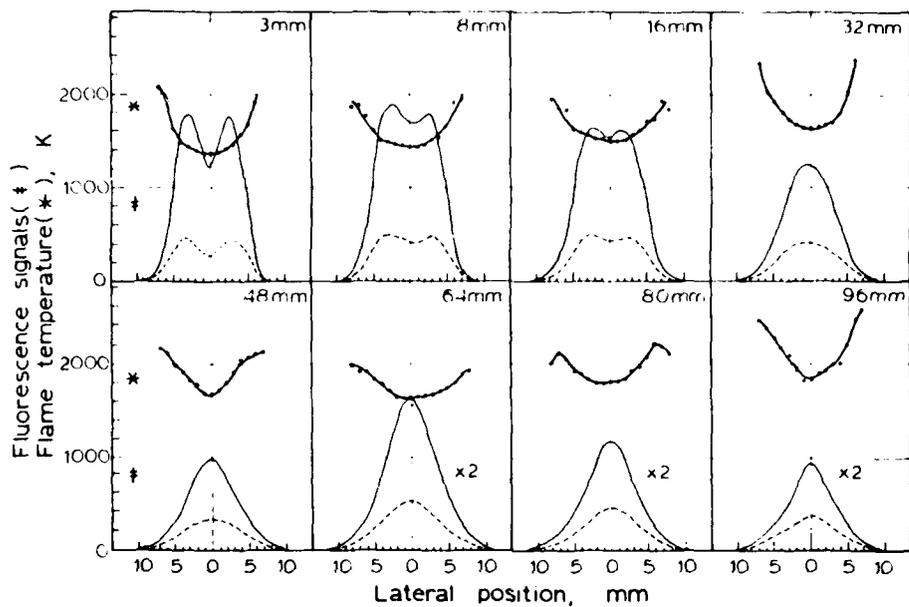


Fig. 1. Temperature profiles in the air-hydrogen flame (air: 7.6 liters min^{-1} ; hydrogen: 11 liters min^{-1}). The circles show the local temperatures at the positions where the calculations were carried out. The profiles below that of temperature show the radial profiles of the direct-line Stokes (—) and anti-Stokes (---) atomic fluorescence intensity at each vertical height.

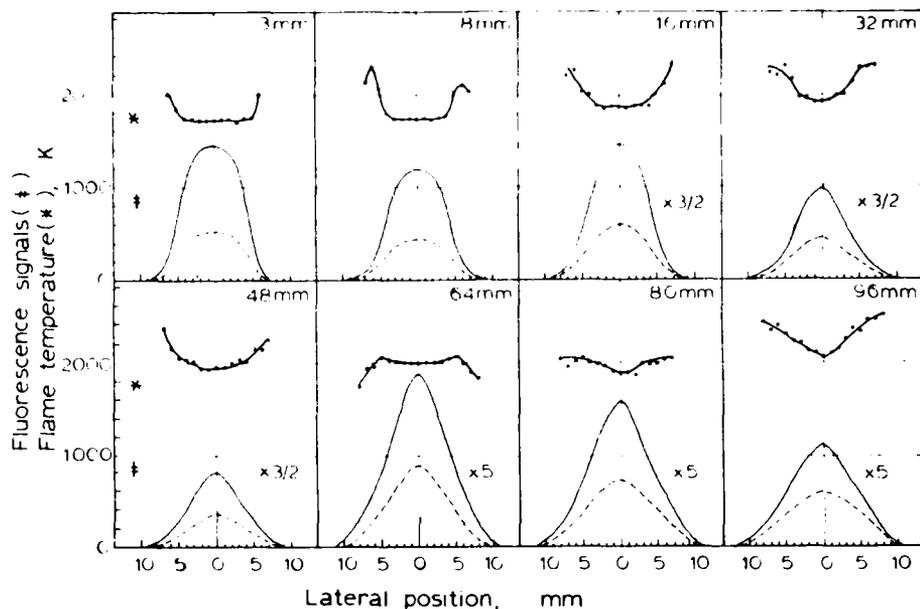


Fig. 2. Temperature profiles in the air-hydrogen flame (air: 7.6 liters min^{-1} ; hydrogen: 11 liters min^{-1}). The circles show the local temperatures at the positions where the calculations were carried out. The profiles below that of temperature show the radial profiles of the direct-line Stokes (—) and anti-Stokes (---) atomic fluorescence intensity at each vertical height.

In Figures 1 and 2, the lateral temperature profiles of the air-hydrogen flames with two different flow rates of hydrogen at several vertical positions are shown along with the Stokes and anti-Stokes direct-line atomic fluorescence intensity profiles, which were used for the calculations of flame temperatures. The use of indium Stokes (411.18 nm) and anti-Stokes (450.13 nm) atomic fluorescence lines is preferable to the use of thallium lines for the measurements of local flame temperature below ca. 2500°K. It is known that air-hydrogen flames give maximal flame temperatures of ca. 2200 to 2300°K. Therefore, indium fluorescence lines were used for flame temperature measurements in the experiment. The fluorescence intensity profiles used for the temperature calculation were observed by using the optical excitation beam (a 150 W Eimac xenon arc lamp) size of 5 mm, the monochromator entrance slitwidth of 300 μm , and the vertical aperture (in front of

monochromator entrance slit) of 2 mm. Therefore, the flame temperatures were obtained at the spatial (volume) resolution of 5 by 0.3 by 2mm. A solution of indium with the concentration of 50 μg per ml and a capillary burner having a 10 mm diameter were used for all measurements of atomic fluorescence intensity profiles for both lines. Flame temperatures were calculated by using the following equation

$$T_f = \frac{5040V_1}{\log \frac{E_{\lambda_{12}}}{E_{\lambda_{02}}} + 6 \log \frac{\lambda_{20}}{\lambda_{21}} + \log \frac{E_{f12}}{E_{f02}}}$$

The spectral irradiance ratio, $E_{\lambda_{12}}/E_{\lambda_{02}}$, was obtained by the measurement of the outputs of the Eimac lamp at two wavelengths (λ_{20} and λ_{21}), and the ratios of Stokes and anti-Stokes direct-line atomic fluorescence, E_{f12}/E_{f02} , were determined from the intensity profiles shown in Figs. 1 and 2. As can be seen in Figs. 1 and 2, the calculations of the temperature were carried out at radial positions increasing by 1 mm increments from the center to distances of 7 or 8 mm from the center.

The temperature profiles of an air-hydrogen flame with air and hydrogen flow rates of 7.6 and 11 liters min^{-1} , respectively, are shown in Fig. 1. The fuel/oxidant ratio (H_2/O_2) of the flame in Fig. 1 is ca. 7, i.e., the flame is very fuel-rich. In this flame, the radial temperature profiles at all the vertical positions, i.e., 3 to 96 mm, show minimal temperatures at the center of the flame, whereas the temperature increases in the outer region of the flame. The minimal temperature at the center of the flame was obtained at the lowest flame height observed, i.e., 3 mm above the burner head, where the flame temperature was in the range 1400 to ca. 2000°K. In all of the radial temperature profiles, the flame temperature near the flame fringe was about 2000 to 2200°K. The temperature at the flame center increased from 1400°K at a height of 3 mm to 1850°K at 96 mm. However, the temperature at the flame center at a height of 96 mm was still lower than those near the flame fringes studied, indicating that entrained air plays an important role in determining the temperature profiles of this fuel-rich flame.

The temperature profiles of an air-hydrogen flame with the air and hydrogen flow rates of 7.6 and 8 liters min^{-1} , respectively, are shown in Fig. 2; the fuel/oxidant ratio of the flame is ca. 5.3, and so this flame is less fuel-rich. The decreased supply of fuel resulted in flame temperatures at all flame heights being higher by about 200 to 300°K, compared to the more fuel-rich flame shown in Fig. 1. However, lower flame temperatures in the central region of the flame are also observed, although the temperature differences become smaller above a height of 64 mm. Furthermore, the flame temperatures at all flame heights except for those near the fringes between 16 to 48 mm high

are lower than the reported maximal temperature of the air-hydrogen flame, indicating that the oxidant (supplied air + entrained air) in the flame is still insufficient to obtain complete combustion in the present flame. Because the maximal literature flame temperature can be obtained in the outer region of the flame between 16 to 48 mm high, complete combustion may be occurring in those regions due to presence of entrained atmospheric air. The flame temperature near the fringe above the 64 mm high decreases again probably due to the cooling of the flame by the unheated atmospheric air.

In summary the principle of the two-line atomic fluorescence method is based on the use of typical 3-level systems (Tl, In, Ga, Pb) characterized by a metastable level not optically coupled with the ground level. The method senses the thermal population of this metastable level by observing the ratio between the Stokes Direct Line Fluorescence (SDLF) and the Anti-Stokes Direct Line Fluorescence (ASDLF) signals obtained when the fluorescence level is reached by excitation both from the ground and the metastable state. The schematic diagram pertaining to these processes is depicted in Figure 3. V_1 is the excitation potential of the metastable state.

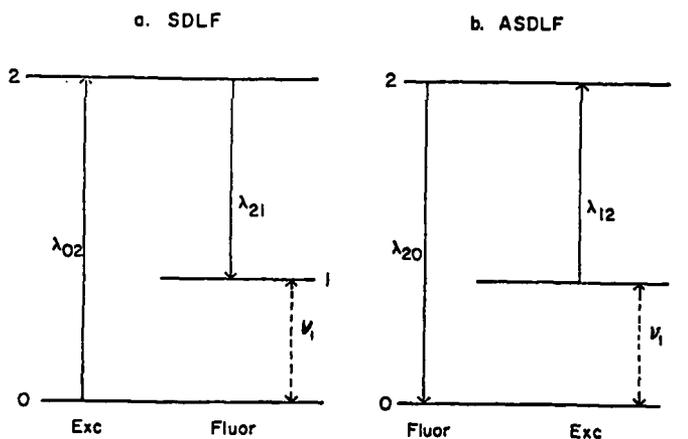
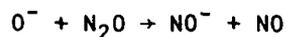
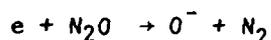


Figure 3

Professor Robert E. Sievers and Michael P. Phillips of the University of Colorado have conceived a novel method for making electron capture gas chromatographic detectors respond more sensitively to compounds which cannot ordinarily be readily detected.

They have demonstrated that it is possible to cause electron capture detectors to be highly sensitive to compounds not normally producing significant responses by the simple expedient of adding a few parts per million of nitrous oxide to the nitrogen used as a carrier gas. This was accomplished by clever application of the following ion-molecule chemistry. In the absence of other eluting gases the following reactions are important in an electron capture detector with the special doped carrier gas devised and studied by Mr. Phillips:



It should be noted that so long as other reactants do not interrupt this reaction sequence there is no net loss of electrons; i.e., each electron emitted from the ^{63}Ni foil which reacts with N_2O in the first reaction is regenerated in the final reaction. Consequently, there is no appreciable loss of electron density, unless some of the intermediates undergo other reactions. O^- and NO^- are quite reactive species, however, and undergo rapid reaction with many compounds that one would like to be able to detect at very low concentrations in the carrier gas eluent from chromatographic columns. For example, O^- reacts readily with compounds such as methane, ethane, propane, butane, pentane, carbon dioxide, hydrogen, and numerous others. They have been able to demonstrate that, by using nitrous oxide as a sensitizer in the carrier gas, they can increase greatly the sensitivity with which many compounds can be seen by electron capture gas chromatography. For example, they were able to detect picogram levels of hydrocarbons, and increased by several orders of magnitude the sensitivity towards certain other compounds over that in the absence of the nitrous oxide. Apparently O^- is the reactant species that is destroyed to interrupt the regeneration of electrons in the reaction scheme above, causing a decrease in free electron density and producing the detector signal. In the following example hydrogen is detected in the sensitized electron capture detector because O^- is removed by the following reaction:



The practical ramifications of this research are very far-reaching. By simply switching from pure nitrogen carrier gas to nitrogen containing nitrous oxide it will be possible to detect many compounds with

unprecedented sensitivity. They have demonstrated that, even though electron capture detectors are normally inferior to flame ionization detectors for non-electrophilic compounds such as hydrocarbons, the situation can be reversed with nitrous oxide sensitization. They have also been able to detect hydrogen at very low concentrations in ambient air samples. Carbon dioxide does not normally produce a significant response in either electron capture or flame ionization detectors. However, they have shown that it can be readily detected at very low levels in the presence of nitrous oxide.

They call this technique Selective Electron Capture Sensitization (SECS). Since Lovelock's initial description of the electron capture detector in the late 1950's many workers have done much research to form stable electrophilic derivatives of various compounds to improve the sensitivity with which they can be detected. These almost invariably require time-consuming procedures to form derivatives and separate reactants before injection into the gas chromatographic apparatus. The beauty of the SECS method is that the chemistry all takes place effortlessly and essentially instantaneously in the detector cell. One can predict that soon after the work is published it will be used for certain analyses in most of the analytical laboratories throughout the world that are equipped with electron capture detectors.

For further details concerning this technique see Journal of Chromatography - 1979 Elsevier Scientific Publishing Company, Amsterdam.

SURFACE CHEMISTRY

CAPTAIN LORELEI A. KREBS

AFOSR maintains a modest research effort in Surface Chemistry, Task 2303/A2. The broad objective of this task is to provide increased understanding of the properties and chemical interactions of surfaces with gases, liquids, and absorbed solids. This knowledge contributes to the many materials limited technologies which are vital to the operational readiness of the Air Force, such as solid state, metallurgy, tribology, mechanics, and propulsion.

Three major problem areas of the Air Force serve as focal points for the AFOSR sponsored research in surface chemistry -- corrosion, lubrication, and adhesion. I will discuss the overall objectives, highlight some of the current programs, and present the new work efforts for each of these areas.

Corrosion

Corrosion is a serious problem to the Air Force affecting operating efficiency, resource conservation, personnel safety and combat readiness, not to mention the millions spent on preventative maintenance and replacement costs. In the AFOSR Surface Chemistry program advanced surface analytical and electrochemical techniques are used to explore the chemical nature of high strength metal surfaces under corrosive attack. Conversely, the various aspects of corrosion control and prevention -- cleaning, passivation, inhibitors, coatings, and films are also of interest.

During FY79, Dr. Theodore Beck of Electrochemical Technology Corporation finished a successful three year effort investigating, both theoretically and experimentally, the mechanisms for corrosion initiation under paint films. An abstract of his work and a publications list are included among the project summaries.

Dr. Gary Stupian and coworkers at Aerospace Corporation have been looking at protective coatings from another angle. Their work involves the search for improved, environmentally acceptable alternatives to the standard chromate conversion coatings now used on aircraft aluminum. Using a conceptual model for corrosion protection of a metal by a surface oxide, they have investigated several solution-deposited oxide systems. There are two general types of systems: those in which the deposition cation species changes oxidation state, and systems in which a change in oxidation state does not occur. Chromate coatings typify the former category. Generally speaking, film-forming cations in this

category can actively react with aluminum metal and thus potentially can create a thick region of mixed oxides. Vanadium, manganese, molybdenum and niobium alkoxides all form films on aluminum by changing their oxidation state. The vanadium system was extensively studied. It penetrates into approximately 100 Å depth of the aluminum oxide film and the resulting corrosion resistance is about two thirds that of the chromate coatings.

Titanium, silicon, indium, tantalum and zirconium also produce mixed oxide films but do not change oxidation state. A model for these systems was developed after extensive work with titanium tetrabutoxide. It is suggested that water promotes coating formation by participating directly in the growth of the oxide film: by oxidizing additional aluminum; and also by causing partial polymerization of the titanium alkoxide.

Ion implantation is another method of modifying surfaces to increase resistance to corrosion. Drs. Stevenson, Legg and colleagues at Georgia Tech are studying high dose ion implantation of Ti, Al, and Ti-Al alloys. Initially they have investigated the effects of implants on grain growth in titanium. Ti samples implanted with erbium (total dose of 5×10^{15} ion cm^{-2}) were annealed at 750°C and the grain structure was studied using optical metallographic techniques. Data showed the erbium inhibits grain growth on both the implanted and surrounding regions. Moreover, the observed segregation and diffusion of the erbium was in agreement with theoretical calculations. Platinum implants have also been found to inhibit grain growth.

Future work in this program will include depth profiling using Rutherford backscattering, AES to monitor oxidation states and the thermobalance to check for weight gain measurements. A cw far IR laser was recently put into operation and will be used to study oxide formation.

A new program using Electron Energy Loss Spectroscopy (EELS) will be starting in May at the University of Texas - Austin. Dr. J. Erskine and Dr. M. White will be using EELS in conjunction with other surface sensitive tools to obtain a firm molecular level description of the structure and reactivity of species on Al and Ti surfaces which have controlled numbers of chemical and physical defects.

Lubrication

The Air Force is continually seeking to develop improved lubricants which are resistant to failure under severe operating conditions. Thus, an understanding of how the molecular structure and property

relationships of fluids in contact with wear surfaces are effected by their thermal and chemical environment is critical.

Dr. J. Lauer at Rensselaer Polytech is looking at the emission spectra produced by lubricants in his unique sliding contact bearing (described in last year's review article). He has reported dramatic changes in the polarized emission spectra of polyphenyl lubricants under conditions conducive to bearing failure. He relates these spectral differences to changes in molecular alignment and other physical properties of the lubricant film.

Considerable progress has also been made in the past year on the experimental determination of the effects of water and oxygen on the rupture strength of boundary films. Drs. Drauglis and Snediker at Battelle's Columbus Laboratories have studied the effects of oxygen on di-2-ethylhexyl sebacate films in the presence of high humidity (65-70%) under various partial pressures of oxygen and concentrations of tricresyl phosphate (anti-wear additive). Post-experiment observations of the specimens by SEM, ESCA, and FTIR revealed the presence of inclusions on the iron surface. These may be nuclei for the chemical reactions responsible for the formation of films. Moreover, ESCA and FTIR analyses indicate that the films are almost exclusively inorganic phosphates.

Two new research efforts in lubrication will be starting this spring. Jakobsen and Drauglis at Battelle's Columbus Laboratories will be using FTIR and a diamond anvil pressure cell to gain a more thorough understanding of the phase changes in straight-chain hydrocarbons, straight-chain aliphatic acids and solutions of these compounds. In particular they will study the effects of high pressure and temperature, composition (in the case of solutions), and chemical nature of the walls of the cell containing the specimen. The data obtained will be of great potential not only in broadening our understanding of the basic physics and chemistry of hydrocarbon - aliphatic acid systems, but also have great potential in practical problems involving the development of better boundary lubricants.

Dr. L. Mahoney and associates of Ford Motor Company have just completed a three-year research effort on lubricant deterioration and wear phenomena occurring in lubricant systems exposed to oxidative environments at high temperatures (ref. project summaries). Complementary to this work their new research effort will study the deterioration reactions of the ester and of n-hexadecane, a model hydrocarbon lubricant at reduced oxygen pressures, 20 kpa and lower. The results derived from low oxygen pressure studies will not only provide a technical basis for improvements in practical lubrication systems operating under ambient oxygen pressures but will also yield basic information on an important but unexplored area of free radical chemistry.

Adhesion

Our interests in this subtask are: the characterization of surfaces prepared for adhesive bonding; an understanding of the reactions between substrates and bond agents; an understanding of the effects of load, temperatures, and environment on bond failure; and the identification of bond failure mechanisms. We have three current research efforts in the adhesion area.

Drs. Lando and Rogers at Case Western Reserve are working to create ordered coupling agent interfaces on glass fiber and graphite fiber substrates. These substrates will then be bonded to a polyester or epoxy matrix and deformation of the adhesive bond will be investigated using a nanotensileometer. The effects of moisture and temperature on the bond strength will also be examined.

At Martin Marietta Laboratories, Dr. Chen and colleagues are using STEM, AES, with depth profiling, XPS, and electrochemical methods to study the oxide morphology and growth mechanism of Al specimens anodized in phosphoric acid solution (PAA). Results indicate that the growth of PAA oxide films is a two-stage process - a fast linear growth stage during which the pore cell structure develops, followed by a slower growth stage during which whiskers are formed on top of the cells. In addition, there was substantial evidence of a field-assisted dissolution process during pore growth. Electron diffraction analysis of oxide films produced by PAA, CAA and FPL (commercial anodization processes) revealed totally amorphous structures. The boehmite (hydrated crystal) structure was found only in hot-water treated specimens. Plans for future work include a study of environmental effects on oxide properties.

And, finally, Drs. Sung and Sung from MIT and Tufts are focusing on the critical question of whether and how any bonding (chemical, ionic or hydrogen bonding) occurs at the interfaces of coupling agents/ sapphire and coupling agents/polymer, and their effects on adhesive joint strength. Experimentally, first, sapphire surfaces will be characterized more rigorously, especially with the objective of cleaning carbon contamination off, and thin layers ($\sim 25\text{\AA}$) of the coupling agent film will be studied by FT-IR and ESCA. Secondly, any interaction of the coupling agents with polymer matrix will be studied. The last part of the research will be directed toward an investigation of the interrelation between the structure of the interface and the joint strength measured by 180° peel strength.

In addition to silane coupling agents, organic titanates will be included as another class of coupling agents, and also E-glass fibers will be studied as a substrate.

Meetings

Three conferences were supported, in part, by the AFOSR Surface Science task during FY79. The technical and societal aspects of war and corrosion were presented at the National Symposium on Wear and Corrosion sponsored by the Division of Industrial and Engineering Chemists of the American Chemical Society. Dr. Ralf Vanselow of the University of Wisconsin-Milwaukee once again hosted the highly successful biennial Summer Institute of Surface Science. We also provided support for the Symposium on Applied Surface Analysis held at the University of Dayton. This somewhat unique meeting was chaired by Dr. John T. Grant and coordinated through Dr. T. W. Haas of the AF Materials Laboratory.

This meeting was significant because it brought together both basic researchers and applications oriented surface scientists. Due to the favorable response from the scientific community, the University of Dayton plans to repeat this symposium in June 1980.

HYDRAZINE FUELS RESEARCH

DR. ANTHONY J. MATUSZKO

The chemical research supported by AFOSR is generally looked upon as long range basic research which could be useful in solving Air Force problems of the future (10, 20, 30 years from now and longer). Sometimes, there is a need to help solve more immediate problems. The following is a brief historical account of how the Directorate of Chemical and Atmospheric Sciences got involved and participated in a near term Air Force problem area.

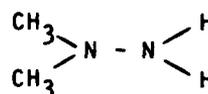
Unsymmetrical dimethylhydrazine (UDMH) is an important component of several liquid rocket fuel mixtures. Its principal use in the Air Force has been in the Titan II and Titan III rockets. Smaller quantities are needed in Army, Navy, and NASA propulsion systems. Hydrazine itself is a widely used high energy fuel; most recently it is the fuel used in the emergency power unit for the F-16. Monomethylhydrazine (MMH) is an important component of the fuel for the space shuttle.



Hydrazine

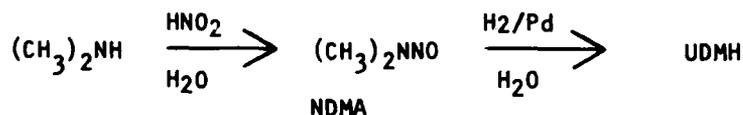


MMH



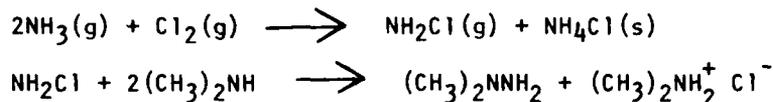
UDMH

Over the years, the Air Force has had the responsibility for the acquisition of hydrazine fuels for the three services and NASA. Up until 1975, UDMH had been economically produced by the nitrosation of dimethylamine and hydrogenation of the nitroso intermediate to the desired product.



The overall yield was good. Unfortunately, the intermediate, N-nitrosodimethylamine (NDMA) proved to be very toxic and was determined to be a human carcinogen. Accordingly, its use and worker exposure was severely limited by the Occupational Safety and Health Administration. These restrictions led to the abandonment by the manufacturer of the nitroso process for producing UDMH, thereby cutting off the only commercial source of this important rocket fuel.

In the search for a new manufacturing process, a method which had been worked on by Sisler and coworkers at the University of Florida involving the chloramination of amines was examined by the Air Force. The main reactions involved were the following:



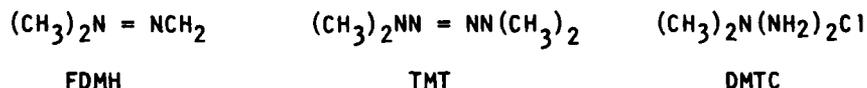
The nitrosamine carcinogen was not involved in the reactions. Additionally, both UDMH and MMH could be made by this reaction sequence.

Martin Marietta was awarded a contract by the Air Force Space and Missiles Systems Organization (SAMSO) to study the economics and feasibility of scaling up the chloramination process. It soon became evident that very little information was available pertaining to the kinetics and mechanisms of the various reactions leading to the desired products as well as the many undesirable reactions taking place. AFOSR was asked by AFSC to assist SAMSO with basic research to help resolve some of these problems.

On hand at the time was an unsolicited joint proposal from Professor Harry Sisler of the University of Florida and Dr. William McQuiston of the Naval Surface Weapons Center entitled "Basic Studies Relating to the Synthesis of Unsymmetrical Dimethylhydrazine and Monomethylhydrazine by Chloramination" which addressed these problems. A program was initiated in the fall of 1975 to do basic research on the kinetics and mechanisms of reactions of the chloramine process (Sisler process) for synthesizing UDMH and MMH.

The mechanism study undertaken at the U. of Florida was aimed at acquiring a better understanding of the mechanisms involved in the formation of the desired reaction products as well as the undesirable side products. Knowledge concerning the mechanisms would be useful in optimizing conditions for obtaining the best yields in the synthesis of UDMH and MMH by the chloramination process.

The findings of the U. of Florida research showed that the reaction between dimethylamine and chloramine formed, in addition to UDMH, at least three major side products. These side products were formaldehyde dimethylhydrazine (FDMH), tetramethyl tetrazene (TMT), and dimethyl-triazanium chloride (DMTC).



It was established that the side products were the result of the reactions of chloramine with the UDMH formed. More detailed accounts of the research results may be found in articles published in the journal *Inorganic Chemistry*, V 16, N 8, p 2043 (1977) and V 18, N 9, p 2350 (1979).

In the kinetic study done at the Naval Surface Weapons Center a stopped flow reaction system was assembled and used to measure the rate of formation of UDMH in anhydrous organic solvents (chiefly chloroform) in the temperature range 15°-30°C. Reaction rates and an activation energy of 9.8 kcal/mole were derived from these measurements. Bench-scale and modeling experiments showed that the reaction rate for the formation of the hydrazone is about 600 times that for the formation of UDMH at 0°C. The second order kinetics model for these consecutive reactions indicated and experiment showed that the concentration of UDMH quickly reaches a steady-state value while the yield of the hydrazone steadily increases with chloramine addition. The conclusions arrived at from this investigation were that large-scale production of UDMH in anhydrous organic solvents by chloramination of dimethylamine did not appear feasible at practical temperatures because of the low ratios (<.3) UDMH to hydrazone obtained in the experiments.

While the AFOSR studies were going on, UDMH and MMH became once again readily available to the Air Force from other commercial sources. The Martin Marietta scaleup operation was discontinued. Nevertheless, the information obtained from the AFOSR research should be useful in any future considerations for alternate sources of UDMH and MMH.

HIGHLIGHTS AIR FORCE STRUCTURAL CHEMISTRY RESEARCH

DR DONALD R. ULRICH

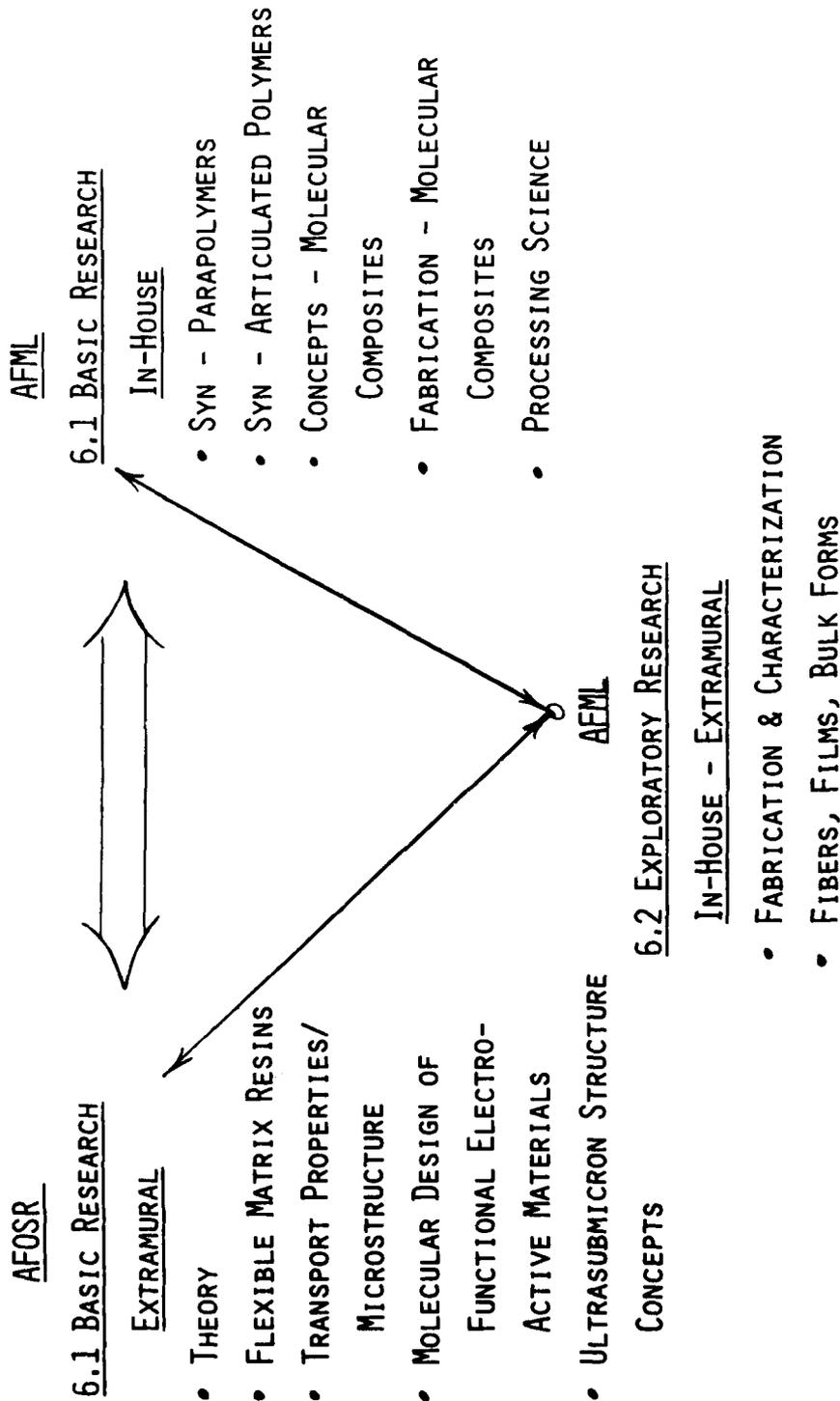
The Structural Chemistry program sponsors research in the chemistry of structural, electromagnetic and containment materials. The objective is to relate processing and properties - mechanical, thermal, physical and rheological, chemical, optical and electrical, and environmental - to bulk and surface structure from the molecular to the microstructural level in nonmetallic materials. The emphasis has been on polymers, glass and glass-ceramics, carbon fibers and carbon-carbon composites, and solid state chemistry.

During FY 79, research on the processing science of carbon-carbon composites neared completion, and transition of the results and work to the Air Force Materials Laboratory was initiated. Phase down of the solid state chemistry research was undertaken as the process of introducing chemical physics into the polymer program was accelerated. This is part of an investment strategy thrust in the microscience or microstructural science of polymers, glass and ceramics for ultrasub-micron structures which will receive increased emphasis and out-year funding. Materials chemistry research for the near future then will emphasize work units in polymer science and the chemistry of glass and ceramics, including powders and particulates.

The Air Force Materials Laboratory and AFOSR are conducting a corporate research program to attain self-reinforced or molecular composites. The organization and interaction of this thrust is schematically illustrated in Figure 1. The unique concept demonstrated here is that AFOSR research in theory, advanced materials, and the molecular design of structure is iteratively interacting with AFML basic and exploratory research in synthesis, processing fabrication and characterization. The AFOSR effort includes principal investigators at Stanford University (Prof Paul Flory), Carnegie-Mellon University (Prof Guy Berry), SRI International (Dr James Wolfe), University of Virginia (Profs Barker and Lawless), The University of Massachusetts (Prof Frank Karasz), and the University of Cincinnati (Prof James Mark).

The long range objective is attainment of mechanical properties from polymers which are comparable with those now being obtained from fiber reinforced composites, but without the use of a fiber reinforcement. (Figure 2). Differing from other known efforts to achieve superior properties through molecular orientation, this goal is being sought with para-polymer materials possessing significantly higher thermal stability and greater environmental resistance than that exhibited

FIGURE 1
 AFOSR / AFML CORPORATE THRUST
 ORDERED POLYMERS



by current structural composites. Besides greater environmental resistance, the prospective pay-offs for processable ordered polymer systems include the possibilities of simpler processing or fabrication methods, elimination of the fiber-matrix interfaces, improved engineering approaches, and better quality control or inspection.

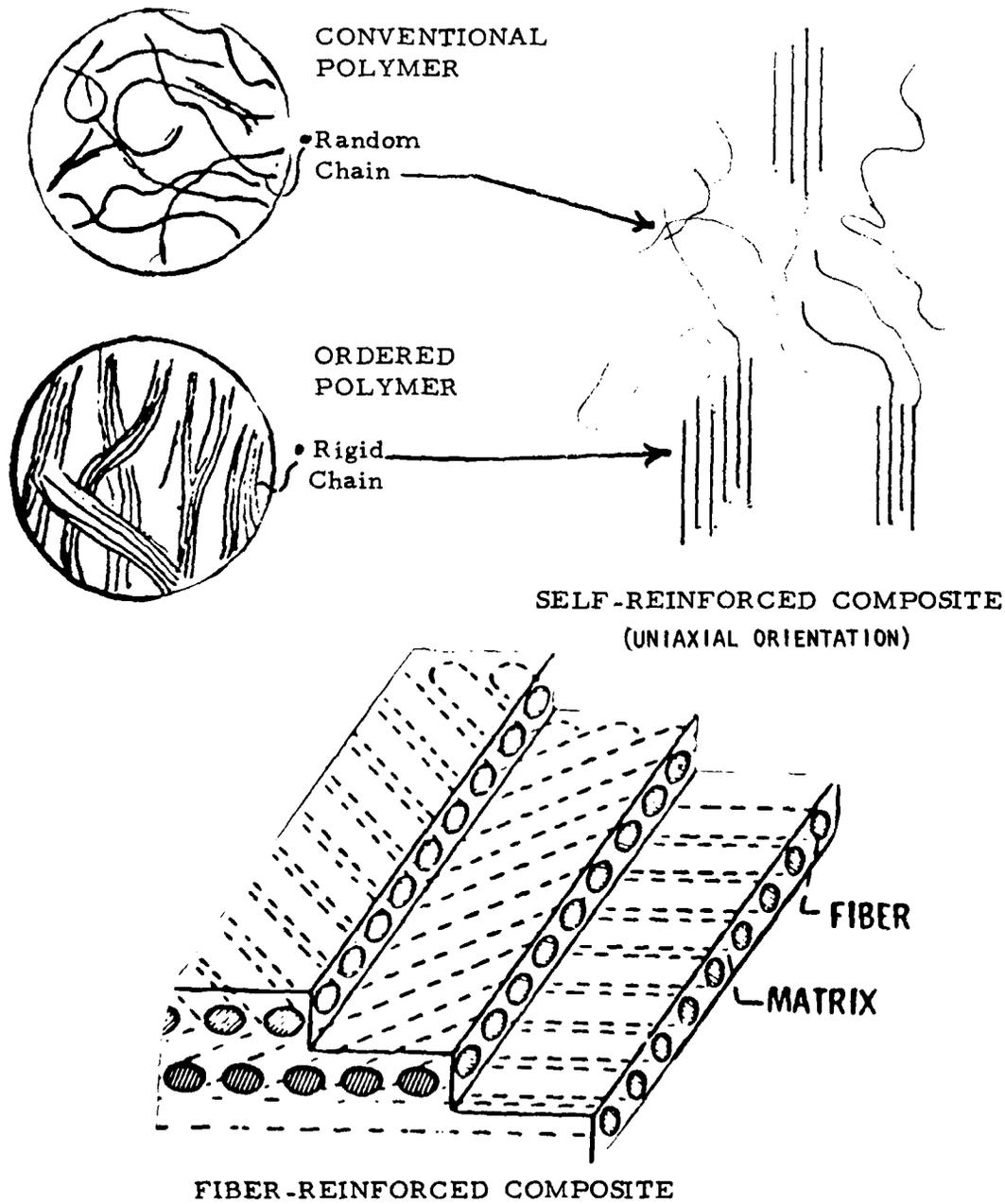
The rigid chain structure can schematically be shown by an "uncooked spaghetti model," while conventional polymers with their unaligned random chains can be represented as a "cooked spaghetti model." (Figure 2). The high degree of order in terms of structure is being accomplished with a para-configured polybenzothiazole (PBT) synthesized by Dr. James Wolfe of SRI International and Dr. Fred Arnold of AFML. Dr. Wolfe has defined the necessary controls for the reproducible preparation of the rodlike polymer poly {benzo(1,2-d:4,5-d')bisthiazole-2,6-diyl}1,4-phenylene}. Bulk forms with a high degree of fibrillar structure in the direction of shear were prepared from PBT/PPA solution. A fractured PBT film is shown on the front cover. The high purity and stability of the polymer now being produced in the program is demonstrated by the excellent isothermal aging weight loss cure (Figure 3) obtained at 371°C (700°F) as compared with another para-polymer polybenzothiazole (PBO) and an aromatic benzamide polymer. These fibers, when heat treated at 475°C for 64 seconds and stretched 4%, have a modulus and tenacity of tensile strength as high as 47×10^6 psi (2,330 g/denier) and 5×10^7 psi, (25 g/denier) respectively. This compares favorably with high performance steel with a typical modulus of 28×10^6 psi and a tensile strength of 3×10^5 psi, or graphite fibers for advanced structural composites with a modulus of 28×10^6 psi and a tensile strength of 4×10^5 psi.

Research is being pursued based on the concept of producing a composite composed of rod-like polymer molecules and coil-like polymer molecules in which the rods act as reinforcement for the coils much like chopped fibers reinforce a resin matrix. (Figure 2). Early experimental work by Drs. T. Helminiak and G. Husman of AFML has shown that the mechanical properties of an amorphous matrix can be improved by rod-like para-polymer molecules.

Dr. Wolfe is now investigating the chemistry of several monomers that form the benzothiazole unit and studying the effects of various synthesis parameters on the formation of high molecular weight, wholly aromatic polymers containing benzothiazole units. This is to provide chemically compatible flexible matrices for the rod-like benzobisthiazole polymer PBT.

Experimental and theoretical iterative interaction has continued between Dr. Robert Evers of AFML, Dr. Paul Flory of Stanford University and Dr. James Mark of the University of Cincinnati in the design and synthesis of articulated polymers, rod-like polymers with a controlled

FIGURE 2
CONCEPT OF MOLECULAR COMPOSITE



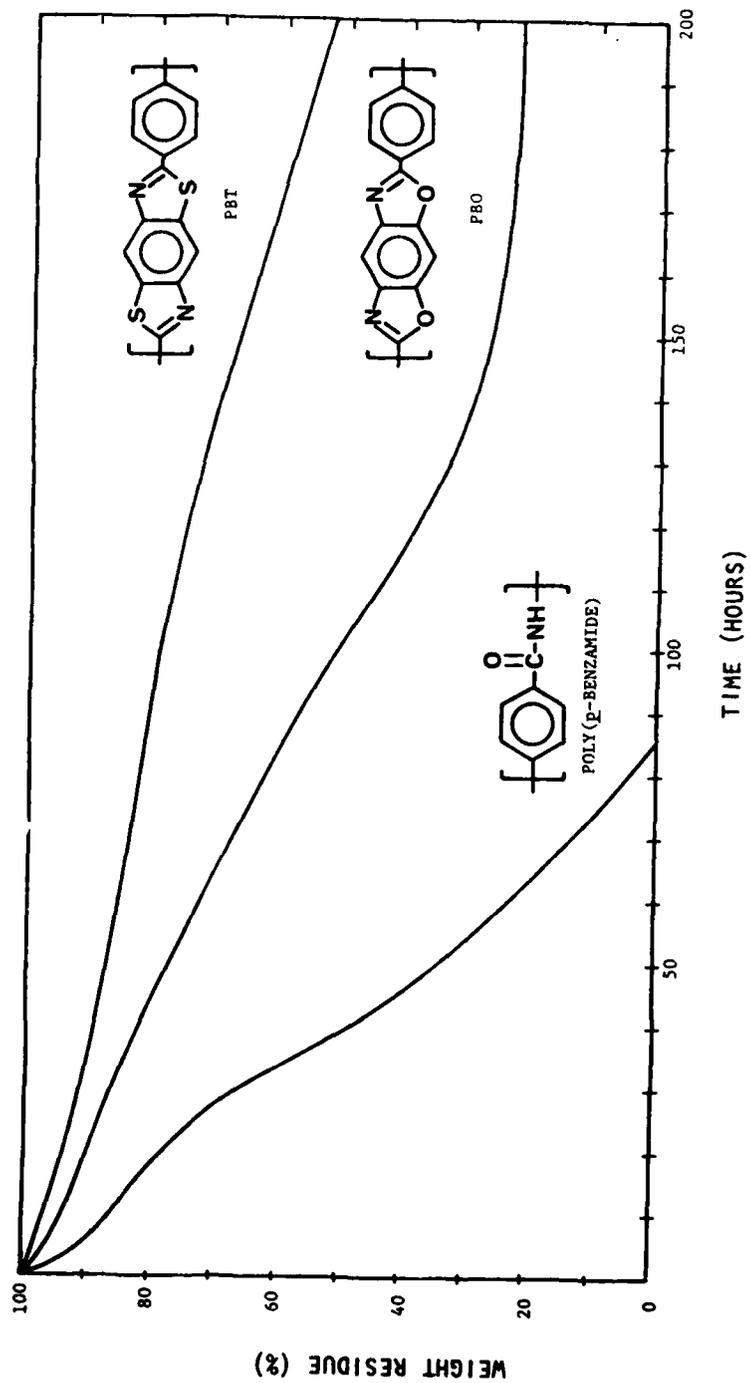


FIGURE 3
 ISOTHERMAL AGING IN CIRCULATING AIR 371°C (700°F)

number of flexibilizing segments. Flory and Mark have postulated that these articulated structures should have increased molecular weights, improved solubilities, and improved molecular packing. Mark used semi-empirical and quantum mechanical methods to calculate intramolecular energies of various conformation of the relatively rigid trans-PBT chains and interaction energies between the chains as they might occur in anisotropic phases. The intramolecular energy calculations elucidated the nonplanarity of trans-PBT, which is of importance with regard to its capability of forming the anisotropic materials. The same types of calculations were used to characterize the flexibility of molecular swivels introduced into these chains in order to facilitate their processing. Simple geometric considerations were used to determine which swivels would be most likely to yield the desirable parallel or collinear continuation of the chains. The effect of the length of the articulated unit in the copolymer synthesis on the ease of the molecules to pack has yielded important information required in the guidance of the synthesis effort. A possible ideal packing scheme of the rigid rod molecule in the bulk film or fiber polymer form has been developed.

In other work on molecular composite concepts or rod-like polymer molecules, Professor William Krigbaum and Dr. Jack Preston of Duke University have succeeded for the first time in synthesizing para-linked aromatic polyamides, polymers known to have high-modulus properties, which form cholesteric phases.

A copolymer of poly (p-benzamide) containing 3 mole % of L-valine was investigated. That is, chirality was inserted by incorporating a few percent of a chiral monomer into the chain. These cholesteric polymers offer the opportunity to achieve a high degree of biaxial orientation (Figure 4) as compared with the uniaxial orientation of nematics (Figure 5). A molecular composite made from a rod-like polymer forming a cholesteric phase would avoid the adhesive problem of heterogeneous composites prepared by laminating uniaxially oriented layers. If the superhelix axis of the cholesteric phase was aligned perpendicular to the film plane, the properties in the plane of the film should be isotropic and the modulus could approach 1/3 that of the fiber.

The technique of Z contrast using the scanning transmission electron microscope has been proven feasible for the study of structure in polymers by Professor Donald Uhlmann of MIT. It has been shown possible with this technique to characterize structural features in polymers by carrying out ultramicrotomy, followed by staining with uranyl acetate and viewing in the scanning transmission electron microscope in the Z contrast mode. Here the bright field image is combined with the annular dark field image to produce an image with greatly increased contrast. This technique offers outstanding promise for investigating the structure of polymers.

FIGURE 4

MOLECULAR COMPOSITE CONCEPT - BIAXIAL ORIENTATION

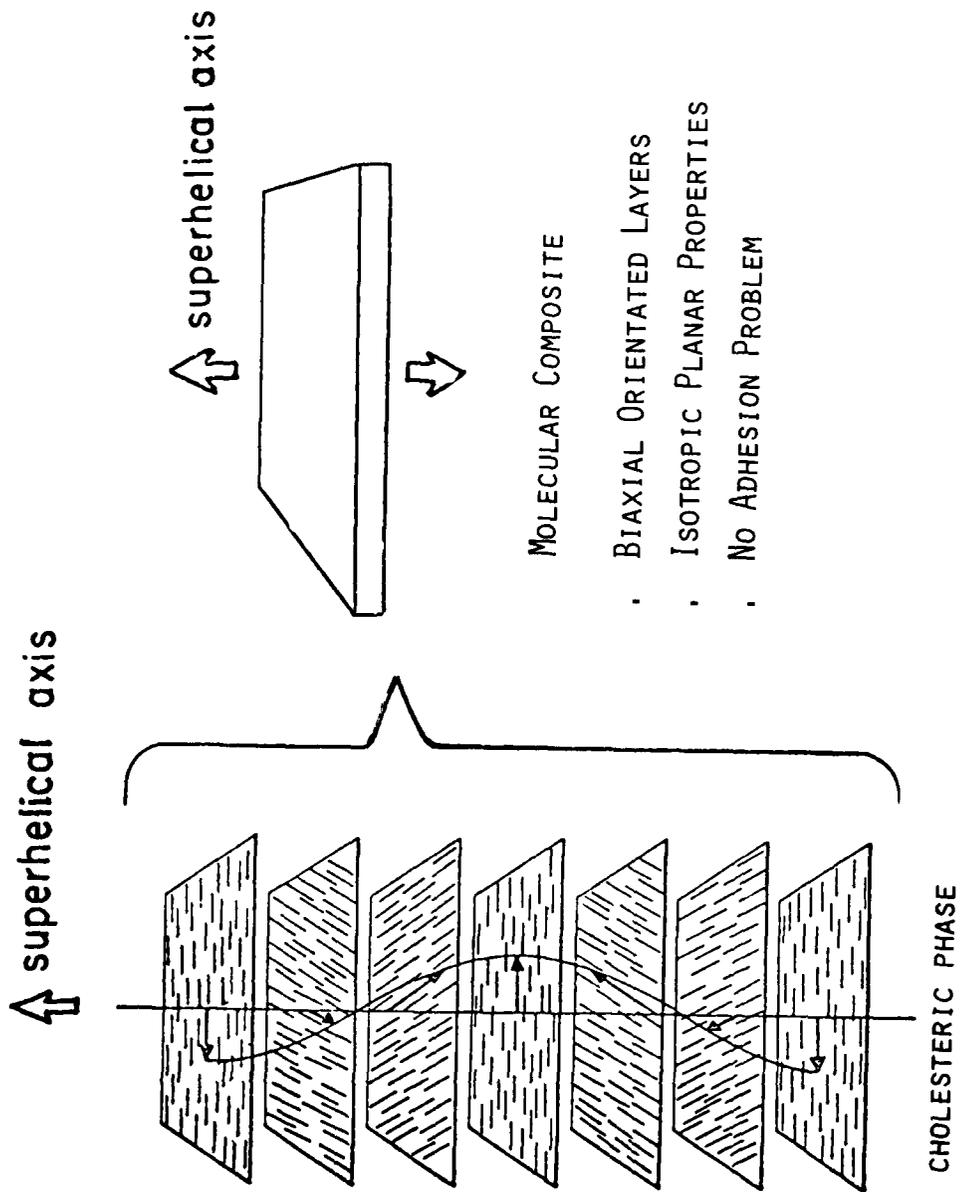
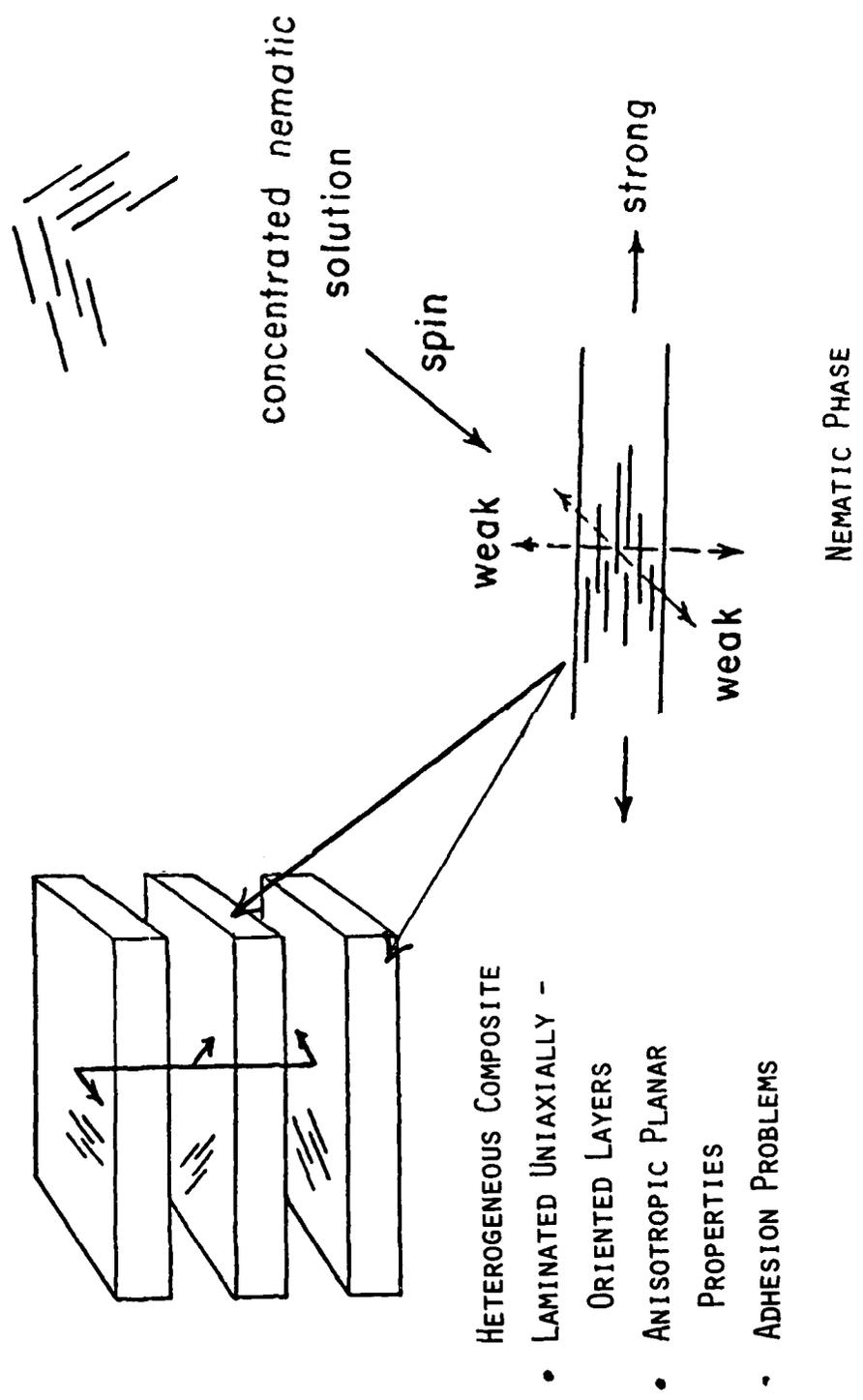


FIGURE 5
 MOLECULAR COMPOSITE CONCEPT - UNIAXIAL ORIENTATION



Results obtained to date using this technique have indicated structural inhomogeneities in both amine-cured and anhydride-cured epoxies, as well as in polyimides. This is shown in the figure on the back cover of this publication for an epon 812 epoxy resin cured with NMA, DDSA and BPMA at 80°C for four hours. The sizes of the inhomogeneities seen in the epoxy resins are similar to those inferred during the previous year from small angle X-ray scattering studies of the same polymers, i.e., in the range of 50-200 Å. From the fact that the heterogeneities are seen in electron microscopy as well as SAXS, it can be inferred that they differ in density from the bulk material by less than 1% of the bulk density. These heterogeneities are very likely regions of different crosslink density, whose now-confirmed presence has important implications for the behavior of the materials in high performance applications. Without the use of uranyl acetate as a staining agent, the microstructure appears homogeneous.

Porous glass-polymer composites have been developed by Professor J. D. Mackenzie of UCLA which are transparent, lightweight and demonstrate improved mechanical properties as compared to glass or polymers. The glass is phase separated by heat treatment to form two separate, interconnecting phases ranging from 40 to 500 Angstroms in diameter (Figure 6). Removal of the leachable phase results in a glass containing 30% by volume of 30 to 500 Angstrom diameter interconnected micropores. The porous glass is impregnated with monomer which is polymerized by low temperature treatment or ultraviolet radiation (Figure 7). Calculations and transmission electron microscopy showed near complete impregnation of the 30Å diameter interconnecting pores with polymer. The resultant glass-polymer composite is stronger than window glass, is 25% lighter in weight, is more transparent (93%) than glass or polymers and has the chemical desirability of glass. The preliminary results are shown in Table 1.

A significant contribution to carbon-carbon materials and structures is the interaction of AFOSR principal investigators with the AFML exploratory development program in analytical processing for improved composites. An example is the work of Dr. Joseph Gebhardt at General Electric Company. In the production of carbon-carbon composites, formation of the matrix is accomplished by pyrolysis of a largely aromatic, commercially available material such as coal tar or petroleum pitch. Gebhardt determined transport properties of the material at various stages of the impregnation-pyrolysis cycle using specially designed, simple laboratory equipment. This accomplished stipulation of process variables in the process environment model without lengthy experimentation. Thermal diffusivity, thermal conductivity and specific heat, which influence heat transfer rates, flow into and out of voids, gas evolution rates and mechanical stresses in the preforms, were determined.

FIGURE 6

PREPARATION OF POROUS GLASS

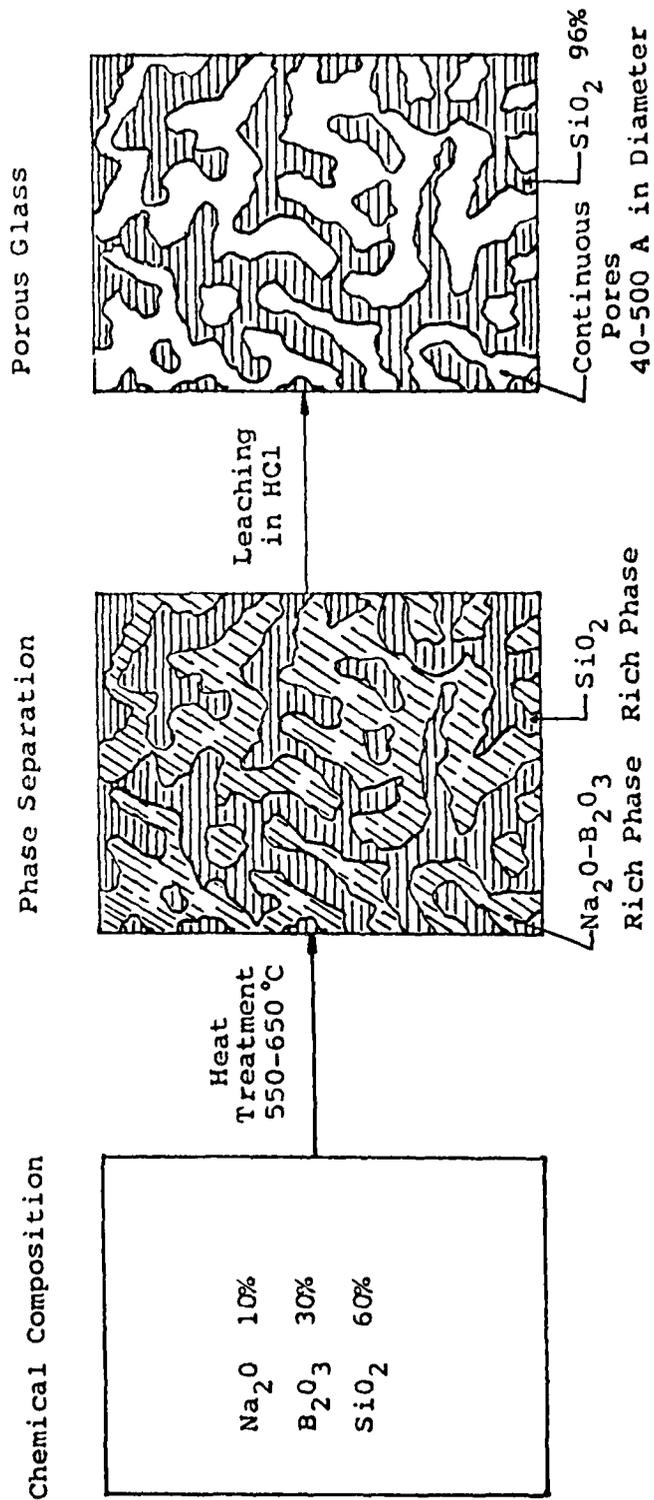


FIGURE 7

PREPARATION OF POROUS GLASS-POLYMER COMPOSITE

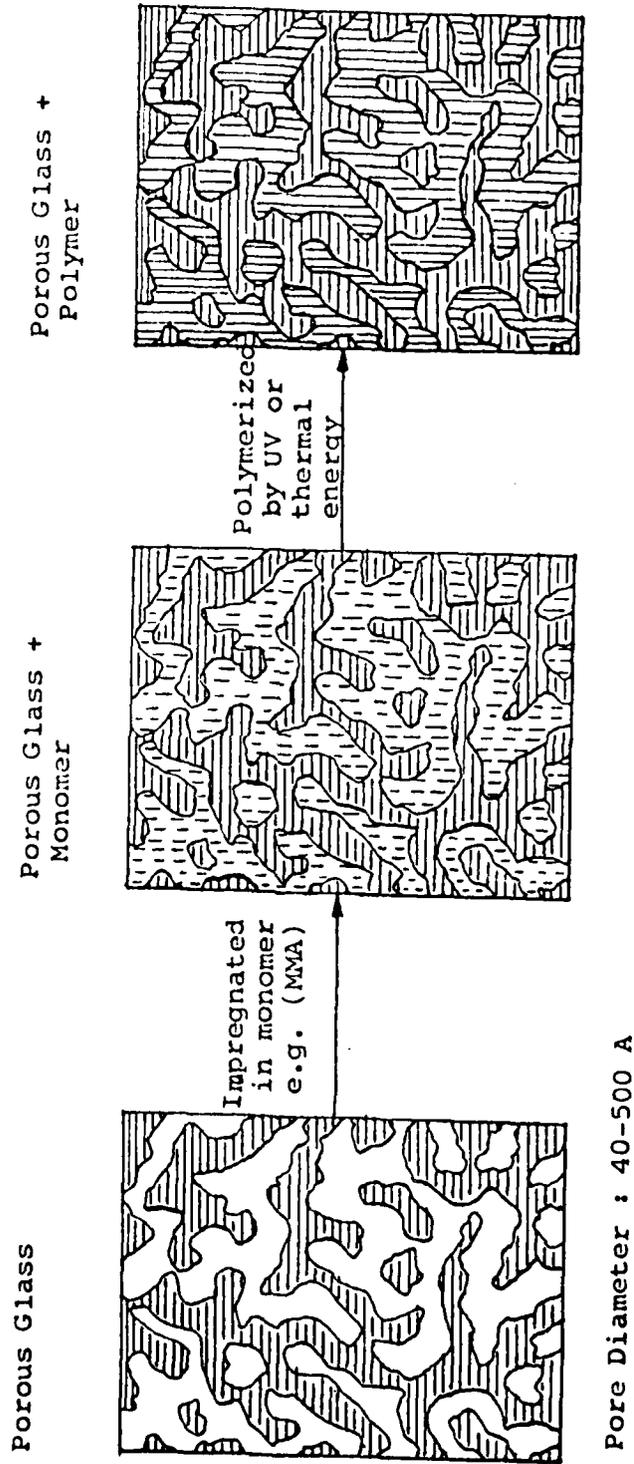


TABLE I

PRELIMINARY RESULTS

	POROUS GLASS-PMMA* COMPOSITE	PMMA	WINDOW GLASS
MODULUS OF RUPTURE (PSI)	18,500	8,000	15,000
YOUNG'S MODULUS (PSI)	3×10^6	4.8×10^5	10×10^6
DENSITY (G/CM ³)	1.83	1.19	2.46
THERMAL EXPANSION COEFFICIENT	1.84×10^{-5}	6×10^{-5}	9×10^{-6}
TRANSMITTANCE**	93%	92%	85%

* PMMA: POLYMETHYL METHACRYLATE, 30 VOL% IN COMPOSITE

** TRANSMITTANCE IN VISIBLE RANGE

CHEMISTRY ANNUAL BUDGET FOR PAST TEN YEARS

<u>FY</u>	<u>Funding (thousands)</u>
70	\$3,169
71	3,205
72	3,210
73	2,512
74	3,080
75 *	3,213
76	3,620
77	4,364
78	4,884
79	5,045

*FY75 total includes \$570,449 from Project 9750 for Kinetics and Thermophysical Properties Research.

FY79 CHEMISTRY PROGRAM STATISTICS

Total number of proposals received.....	248
Total number of inquiries received.....	164
New work efforts initiated.....	46
Renewals.....	81
Proposals declined.....	82
Proposals withdrawn.....	12
Proposals transferred.....	1
Mini-Grants (one year funding).....	1
Conferences and Symposia.....	10
Proposals pending disposition/deferred.....	25

CONFERENCES AND SYMPOSIA

The following conferences and symposia were held during FY 79 with funds provided in part or wholly by the Directorate of Chemical and Atmospheric Sciences as a means of furthering areas of scientific research of particular interest to the Air Force.

ACS National Symposium on Wear and Corrosion

Dr. Robert S. Sahne
Washington, D.C.
4-6 June 1979

AFML/AFOSR Applied Surface Analysis Workshop

Dr. T. W. Haas
Dayton, Ohio
11-15 June 1979

University of Akron Institute of Polymer Sciences Research Workshop on the Relation of Molecular Structure to Adhesion

Dr. A. N. Gent
Akron, Ohio
31 May - 1 June 1979

University of Dayton Workshop on Status of Chemical Instrumentation and Analytical Programs in the Air Force

Dr. Wendell E. Rhine
Dayton, Ohio
14-15 June 1979

University of Dayton Symposium on Ordered Polymers

Dr. D. R. Wiff
Dayton, Ohio
11-13 June 1979

Gordon Research Conference on Elastomers

Dr. James E. McGrath
Colby-Sawyer College
New London, New Hampshire
16-23 July 1979

Gordon Research Conference on Electrochemistry

Dr. Ralph J. Brodd
Santa Barbara, California
8-12 January 1979

University of Utah - The Fourth International Conference
on Boron Chemistry (IMEBORON IV)

Dr. Robert W. Parry
Salt Lake City, Utah
8-13 July 1979

University of Wisconsin-Milwaukee 4th International Summer
Institute of Surface Science (SISS 1979)

Dr. Ralf Vanselow
Milwaukee, Wisconsin
13-17 Aug 1979

NSF/AFOSR Workshop on the Mechanics and Structure of Materials

Dr. M. L. Williams
Cincinnati, Ohio
1-4 May 1979

ACTIVE RESEARCH EFFORTS

CHEMISTRY

AS OF 1 OCTOBER 1979

ALPHABETICAL BY PRINCIPAL INVESTIGATOR

Photoionization of Molecular Clusters (RAA) AFOSR-78-3638, 2303/B1	Ronald P. Andres Joseph M. Calo Department of Chemical Engineering Princeton University Princeton, New Jersey 08540
Inter-Relationships Between Microstructural and Transport Properties of Extended-Chain Polymers (DRU) AFOSR-80-0014, 2303/A3	R. Edward Barker, Jr. Kenneth P. Lawless Department of Materials Science University of Virginia Charlottesville, Virginia 22901
Diagnostics and Chemical Applications of Multiphoton Absorption Processes (RAA) AFOSR-77-3279, 2303/B1	Sidney W. Benson Department of Chemistry University of Southern California Los Angeles, California 90007
Investigations of Cooperative and Dynamic Phenomena in Molecular Solids (DRU) AFOSR-77-3317, 2303/A3	Elliot R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521
Property-Structure-Processing Relations in Polymeric Materials (DRU) AFOSR-77-3404, 2303/A3	Guy C. Berry Herschel Markovitz Department of Chemistry Carnegie-Mellon University Pittsburgh, Pennsylvania 15213
Reactions and Transfer of Excited Molecules (RAA) AFOSR-78-3463, 2303/B1	Philip R. Brooks Department of Chemistry Rice University Houston, Texas 77001
Underpotential Metal Deposition and Trace Analysis Using Solid Electrodes (DRU) AFOSR-78-3621, 2303/A1	Stanley Bruckenstein Department of Chemistry State University of New York Buffalo, New York 14214

Energy Transfer and Chemical
Reactions Important in Molecular
Lasers (RAA)
AFOSR-75-2856, 2303/B1

Program to Investigate Laser Induced
Synthesis of Chemical Materials (AJM)
F49620-78-C-0113, 2303/B2

Fast Ion Transport in Solids (DWE)
AFOSR-77-3427, 2303/A1

Effects of Surface Morphology and
Chemical Composition on the Dura-
bility of Adhesively Bonded Aluminum
Structures (LAK)
F49620-78-C-0097, 2303/A2

Kinetics Studies Involving
Electronically-Excited Interhalogens
and Halogens (RAA)
AFOSR-75-2843, 2303/B1

Chemical Kinetic Studies Involving
NF Radicals (RAA)
AFOSR-78-3507, 2303/B1

Excited State Chemistry of Halogen
Azides (RAA)
F49620-79-C-0053, 2303/B1

Structural Electronic Relationships
in Polymeric Solids (DRU)
AFOSR-80-0038, 2303/A3

Theoretical Studies of Metal Oxides
(RAA)
AFOSR-78-3677, 2303/B1

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Double Layer Structure and Electrode
Kinetics (DWE)
AFOSR-76-3027, 2303/A1

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New Laser Dye Systems Based on
Luminescent Transition Metal
Complexes (AJM)
AFOSR-78-3590, 2303/B2

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Development of Practical MO Techniques
for Prediction of the Properties and
Behavior of Materials (AJM)
AFOSR-79-0008, 2303/B2

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Relation of Structure to Properties
in Graphite Fibers (DRU)
AFOSR-77-3436, 2303/A3

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Investigation of Electron Attachment
Processes in Polyatomic Molecules
(RAA)
F49620-77-C-0071, 2303/B1

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Evaluation of Chemical Research
Relevant to Current and Project
U.S. Air Force Interests (DWE)
F49620-79-C-0144, 2303/A1

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Picosecond Laser Studies of Excited
State Proton Transfer (AJM)
AFOSR-77-3407, 2303/B2

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Time Resolved Spectroscopy of
Reactive Chemical Systems (DWE)
AFOSR-78-3617, 2303/A1

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Intramolecular Energy Exchange by
Infrared Radiometry (RAA)
F49620-79-C-0036, 2303/B1

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Structure-Property-Environmental
Relations in Glass and Glass-
Ceramics (DRU)
AFOSR-77-3210, 2303/A3

Energy Disposal in Electronically
Excited Halogen Atoms and Molecular
Oxygen (RAA)
AFOSR-78-3513, 2303/B1

Synthesis and Characterization of
Transition Metal Complex Systems
with Novel Solid State Properties
(AJM)
F49620-79-C-0051, 2303/B2

NMR Study of Viscoelastic Fluids and
Elastomers under Extreme Conditions
of Temperature and Pressure (DRU)
AFOSR-77-3185, 2303/A3

Multiphoton Dynamics: Energy
Disposal During Decomposition of
Molecules (RAA)
F49620-78-C-0107, 2303/B1

Electrochemical Impregnation for
Fabrication of Cadmium Electrodes
(DWE)
AFOSR-79-0104, 2303/D9

Effect of Structure on Physical
Polymer Interactions and Properties
(DRU)
AFOSR-76-2983, 2303/A3

Energy Partitioning and Transfer
in H + HI System (RAA)
AFOSR-78-3612, 2303/B1

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One- and Two-Photon Optically
Pumped Laser Devices: New Chemical
Laser Diagnostics and Kinetic Probes
(RAA)
AFOSR-76-3056, 2303/B1

The Structure and Properties of
Polymeric Materials (DRU)
AFOSR-77-3293, 2303/A3

Chemical and Physical Aspects of
Mesophase Formation During Carbon
Carbon Composite Processing (DRU)
F49620-78-C-0006, 2303/A3

Microscopic Theory of Electronic
Transitions in Molecular Rate
Processes (RAA)
F49620-78-C-0005, 2303/B1

Exploratory High Pressure
Chemistry (AJM)
AFOSR-79-0092, 2303/B2

Spectroscopic Studies of the
Products of the Reactions of
Noble-Gas Atoms (RAA)
AFOSR-79-0089, 2303/B1

New Materials for Electrochemical
Cells (DWE)
AFOSR-77-3402, 2303/A1

Spectroscopic Investigations
of PbF (RAA)
AFOSR-80-0019, 2303/D9

Energy Transfer in Chemically
Reacting Systems and in Surface
Characterization (RAA)
AFOSR-77-3138, 2303/B1

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Measurement of Rate Constants of
Elementary Gas Reactions of
Importance to Upper Atmosphere
and Combustion Systems (RAA)
F49620-79-C-0155, 2303/B1

Computer Modeling of Pulsed
Chemical Lasers (RAA)
AFOSR-80-0003, 2303/B1

Spectroscopic Determination of
Intermolecular Potentials of Gas
Laser Components and of Major
Atmospheric Constituents (RAA)
AFOSR-77-3269, 2303/B1

The Measurement of Vibrational
Intensities for Infrared Active
Exhaust Plume Species from Advanced
Propellant Rocket Boosters (RAA)
F49620-77-C-0075, 2303/B1

An Approach to Molecular Composites
(DRU) (AJM)
AFOSR-79-0080, 2303/A3 and 2303/B2

The Quantum Dynamics of Chemical
Reactions (RAA)
F49620-79-C-0187, 2303/B1

Chemically Modified Electrodes
and Oxygen Electrocatalysis (DWE)
AFOSR-78-3672, 2303/A1

Studies of Polymer-Bound Macrocyclic
Polytertiary Phosphines (AJM)
AFOSR-79-0090, 2303/B2

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Synthesis of Novel Fluorine
Compounds - New Experimental
Challenges in Elemental Fluorine
Chemistry (AJM)
AFOSR-78-3658, 2303/B2

Controlled Structural Adhesive
Interphases (LAK) (DRU)
AFOSR-78-3692, 2303/A2 and 2303/A3

Analysis of Lubricant Films in
Bearings under Incipient Failure
Conditions (LAK)
AFOSR-78-3473, 2303/A2

Infrared Chemiluminescence Studies
of Ion-Molecule Reactions in a
Flowing Afterglow (RAA)
AFOSR-78-3565, 2303/B1

Energy and Chemical Change (RAA)
AFOSR-77-3135, 2303/B1

Laser Hole Burning Spectroscopy -
A High Resolution Probe of Molecular
Environments (DRU)
F49620-79-C-0108, 2303/A3

Preparation and Properties of
Halide Glasses and Glass-Polymer
Composites (DRU)
AFOSR-80-0059, 2303/A3

Chemical Structure by Laser-
Produced X-Rays (DWE)
AFOSR-78-3575, 2303/A1

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Low Temperature Fluorine Chemistry
of Electronegative Elements (AJM)
AFOSR-77-3165, 2303/B2

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Anisotropic and Electro-Optical
Effects in Liquid Crystals (DWE)
F49620-77-C-0017, 2303/A1

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Intermolecular Flexibility of
Rigid Polymers and Intermolecular
Interactions in Ordered Systems (DRU)
AFOSR-78-3683, 2303/A3

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Fabricable Polymers for Matrices
and Adhesives which Are Extremely
Stable to Heat, Oxidation and
Hydrolysis (AJM)
AFOSR-77-3112, 2303/B2

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Structure and Chemistry of
Surfaces (LAK)
F49620-77-C-0118, 2303/A2

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Calculation of the Energetics and
Collision Dynamics for Electronic
Transitions (RAA)
F49620-77-C-0064, 2303/B1

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Energy Paths in Chemical Reactions
(RAA)
AFOSR-78-3535, 2303/B1

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Investigation of Electrochromic
Diphthalocyanines (AJM)
F49620-79-C-0104, 2303/B2

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Electronically Excited Molecular
Oxygen (RAA)
AFOSR-79-0088, 2303/B1

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Electrochemistry and Electrochemical
Methodology in Molten Salts (DWE)
F49620-79-C-0142, 2303/A1

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Synthesis of Phosphotriazines for
Potential High Temperature Fluids
and Elastomers Applications (AJM)
F44620-79-C-0037, 2303/B2

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High Resolution Vacuum Ultraviolet
Spectroscopy of Small Molecules (RAA)
F49620-77-C-0010, 2303/B1

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Cyclic Polyfluorosilicone Polymers
and Copolymers (AJM)
F49620-77-C-0012, 2303/B2

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Carbon-Carbon Composite Matrix
Decomposition Reactions and
Densification Response (DRU)
F49620-79-C-0068, 2303/A3

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Raman Study of Solid State
Reactions (DRU)
F49620-79-C-0229, 2303/A3

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Studies of Non-Radiating Species
in Metal + Oxidant Chemiluminescent
Flames (RAA)
F49620-79-C-0023, 2303/B1

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Studies in Non-Equilibrium
Statistical Mechanics (RAA)
AFOSR-78-3724, 2303/B1

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Computational Study of Nonadiabatic
Effects in Atom-Molecule Reactive
Scattering (RAA)
F49620-79-C-0050, 2303/B1

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Experimental and Theoretical Studies
of Intramolecular and Intermolecular
Dynamics (RAA)
F49620-76-C-0017, 2303/B1

Theory and Experiments on
Chemical Dynamics and Instabilities
(RAA)
AFOSR-80-0094, 2303/B1

Inorganic Reactants for Synthesis of
Novel Fluorocarbon Derivatives (AJM)
F49620-77-C-0038, 2303/B2

Mechanisms of Photochemical Degrada-
tion in Xanthene Laser Dyes (AJM)
AFOSR-77-3313, 2303/B2

Organosilicon Compounds and Organo-
silicon Polymer Intermediates (AJM)
AFOSR-79-0007, 2303/B2

Impact Initiated Damage in Laminated
Composites (DRU)
F49620-80-C-0050, 2303/A3

New Solid Superionic Conductors
Containing Cu^+ , Ga^+ , In^+ and Tl^+
(DWE)
AFOSR-77-3227, 2303/A1

Experimental Studies of the State-to-
State Chemical Dynamics of Reactions
Involving Air Triatomics (RAA)
AFOSR-77-3348, 2303/B1

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New Chemical Analysis Techniques (DWE)
AFOSR-80-0011, 2303/A1

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Synthesis of Monomethylhydrazine
and Problems Relating to the
Protection of the Environment from
Hydrazine Vapors (AJM)
AFOSR-80-0007, 2303/B2

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Reactive Atomic Species Generated at
High Temperatures and Their Low
Temperature Reactions to Form Novel
Substances (AJM)
AFOSR-79-0063, 2303/B2

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Studies of Energy Transfer and
Selective Chemical Reaction Using
Tunable IR Radiation (RAA)
AFOSR-77-3240, 2303/B1

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Defect Chemistry of Crystalline
Inorganic Materials (DRU)
AFOSR-78-3505, 2303/A3

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Effects of Oxygen and Water Vapor on
the Compressive Strength of Boundary
Films on Iron Crystals (LAK)
AFOSR-76-3051, 2303/A2

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Lithium-Based Anodes for Solid State
Batteries (DWE)
AFOSR-77-3460, 2303/A1

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Spectroscopy and Chemistry of
Molecules with High Vibrational
Energy Content (RAA)
AFOSR-78-3725, 2303/B1

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High Dose Ion Implantation of
Aluminum and Titanium Alloys (LAK)
AFOSR-79-0011, 2303/A2

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Synthesis of New Inorganic and
Organometallic Materials (AJM)
AFOSR-76-3102, 2303/B2

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Multicomponent Oxide Systems for
Corrosion Protection (LAK)
AFOSR-77-3334, 2303/A2

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Role of Coupling Agents in Metal-
Polymer Adhesion (LAK)
F49620-79-C-0085, 2303/A2

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Photofragment Momentum
Spectroscopy of NSO⁺ and D2⁺ at 334.1
nm (RAA)
F49620-79-C-0167, 2303/B1

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Structural and Dynamic Studies of
Materials Possessing High Energy
Content (AJM)
AFOSR-78-3502, 2303/B2

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Microstructure of Amorphous and
Semi-Crystalline Polymers (DRU)
AFOSR-77-3226, 2303/A3

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Stabilization and Graphitization of
Acrylic Fibers and Carbon Composite
Matrices (DRU)
AFOSR-77-3466, 2303/A3

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Applied Quantum Chemistry of
Nonmetallic Materials (AJM)
AFOSR-77-3145, 2303/B2

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Radiation and Laser Potential of
Homo- and Hetero-Nuclear Rare Gas
Diatomic Molecules (RAA)
AFOSR-77-3137, 2303/B1

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Correlation of Electrode Kinetics
with Molecular Structure (DWE)
AFOSR-77-3408, 2303/A1

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Organosilicon Chemistry (AJM)
AFOSR-80-0006, 2303/B2

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High Temperature Molecules and
Molecular Energy Storage (RAA)
AFOSR-76-2906, 2303/B1

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Multiphoton Gas Phase Spectroscopy
(DWE)
AFOSR-77-3438, 2303/A1

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Chemical Reactions and Properties of
Organosilicon Compounds Related to
New Materials (AJM)
AFOSR-78-3570, 2303/B2

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Gas-Surface Dynamics, High Power
Laser-Solid Interactions (LAK)
AFOSR-77-3186, 2303/A3

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Atomic and Molecular Gas Phase
Spectrometry (DWE)
F49620-80-C-0005, 2303/A1

James D. Winefordner
Department of Chemistry
University of Florida
Gainesville, Florida 32611

X-Ray Photoelectron Spectroscopy
(XPS) and Secondary Ion Mass
Spectrometry (SIMS) (DWE)
AFOSR-80-0002, 2303/A1

Kinetic Studies of Gas Phase Free
Radicals (RAA)
AFOSR-78-3693, 2303/B1

Polybenzothiazoles - Synthesis
and Characterization Polymers
(DRU)
F49620-78-C-0110, 2303/A3

Alkaline Earth - Noble Gas Excimers
(RAA)
F49620-79-C-0049, 2303/B1

A First Principles Approach to
Electronic Energy Transfer Processes
in Reactions of the Form $Me + O-A =$
 $MeO + A$ (RAA)
AFOSR-79-0073, 2303/B1

The State Identification of Reaction
Products (RAA)
AFOSR-77-3363, 2303/B1

Nicholas Winograd
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Curt Wittig
Department of Electrical Engineering
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Durham, New Hampshire 03824

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Department of Chemistry
The Johns Hopkins University
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Richard N. Zare
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Stanford University
Stanford, California 94305

ACTIVE RESEARCH EFFORTS

ATMOSPHERIC SCIENCES

AS OF 1 OCTOBER 1979

ALPHABETICAL BY PRINCIPAL INVESTIGATOR

Modelling the Ionospheric and
Plasmaspheric Effects Produced
by a Simulated Saturn V Launch
(TSC)
AFOSR-ISSA-80-00016, 2310/A2

David N. Anderson
Space Environment Laboratory
NOAA Environmental Research Labs
Boulder, Colorado 80303

Analysis and Prediction of Severe
Storm Environment (TSC)
AFOSR-79-0125, 2310/A1

R. A. Anthes
T. N. Carlson
Pennsylvania State University
University Park, Pennsylvania 16802

The Morphology of Stratospheric
Planetary Waves (TSC)
F49620-79-C-0160, 2310/A2

Arthur D. Belmont
Control Data Corporation
Minneapolis, Minnesota 55440

Low Level Convergence and the Pre-
diction of Convective Precipitation
(TSC)
AFOSR-ISSA-80-00029 2310/A1

Dr. Stanley Changnon
Dr. Bernice Ackermann
University of Illinois
Illinois State Water Survey
Box 232
Urbana, Illinois 61801

Studies of the Morphology of the
High Latitude Ionosphere (TSC)
F19628-80-C-0002, 2310/A2

J. V. Evans
W. L. Oliver
Lincoln Laboratory
Massachusetts Institute of Technology
Lexington, Massachusetts 02173

Structure of the Upper Atmosphere
(TSC)
AFOSR-77-3223, 2310/A2

Jeffrey M. Forbes
Space Data Analysis Laboratory
Boston College
Newton, Massachusetts 02159

Analysis of Coherent Satellite
Scintillation Data (TSC)
F49620-78-C-0014, 2310/A2

Edward J. Fremouw
Physical Dynamics Inc.
Bellevue, Washington 98005

Analysis of Severe Weather Using
Digital Doppler and Noncoherent
Radar Data (TSC)
AFOSR-80-0063, 2310/A1

Extratropical Cyclonic Storms -
The Cycles Project (TSC)
F49620-77-C-0057, 2310/A1

Cloud Simulation Chamber (TSC)
AFOSR-MIPR-79-0029, 2310/A1
Navy Contract N00014-79-C-0545

Analysis of the NOAA Alaskan MST
Radar System Data (TSC)
AFOSR-80-0020, 2310/A2

Experiments in Regional Scale NWP
Including SESAME '79 Data (TSC)
F49620-79-C-0208, 2310/A1

Corona from Ice, Thunderstorm
Electrification and Lightning
Suppression (TSC)
AFOSR-77-3429, 2310/A1

Experimental Evaluation of Angular
Scattering and Absorption Properties
of Ice Clouds at 10.6 μm CO₂ Laser
Line (TSC)
F49620-79-C-0198, 2310/A1

Propagation of Transient Signals
through Non-Linear Ionized Media
(TSC)
AFOSR-78-3729, 2310/A2

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College Station, Texas 77843

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University of Washington
Seattle, Washington 98195

James L. Kassner, Jr.
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Physics Research
Department of Physics
University of Missouri-Rolla
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Institute of Science and Technology
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Kenneth Sassen
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University of Utah
Salt Lake City, Utah 84112

Robert E. McIntosh
Department of Electrical and
Computer Engineering
University of Massachusetts
Amherst, Massachusetts 01003

Near-Infrared Spectrometric Airglow
Measurements During the Total Solar
Eclipse of 26 Feb 1979 (TSC)
AFOSR-79-0040, 2310/A2

Aerosol Profiles vs Meteorological
Conditions in West Germany (TSC)
AFOSR-77-3228, 2310/A1

Scattering by Non-Spherical
Particulates (TSC)
AFOSR-MIPR-80-00014, 2310/A1

Auroral-Region Dynamics Determined
with the Chatanika Radar (TSC)
F49620-78-C-0018, 2310/A2

William R. Pendleton, Jr.
Electro-Dynamics Laboratory
Utah State University
Logan, Utah 84322

Reinhold Reiter
Institute for Atmospheric Environ-
mental Research
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Space Astronomy Laboratory
State University of New York
Albany, New York 12222

Vincent Wickwar
Stanford Research International
Menlo Park, California 94025

RESEARCH EFFORTS COMPLETED IN FY79

ALPHABETICAL BY PRINCIPAL INVESTIGATOR

- | | |
|---|--|
| A Study of Transport Processes and Initiation of Corrosion under Paint Films | Theodore R. Beck
Electrochemical Technology Corporation
3935 Leary Way N.W.
Seattle, Washington 98107 |
| Theoretical and Experimental Analysis of Alkaline Zinc Batteries | Douglas N. Bennion
Chemical, Nuclear, and Thermal Engineering Department
University of California,
Los Angeles
Los Angeles, California 90024 |
| Synthesis and Spectroscopic Investigation of Inorganic Materials Possessing Unusual Electronic Properties | G. A. Crosby
Department of Chemistry
Washington State University
Pullman, Washington 99164 |
| Development of Practical MO Techniques for Prediction of the Properties and Behavior of Materials | Michael J. S. Dewar
Department of Chemistry
University of Texas
Austin, Texas 78712 |
| Rates of Rapid Chemical Reactions | Edward M. Eyring
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112 |
| Kinetic Spectroscopy of Metal Atom/Oxidizer Chemiluminescent Reactions for Laser Applications | Arthur Fontijn
AeroChem Research Laboratories, Inc.
P.O. Box 12
Princeton, N.J. 08540 |
| Selective Chemical Pumping of Electronic States; Formation and Deactivation Processes in Electronic Transition Chemically Pumped Lasers | James L. Gole
Department of Chemistry
Georgia Institute of Technology
Atlanta, Georgia 30332 |
| Photoluminescence Spectroscopy with a CW Dye Laser: A Study of the Diatomic Alkaline Earth Metal Halides and Oxides | David O. Harris
Department of Chemistry
University of California
Santa Barbara, California 93106 |

Processing Mechanisms, Structure and Morphology of High-Temperature Polymeric Alloys

Ian L. Hay
Celanese Corporation
Celanese Research Company
Box 1000
Summit, New Jersey 07901

Novel Organophosphorus and Organonitrogen Derivatives and Their Use for the Synthesis of Unusual Transition Metal Complexes

R. B. King
Department of Chemistry
University of Georgia
Athens, Georgia 30602

Structure and Properties of Glasses

John D. Mackenzie
Materials Department
University of California
Los Angeles, CA 90024

Time-Temperature Studies of High Temperature Deterioration Phenomena in Lubricant Systems: Synthetic Ester Lubricants

Lee R. Mahoney
Fuels and Lubricants Department
Ford Motor Company
Dearborn, Michigan 48121

Basic Studies Relating to the Synthesis of 1,1-Dimethylhydrazine by Chloramination

William E. McQuiston
Propellant Sciences Department
Naval Surface Weapons Center
Silver Spring, Maryland 20910

Ion Photofragment Spectroscopy - Potential Surfaces of Molecular Ions

John T. Moseley
Molecular Physics Laboratory
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Photodissociation and Photodetachment of Atmospheric Negative Ions

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L. C. Lee
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Electrochemistry of Solutes in Chloroaluminate Melts and the Development of Related Electrochemical Methodology

Robert Osteryoung
Janet Osteryoung
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

- Viscosity of Chloroaluminate Melts
Harald A. Øye
Institute of Inorganic Chemistry
University of Trondheim
7034 Trondheim NTH 9, Norway
- Syntheses of Phosphotriazines for
Potential High Temperature Fluids
Applications
K. L. Paciorek
Ultrasystems, Inc.
2400 Michelson Drive
Irvine, California 92715
- Studies of HnFn Oligomeric Species
Richard L. Redington
Department of Chemistry
Texas Tech University
Lubbock, Texas 79409
- Studies of Ionization Processes
Erhard W. Rothe
Research Institute for
Engineering Sciences
College of Engineering
Wayne State University
Detroit, Michigan 48202
- Power Spectral Performance of a
cw Chemical Laser
Lee H. Sentman
Aeronautical and Astronautical
Engineering Department
University of Illinois
Urbana, IL 61801
- Studies of New Chemical Analysis
Techniques
Robert E. Sievers
Department of Chemistry
University of Colorado
Boulder, Colorado 80309
- Evaporation and Dispersion of
Hazardous Materials from Acci-
dental Spills
Charles Springer
Department of Chemical Engineering
University of Arkansas
Fayetteville, Arkansas 72701
- New Perfluoropolymer-forming
Reactions
Madeline S. Toy
Science Applications, Inc
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Kinetic Aspects of Gas Phase Metal
Atom Oxidation Reactions

John Wiesenfeld
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Cornell University
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Atomic and Molecular Gas Phase
Spectrometry

James D. Winefordner
Department of Chemistry
University of Florida
Gainesville, Florida 32611

COMPLETED PROJECT SUMMARY

1. TITLE: A Study of Transport Processes and Initiation of Corrosion under Paint Films
2. PRINCIPAL INVESTIGATOR: Dr. Theodore R. Beck
Electrochemical Technology Corporation
3935 Leary Way N.W.
Seattle, Washington 98107
3. INCLUSIVE DATES: 1 September 1976 - 30 September 1979
4. CONTRACT NUMBER: F49620-76-C-0029
5. COSTS AND FY SOURCE: \$48,370, FY77; \$45,186, FY78; \$47,117, FY79
6. OTHER RESEARCH PERSONNEL INVOLVED: Dr. Robert T. Ruggeri, a chemical engineer, carried out the mathematical modeling and supervised the experimental work. He was guided in the mathematical modeling effort by Professor Douglas N. Bennion who was at Electrochemical Technology Corp. on industrial leave from UCLA during the academic year 1977-1978. Olwen M. Morgan and Sandra G. Chan, chemists, and Raymond Carveth and Michael LaScala, chemical technicians, assisted in the experimental work.
7. PUBLICATIONS:
 - "Effect of Hydrodynamics on Pitting," T. R. Beck, Corrosion, **33**, 9 (1977).
 - "Techniques for Studying Initial Film Formation on Newly Generated Surfaces of Passive Metals," T. R. Beck, in Electrochemical Techniques for Corrosion, R. Baboian, Ed., NACE, Houston, 1977.
 - "Improvements in Energy Efficiency of Industrial Electrochemical Processes," T. R. Beck, Argonne National Laboratory Report, ANL/OEPM-77-2.
 - "Passivation of New Titanium Surfaces," T. R. Beck, Conference Proceedings, 4th International Symposium on Passivity, Kruger and Frankenthal, Eds., The Electrochemical Society, 1978.
 - "Occurrence of Salt Films During Repassivation of Newly Generated Metal Surfaces," R. Alkire, D. Ernsberger and T. R. Beck, J. Electrochem. Soc., **125**, 1382 (1978).
 - "Industrial Electrolysis," T. R. Beck, in Techniques of Electrochemistry, Vol. 3, p 1-47, E. Yeager and A. J. Salkind, Eds., John Wiley, New York, 1978.

"A Model for Mass Transport in Paint Films," R. T. Ruggeri and T. R. Beck, submitted to Symposium Volume, Corrosion Control by Coatings, H. Leidheiser, Ed., Lehigh University, 1978.

"Surface Stress Curves for Platinum," T. R. Beck and K. F. Lin, J. Electrochem. Soc., 126, 252 (1979).

"The Thermodynamic Theory of Electrocapillarity for Solid Metals," D. M. Mohilner and T. R. Beck, J. Phys. Chem., 83, 1160 (1979).

"Energy Consumption and Efficiency of Industrial Electrochemical Processes," T. R. Beck and R. T. Ruggeri, Advances in Electrochemistry and Electrochemical Engineering, Vol. 12, C. W. Tobias and H. Gerischer, Eds., submitted for publication.

"A Survey of Organic Electrolytic Processes," T. R. Beck, R. T. Ruggeri, R. C. Alkire, M. A. Stadtherr, and N. L. Weinberg, Argonne National Laboratory Report, ANL/OEPM-79-5.

"Occurrence of Salt Films During Initiation and Growth of Corrosion Pits," T. R. Beck and R. C. Alkire, J. Electrochem. Soc., 126, 1662 (1979)

"Mass Transport Analysis of Filiform Corrosion," R. T. Ruggeri and T. R. Beck, J. Electrochem. Soc., to be submitted.

"The Transport Properties of Polyurethane Paint," R. T. Ruggeri and T. R. Beck, to be submitted to symposium on Corrosion Control by Coatings, Lehigh University, 1980.

"A Study of Transport Processes and Initiation of Corrosion Under Paint Films," T. R. Beck, Final Technical Report

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Corrosion of metals coated with paint films has previously been extensively studied, but a general quantitative treatment was unavailable. To this end, general mathematical and computer models were developed to quantitatively describe the diffusion and migration of mobile species (solvents and ions) through polymer films. The models required thermodynamic data and transport parameters which were not available. A series of experiments was therefore performed to obtain this required information using a single polyurethane paint type. Based on these data a test of the

applicability of the models was conducted. New thermodynamic data were obtained, and the applicability of the model was supported; however, because the available thermodynamic data are incomplete, a critical test of the model remains to be performed. The experiments indicate that the diffusion coefficient of ions through polyurethane is exceedingly low ($D_{Na^+} < 10^{-9}$ cm²/s) and that under most conditions the transport of ions through the paint can be ignored. The diffusivity of water was found to be 3.2×10^{-8} cm²/s with a solubility, at unit water activity and 21°C, of 1.3×10^{-2} g-water/g-paint. Under normal field conditions it is likely the ions beneath the paint were present before the coating was applied or they entered through defects, and the corrosion is limited by either the oxygen or water diffusion through the paint.

As a result of the studies of the diffusional properties of paint films, filiform corrosion was investigated. This investigation revealed a new mechanism for filiform growth: diffusion of oxygen and water toward the head through a porous tail. This new mechanism explains for the first time the major features of filiform corrosion.

AFOSR Program Manager: Lorelei A. Krebs, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Theoretical and Experimental Analysis of Alkaline Zinc Batteries

2. PRINCIPAL INVESTIGATOR: Professor Douglas N. Bennion
Chemical, Nuclear, and Thermal
Engineering Department
University of California, Los Angeles
Los Angeles, California 90024

3. INCLUSIVE DATES: 15 April 1976 - 30 September 1978

4. CONTRACT NUMBER: F44620-76-C-0098

5. COSTS AND FY SOURCE: \$30,000, FY 76; \$15,000, FY77; \$40,000,
FY77; \$37,399, FY78

6. SENIOR RESEARCH PERSONNEL: Dr. John Newman

7. JUNIOR RESEARCH PERSONNEL:

Won G. Sunu
Siddhartha Ghosh
Bruce M. Eliash
Manojit Sinha

8. PUBLICATIONS:

"Transport Parameters for Potassium Hydroxide-Water Solution in a Cation Exchange Membrane," Manojit Sinha and Douglas N. Bennion, J. Electrochem. Soc., 125, 556-561 (1978).

"Mass Transfer in Concentrated Ternary Electrolytes," Won G. Sunu, Douglas N. Bennion, and John Newman, (to be submitted Ind. Eng. Chem. Fundam., 1979).

"Transient and Failure Analysis of Porous Zinc Electrodes, I, Theoretical," Won G. Sunu and Douglas N. Bennion, (to be submitted J. Electrochem. Soc., 1979).

"Transient and Failure of Porous Zinc Electrodes, II, Experimental," Won G. Sunu and Douglas N. Bennion, (to be submitted J. Electrochem. Soc., 1979).

"Removal of Copper from Dilute Solutions by a Flow-through Porous Electrode," Siddhartha Ghosh and Douglas N. Bennion, (to be submitted J. Appl. Electrochem., 1979).

"Zinc Electrode Concentration Profiles," Bruce M. Eliash and Douglas N. Bennion, (to be submitted J. Electrochem. Soc., 1980).

"Performance Controlling Processes in a Porous Nickel Oxide Battery Electrode," Manojit Sinha and Douglas N. Bennion, (to be submitted J. Electrochem. Soc., 1980).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The processes that control the useful life time and performance rates in non-flowing zinc electrodes for electrical storage batteries have been investigated. In particular, the chemical reaction rates, concentration, and electrical potential distributions have been predicted theoretically and measured experimentally as functions of position in the electrode and time for both charge, discharge, and multiple cycles. Changes in crystal structure and solid distributions have also been measured and examined theoretically. Similar rates and distributions have been measured and correlated for RAI P2291 ion exchange membrane separators used in zinc secondary batteries such as the nickel-zinc battery (Zn/KOH, H₂O/NiOOH). Distributions in flow through electrodes were also observed experimentally and calculated theoretically, using the copper deposition reaction for experimental convenience.

A number of factors have been found to be important in the operation and control of zinc electrodes. During discharge, zinc metal (Zn) reacts with hydroxyl ions (OH⁻) to yield water and electrons which are "pumped" into the external electrical circuit. Initially OH⁻ ions within the porous, zinc electrode are consumed. When those OH⁻ ions are consumed, further reaction must be supported by transport of OH⁻ across the separator from the counter electrode, nickel oxide. For RAI P2291 membrane separators, it was found that reaction rates of 50 mA/cm² could not be supported by the ion transport, but 20 mA/cm² could be supported. The supply of OH⁻ ions across the separator is one factor, along with the electric potential distribution, which causes the discharge reaction to concentrate in a narrow zone close to the membrane. At 20 mA/cm² the zone is about 0.3 mm across. At 50 mA/cm² the zone shrinks to about 0.1 mm. The reaction zone thickness has important implications for electrode design.

During charging of the zinc electrode, OH⁻ ions are produced within the porous electrode. This situation causes the OH⁻ ion concentration to increase in the depth of the porous electrode favoring a broad reaction zone and lower potential losses at higher current densities as compared to the discharge reaction. The implication is that the zinc electrode can be safely charged at higher rates than discharged. There are other considerations which enter, however. The nickel electrode becomes OH⁻ ion "starved" during charging and wild, dendrite type zinc deposits get worse at high charge rates. Thus high charge rates are not really possible.

Two types of zinc electrode passivation have been identified, surface coverage of otherwise reactive zinc area and pore blockage. The exposed, reactive zinc is gradually covered up by ZnO precipitation as the discharge reaction proceeds. At modest current densities and reasonably high OH⁻ concentrations, above about 1.0M, the precipitate is a porous, fluffy type deposit which slowly inhibits access to the active zinc. However, this form of surface coverage allows large, useful fractions of active zinc to continue to react. It appears that when the surface concentration of OH⁻ ions get too low, the form of the precipitate becomes monolithic, impervious, and totally blanks off any further reaction. The electrode, or at least the affected area of the porous electrode, is passivated. More detailed observations of this passivation mechanism are needed; but the evidence is that OH⁻ ion concentration is a significant factor.

Porosity of the porous zinc electrode is shown to be a critical parameter. Zinc oxide (ZnO) has a much larger molar volume than zinc. As zinc is converted to zinc oxide, the local volume fraction of solid increases and the volume fraction of electrolytic solution (KOH, K₂ZnOH₄, H₂O) decreases. As has been shown, the reaction rate is largest at the face of the electrode leading to pore plugging at the face if there is not sufficient space for the ZnO to precipitate. When the face of the electrode plugs, further discharge is impossible. For a porosity (fraction of volume filled with electrolytic solution) of 0.33 pore plugging at the face was the failure mode. For a porosity of 0.6, pore plugging at the face did not occur. However, tests on cycling performance showed that with increasing number of cycles more and more zinc and zinc oxide accumulated in the high reaction rate region, that is, in the face of the electrode. Long term cycle tests have not yet been done, but the clear implication of the results is that as cycling proceeds zinc transports from the central region of the electrode to the surface. This transport of zinc causes increasing porosity in the central region and decreasing porosity at the face. When the face porosity goes below a critical value of about 0.5, failure by pore plugging will occur and electrode life can be expected to end.

The OH⁻ concentration distributions have been shown to control many factors which govern electrode performance. Experiments to measure experimentally the actual KOH and K₂ZnOH₄ concentrations are now under way.

It can be shown that once zinc electrodes are produced which approximate the practical limit implied by the model calculations, the nickel oxide electrode will become performance limiting. A theoretical model of the nickel electrode has been completed which shows the interrelationships of water and OH⁻ ion transport along with potential and reaction rate distributions and their relation to properties of the nickel oxide film and associated charge transport steps.

Flow through porous electrodes are an alternative design to the more customary electrodes with limited or no convective flow. In convection designs, the working electrode is inert, and the ZnO precipitates in a storage tank external to the electrode stack. Experimental and theoretical work has been completed demonstrating the interrelationships between flow rates, applied potential, input and output concentration, electrode length, and electrode thickness with potential, current and reaction distribution and cost effectiveness. The experimental work was done with copper deposition at 600 ppm input concentration. The optimum conditions were found to be electrode thickness of 0.6cm, applied potential of 1.4V, and superficial velocity of about 11 cm/s. The minimum in velocity was very broad.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis and Spectroscopic Investigation of Inorganic Materials Possessing Unusual Electronic Properties
2. PRINCIPAL INVESTIGATOR: Professor G. A. Crosby
Department of Chemistry
Washington State University
Pullman, Washington 99164
3. INCLUSIVE DATES: 16 September 1975 - 30 September 1979
4. GRANT NO: AFOSR 76-2932
5. COSTS AND FY SOURCE: \$69,500, FY76; \$69,025, FY77; \$55,000, FY78;
\$56,000, FY79
6. SENIOR RESEARCH PERSONNEL:

Professor H. Rau
Dr. K. D. Spitzer
7. JUNIOR RESEARCH PERSONNEL:

S. F. Agnew
T. L. Cremers
A. D. Crosby
J. L. Crosby
W. A. Fordyce
A. Frankenfield
K. W. Hipps

B. R. McGuire
G. A. Merrell
W. L. Parker
M. S. Pearce
F. J. Schuetze
M. L. Stone
K. A. Truesdell
8. PUBLICATIONS:

"Luminescence as a Probe of Excited State Properties," G. A. Crosby, Advances in Chemistry, 150, American Chemical Society, 1976, Chapter 13.

"Excited States of Mixed Ligand Chelates of Ruthenium(II) and Rhodium(III)," G. A. Crosby and W. H. Elfring, Jr., Journal of Physical Chemistry, 80, 2206 (1976).

"Geometrical Distortion of the Excited States of d^6 Transition Metal Complexes: Systems of O and D_4 Symmetry," K. W. Hipps, G. A. Merrell, G. A. Crosby, Journal of Physical Chemistry, 80, 2232 (1976).

"The Molecular Theory of Polarized Emission: Linear, Circular, and Magnetically Induced Circular Polarization of Emission," K. W. Hipps, Chemical Physics, 23, 451 (1977).

"Magnetically Induced Circular Polarization of Emission: Application to Inorganic Complexes," K. W. Hipps and G. A. Crosby, SPIE, 112, 132 (1977) and Optical Engineering, 17, 176 (1978).

"Infrared-Optical Double Resonance and Thermal Modulation Spectroscopy of the Tris(2,2'-bipyridine)ruthenium(II) Cation," D. C. Baker, K. W. Hipps, G. A. Crosby, Chemical Physics Letters, 53, 333 (1978).

"Applications of the Photoelastic Modulator to Polarization Spectroscopy," K. W. Hipps and G. A. Crosby, Journal of Physical Chemistry, 83, 555 (1979).

"Excited States of Mixed-Ligand Chelates of Ruthenium(II): Quantum Yield and Decay Time Measurements," W. H. Elfring, Jr. and G. A. Crosby, Journal of Physical Chemistry, submitted.

"Charge-Transfer Excited States of Osmium(II) Complexes: I. Assignment of the Visible Absorption Bands," B. J. Pankuch, D. E. Lacky, G. A. Crosby, Journal of Physical Chemistry, submitted.

"Charge-Transfer Excited States of Osmium(II) Complexes: II. Quantum Yield and Decay Times Measurements," D. E. Lacky, B. J. Pankuch, G. A. Crosby, Journal of Physical Chemistry, submitted.

"Synthesis and Spectroscopic Investigation of Inorganic Materials Possessing Unusual Electronic Properties," G. A. Crosby, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A comprehensive program of synthesis, chemical characterization and optical investigation of complexes of $(nd)^6$ configuration possessing charge-transfer (CT) excited states was carried out. Approximately sixty molecules of Ru(II) and Os(II) were examined, a dozen of Ir(III) and six of Pt(IV). Absorption spectra (300 and 77 K), luminescence spectra (77 - 1.5 K) and temperature dependent decay times, quantum yields and emission spectra were examined. Several systems were subjected to intense magnetic fields at low temperatures. Group theoretical models for the CT excited states of Ru(II) and Os(II) complexes were devised for systems of D_3 and D_{2d} symmetry. A new criterion was found for classifying $d\pi^*$ and $\pi\pi^*$ states employing Ir(III) complexes and a configuration-interaction model for rationalizing $d\pi^*-\pi\pi^*$ interactions in complexes was devised.

Several new luminescent systems useful for photochemical energy donors were discovered. The project carried the laboratory significantly further toward its stated goal of defining the principles by which new

substances with potential value as media for electrooptical devices
can be designed and synthesized in the laboratory.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Development of Practical MO Techniques for Prediction of the Properties and Behavior of Materials
2. PRINCIPAL INVESTIGATOR. Dr. Michael J. S. Dewar
Department of Chemistry
University of Texas
Austin, Texas 78712
3. INCLUSIVE DATES: 1 September 1974 - 31 October 1978
4. GRANT NUMBER: AFOSR-75-2749
5. COSTS AND FY SOURCE: \$99,743, FY75; \$99,992, FY76; \$16,631, FY77;
\$99,965, FY77; \$99,998, FY78

6. SENIOR RESEARCH PERSONNEL:

Dr. David Landman	Dr. Taylor Jones
Dr. Ignatius Turchi	Dr. Santiago Olivella
Dr. Anselm Griffin	Dr. Yukio Yamaguchi
Dr. Mike McKee	Dr. Hans Lindner
Dr. Huo M. Chang	Dr. John Buschek
Dr. Paul Weiner	Dr. George Ford

7. JUNIOR RESEARCH PERSONNEL:

Francisco Carrion	Kathryn Mussatto
Steven Kirschner	Donald E. David
Joel Adcock	Lek Chantranupong
Diane Cabelli	

8. PUBLICATIONS:

"MINDO/3 Calculations of Molecular Electric Polarizabilities,"
Michael J. S. Dewar, Robert C. Haddon and Sung Ho Suck, J. Chem.
Soc., Chem. Commun., 611 (1974).

"Additivity of Bond Energies in the Light of the Maximum Overlap
Approximation (MOA) and MINDO/3," Michael J. S. Dewar, Donald H. Lo,
and Zvonimir B. Maksic, Croat. Chim. Acta., 46, 7 (1974).

"MINDO/3 Study of the Thermal Conversion of Cyclobutene to 1,3
Butadiene," Michael J. S. Dewar, Steven Kirschner, J. Amer. Chem.
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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A new semiempirical method (MNDO), based on NDDO, has proved superior to MINDO/3 in nearly all respects. Parameters are available for H, Be, B, C, N, O, F, and (without 3d AOs) Si, P, S, and Cl. MINDO/3 and MNDO give good estimates of molecular vibration frequencies and isotopic shifts, and hence of entropies, specific heats, entropies of activation, and kinetic isotope effects. MINDO/3 and MNDO have been successfully applied to the calculation of ESCA chemical shifts, ionization potentials and electron affinities of molecules and radicals, nuclear quadrupole coupling constants, energies of lowest excited singlet and triplet states, and molecular polarizabilities and hyperpolarizabilities. MINDO/3 and MNDO led to good estimates of the geometry, vibration frequencies, and electronic band structure of polyethylene. MNDO calculations for boron hydrides, boron hydride anions, and carboranes led to results in good overall agreement with experiment. A MNDO study of beryllium borohydride resolved a conflict in the experimental evidence concerning its structure. MINDO/3 calculations for benzyne led to a reassignment of its IR spectrum. MINDO/3 is especially good for carbocations both "classical" and "nonclassical."

MNDO calculations were carried out for a number of normal and mesoionic oxazoles and imidazoles and for pentadienyl ions and their methyl derivatives. MINDO/3 gave results of mechanistic interest and in agreement with experiment for: the conversion of phenylcarbene to cycloheptatrienacarbene; the Cornforth rearrangement of oxazoles; the Cope rearrangement of 1,5-hexadiene; the retro-Diels-Alder reaction of cyclohexene (to ethylene and butadiene); additions of methyl radical to olefins and acetylenes; the conversions of dioxetane to formaldehyde, of Dewar benzene to benzene, of cyclobutyl radical ions to butadiene radical ions, of bicyclobutane to butadiene, of benzvalence to benzene, of bicyclo[2,1,0]pentene and its 1- and 2- methyl derivatives to pentadienes, of vinylcyclopropane to cyclopropene, and of cyclopropylallene to methylenecyclopentene; the Norrish Type II photoreaction of butanal and the di- π -methane reaction of triplet excited 1,4-pentadiene; additions of singlet $^1\Delta_g$ O₂ to olefins and acetylenes; and for the retroene conversion of vinylacetic acid to propene + CO₂. MNDO calculations for hydroboration and borohydride reduction explained these apparent deviations from the Woodward-Hoffman rules. MNDO calculations have been carried out for the conversions of 1- and 2- aza-Dewar benzenes to pyridine and of cyclobutene to butadiene.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Rates of Rapid Chemical Reactions
2. PRINCIPAL INVESTIGATOR: Dr. Edward M. Eyring
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112
3. INCLUSIVE DATES: 1 February 1977 to 30 November 1978
4. GRANT NO: AFOSR 77-3255
5. COSTS AND FY SOURCE: \$55,000, FY77; \$28,000, FY78
6. SENIOR RESEARCH PERSONNEL: Dr. Michael M. Farrow
Dr. Licesio J. Rodriguez
Dr. Frank Strobusch
7. JUNIOR RESEARCH PERSONNEL:

Roger K. Burnham	Lindsay B. Lloyd
Wayne L. Chandler	David B. Marshall
Sherman K. Epperson	Linda Millsaps
Harvey A. Jacobs	Steven L. Olsen
Barbara K. Kajiya	Peter Rose
Steven M. Kuznicki	

8. PUBLICATIONS:

"Ultrasonic Absorption Kinetic Studies of the Complexation of Aqueous Li^+ , Na^+ , Rb^+ , Tl^+ , Ag^+ , NH_4^+ , and Ca^{2+} by 18-Crown-6," G. W. Liesegang, M. M. Farrow, F. A. Vazquez, N. Purdie, and E. M. Eyring, J. Am. Chem. Soc., 99, 3240 (1977).

"Equilibrium and Kinetic Investigation of Salt-Cycloamylose Complexes," R. P. Rohrbach, L. J. Rodriguez, Edward M. Eyring, and J. F. Wojcik, J. Phys. Chem., 81, 944 (1977).

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"Fourier Transform Photoacoustic Spectroscopy," M. M. Farrow, R. K. Burnham, and E. M. Eyring, loc. cit., in press.

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"Titanium Corrosion by a Hot Perfluoropolyether," W. L. Chandler, L. B. Lloyd, M. M. Farrow, R. K. Burnham, and E. M. Eyring, in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objective of this research was the development of techniques to investigate the kinetics and mechanism of the corrosion of titanium metal by a hot perfluoropolyether lubricant. The method originally expected to be most appropriate was photoacoustic spectroscopy using

piezoelectric detection. Such an apparatus was found to be quite suitable for measuring the visible absorption spectrum of static solid systems such as a neodymium(III) glass laser rod. However, a Fourier transform photoacoustic spectrometer assembled from a Michelson interferometer and a dedicated minicomputer proved to be more suitable for measuring rapid transient, visible absorption spectra of surfaces.

The heated sample cell in which the perfluoropolyether lubricant corroded a polished titanium metal surface proved to be an inhospitable environment for the piezoelectric detector of the photoacoustic spectrometer. A CW argon-ion laser was then adapted for a reflectance study of the titanium corrosion reaction. The rate of corrosion is a strong function of the amount of oxygen available in and above the hot lubricant. The degradation of the lubricant and resultant formation of TiF_3 on the titanium surface is accelerated by TiF_3 corrosion products but is unaffected by the intense laser illumination. From kinetic data covering the 215 to 270°C temperature range one finds an activation energy for the overall corrosion process of 19 kJ/mole. When the titanium surface is carefully polished to remove all traces of corrosion products an extended induction time precedes the exponential corrosion process.

The most significant accomplishment to emerge from these studies was the reduction to practice of a Fourier transform photoacoustic spectrometer that is adaptable to transient mid-infrared surface absorption spectral measurements.

Incidental byproducts of this research were complex ion formation and proton transfer kinetic studies (in liquid water, methanol, and acetonitrile) carried out primarily by unpaid foreign visitors to our laboratory on minicomputer controlled ultrasonic absorption and electric field jump equipment paid for by previous AFOSR grants.

AFOSR Program Manager: Lorelei A. Krebs, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Kinetic Spectroscopy of Metal Atom/Oxidizer Chemiluminescent Reactions for Laser Applications
2. PRINCIPAL INVESTIGATOR: Dr. Arthur Fontijn
AeroChem Research Laboratories, Inc.
P.O. Box 12
Princeton, N.J. 08540
3. INCLUSIVE DATES: 1 May 1976 to 30 April 1979
4. GRANT NUMBER: F44620-76-C-0108
5. COSTS AND FY SOURCE: \$24,769, FY76; \$44,959, FY77; \$42,795, FY78;
\$47,640, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. William Felder
Dr. Dennis M. Manos
7. JUNIOR RESEARCH PERSONNEL:

James J. Houghton
William R. Frenchu
8. PUBLICATIONS:

"HTFFR Kinetics Studies: A Chemiluminescence Titration Method for Determination of Absolute Sn Concentrations," A. Fontijn and W. Felder, Chem. Phys. Lett., 47, 380 (1977).

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"High Temperature Flow Tubes - Generation and Measurement of Refractory Species," A. Fontijn and W. Felder, in Reactive Intermediates in the Gas Phase: Generation and Monitoring, D. W. Setser, Ed. (Academic Press, New York), to be published.

"Studies of Elementary Reaction Kinetics of High-Temperature Species Using Optical Measurement Techniques," A. Fontijn, in Characterization of High Temperature Vapors and Gases, J. W. Hastie, Ed. (The National Bureau of Standards), to be published.

"HTFFR Kinetics Studies of the Ge/N₂O Chemiluminescent Reaction," A. Fontijn and W. Felder, J. Chem. Phys., submitted.

"Additional HTFFR Observations on Chemiluminescent Sn-Oxidizer Reactions," D. M. Manos and A. Fontijn, J. Chem. Phys., submitted.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The goals of this program were to provide quantitative kinetic information on reactions having a large branching ratio for excited state production. A major interest in these reactions arises from their potential usefulness as chemical electronic transition laser (CETL) pumps.

The general types of information obtained were:

- a. Overall (production of all states) rate coefficients, as a function of temperature.
- b. Photon yields (i.e., the fraction of reactive events leading to production of a photon) as a function of temperature; in the limit of no quenching these yields equal the branching ratios, which are the more fundamental quantity of interest to CETL development.
- c. Stern-Volmer coefficients, τk_Q , for quenching by reactants, bath gases, and products.
- d. Mechanistic information.

These studies were performed in high-temperature fast-flow reactors (HTFFR) which are uniquely suited to obtaining kinetic and kinetic spectroscopic information over large temperature ranges (300-1900 K). Temperatures from 300-1300 K were used in this study and pressures were generally in the 3-100 Torr range.

In previous studies we had found that the Sn/N₂O reaction produced SnO in its lowest excited state ($a^3\Sigma$) with an exceptionally high photon yield (0.53 ± 0.26). The work therefore concentrated on

obtaining more accurate and detailed information on this reaction and on making a comparison to other Group IVA element/oxidizer chemiluminescent reactions to establish trends. It was found that the Sn/N₂O reaction is unique among these N₂O reactions in producing such high yields. Yields of the Ge/N₂O reaction are two to three orders of magnitude lower and literature data suggest similarly low yields for Si/N₂O, while Pb/N₂O is insufficiently exothermic to produce electronically excited PbO. GeO(a) is moreover efficiently quenched by N₂O while SnO(a) is not quenched by Sn, N₂O, Ar, or N₂ in the concentrations investigated. A more qualitative investigation of the Sn/O, Sn/O₂, and Sn/O/O₂ reactions provided further insights for the Sn/N₂O system but did not suggest a useful alternative laser pumping reaction.

A possible limitation on the use of Sn/N₂O as a chemical laser pumping reaction is the finding that the precursor of SnO(a) is quenched by products of this reaction. This process occurs in competition with the desired transfer, by bath gas molecules, of molecules from this reservoir state to the SnO(a) state. High pressures would thus be beneficial to a Sn/N₂O based CETL and quantitative relations for the influence of the ratio of bath gas to product concentrations on the SnO(a) yield were derived.

Additionally, an extensive review chapter was prepared for a book on generation and monitoring of reactive species in the gas phase. This chapter contains discussions of (i) the HTFFR technique and (ii) other methods for studying metal atom oxidation reactions. In the sections on the HTFFR technique much detail is assembled on HTFFR measurement methods which was not obtainable in convenient form from our previous publications. In addition, this preparation led us to examine several fine points regarding accuracy of measurements which benefitted our subsequent work under this contract. Several such points, including for example, the accuracy of absolute atom concentration (and hence also photon yield) measurements by absorption, are of equal significance to measurements made by other experimental techniques. The sections on such other techniques include a discussion of their relative advantages and disadvantages for given types of measurement. The review provides extensive data summaries in tabular form which should be helpful in assessing the status of CETL research.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Selective Chemical Pumping of Electronic States; Formation and Deactivation Processes in Electronic Transition Chemically Pumped Lasers
2. PRINCIPAL INVESTIGATOR: Dr. James L. Gole
Department of Chemistry
Georgia Institute of Technology
Atlanta, Georgia 30332

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Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
3. INCLUSIVE DATES: 1 September 1974 to 1 October 1978
4. GRANT NUMBER: AFOSR-78-3515; AFOSR-78-2758
5. COSTS AND FY SOURCE: \$37,667 (\$75,333/2)*, FY75; \$38,880 (\$77,759/2)*, FY76; \$12,103 (\$84,206/2)*, FY77; \$36,500, FY78

*Joint with J. I. Steinfeld, M.I.T.

6. SENIOR RESEARCH PERSONNEL:

Dr. Gerald Stewart
Professor Derek Lindsay
Dr. S. Anthony Pace

7. JUNIOR RESEARCH PERSONNEL:

Carl L. Chalek	Steven B. Oblath
Donald R. Preuss	Gary J. Green
Michael J. Sayers	Alfred Hanner
David Liu	Winfred Crumley
Lawrence H. Dubois	Andrew Langford

8. PUBLICATIONS:

"Single Collision Selective Chemical Reaction of Group III Metals (Sc, Y, La) and Halogens, (F₂, ClF, SF₆ and Cl₂)," C. Chalek, D. R. Preuss and J. L. Gole, in Proceedings, 2nd Summer Colloquium on Electronic Transition Lasers (J. I. Steinfeld, ed.), p. 50, M.I.T. Press, Cambridge, MA, 1976.

"Kinetics of Metastable Excited State Products in a Beam-Gas Chemiluminescent Reaction," J. L. Gole, D. R. Preuss and C. L. Chalek, J. Chem. Phys., 66, 548 (1977).

"Al + O₃ Chemiluminescence: Perturbations and Vibrational Population Anomalies in the B²Σ⁺ State of AlO," D. M. Lindsay and J. L. Gole, J. Chem. Phys., 66, 3886 (1977).

"Characterization of the Ground and Excited States of Lanthanum Oxide through Bimolecular Oxidation of La Metal with O₂, NO₂, N₂O and O₃," J. L. Gole and C. L. Chalek, J. Chem. Phys., 65, 4384 (1976).

"Correlation of Molecular Dynamics and Molecular Electronic Structure Demonstrating a Probable Inflection in the D²Σ⁺ State of Lanthanum Oxide," J. L. Gole, J. Chem. Phys., in press.

"Reactions of Silanes with Halogens: Chemiluminescent Products in the UV-Visible Regions," C. P. Conner, G. W. Stewart, D. W. Lindsay and J. L. Gole, J. Amer. Chem. Soc., 99, 2540 (1977).

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"The Temperature Dependence of Chemiluminescent Reactions - Activation Energies for Excited State Formation," D. R. Preuss and J. L. Gole, in Proceedings, 3rd Summer Colloquium on Electronic Transition Lasers (J. I. Steinfeld, S. Suchard and L. E. Wilson, eds.), p. 176, M.I.T. Press, Cambridge, MA, 1977.

"High Temperature Chemistry: Modern Research and New Frontiers," J. L. Gole, Ann. Rev. Phys. Chem. 27, 525 (1976).

"Beam-Gas Chemiluminescent Reactions of Group IIIB Metals and Halogen Molecules - Evidence for Selective Excited State Emission," with Carl L. Chalek, J. Chem. Phys. (accepted with revision).

"A Comparative Study of Excited State Cross Sections for Group IIIB Halide and Oxide Production - Lower Bounds for Excited State Quantum Yields," with Carl L. Chalek, J. Chem. Phys. (accepted with revision).

"A Proposed Model for Selective Excited State Production in Electron Transfer Metal Oxidation," J. L. Gole and C. L. Chalek, to be published.

"A Comparative Study of Group IIIB - Halogen Reactions. II. Observation of ScCl_2 , ScBr_2 and ScI_2 Chemiluminescence, J. L. Gole, (in preparation).

"Dynamic Constraints Observed in Scandium and Yttrium Oxidation," Burke Ritchie, C. L. Chalek and James L. Gole, (in preparation).

"A Comparative Study of Group IIIB - Halogen Reactions. Possible Applications to Chemical Laser Development," with Carl L. Chalek, Proceedings of the Electrochemical Society, Electrothermics and Metallurgy, Atlanta, GA, 1977, Proceedings on "High Temperature Metal Halide Chemistry," Vol. 78-1, p. 278, The Electrochemical Society.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A variety of high temperature techniques have been combined with molecular beam and laser technology to analyze energy partitioning and chemical reaction dynamics in both simple and complex metatheses. Emphasis has been on chemiluminescent systems and their potential development into visible chemical lasers.

In approaching this problem we have operated under the following criteria:

- a. We have searched for systems characterized by selective excited state formation.
- b. We have required that selectively formed states be formed with high quantum yields (copious excited state production). A high quantum yield virtually assures that certain upper state vibrational levels show inversion with respect to other ground state vibrational levels.
- c. The lifetimes of those excited states in which we focus interest should be on the order of 10^{-6} to 10^{-4} seconds. This criteria is determined by the time necessary for intimate reactant mixing at typical laser operating pressures. At 6 torr the requisite mixing time is $\approx 10^{-5}$ secpmds.
- d. Excluding collision-induced transfers among excited states at higher pressures, the criteria of selectivity and high quantum yield virtually require that the activation energy for excited state product formation be less than or equal to the activation energy for ground state product formation in a given system. Hence, one must establish the temperature coefficient for any metatheses producing the excited states of interest.

e. In studying reactions from low ($< 10^{-5}$ torr) to high pressures (≤ 10 torr), excited state deactivation (quenching) should be at a minimum.

f. At higher pressures, rapid collisional transfer rates among excited electronic states, especially those involving long-lived reservoir states, must be catalogued.

In approaching these criteria, our most notable accomplishments may be summarized as follow:

Development of an Approach to Selectivity - A screening principle for obtaining selective excited state production was developed. The application of this screening principle led to the discovery of a series of reactions satisfying the six criteria which we have outlined. It appears that the reactions of group IIIB metals (Sc, Y) and halogens (both homo- and hetero-nuclear) result in the production of a long-lived, selectively formed excited electronic state which undergoes minimal quenching at higher pressures. Based on a comparative study of Group IIIB halogenation and oxidation (monohalide or oxide formation) a model for selective excited state production in electron transfer metal oxidations has been proposed.

Determination of Activation Energies for Formation of Excited Electronic States - A good portion of our research effort has focused on the determination of activation energies for excited state formation using our recently developed procedure for the analysis of beam-gas chemiluminescent reactions. This work is in large part an outgrowth of the fourth criteria outlined above. The activation energies for excited state formation in several systems have been compared. The methodology has also been formulated whereby one can determine whether or not a metathesis results from reaction of ground or excited state metal atoms.

Quantum Yield Determinations - Techniques have been developed to determine the branching ratios for ground and excited state formation in various metatheses. Comparative studies of quantum yields defined as

no. of excited states formed/total no. of molecules formed

have been made for several Group IIIB halogenations and oxidations. In addition, comparisons have been made with Group IIA - halogen reactions. These studies indicate that the group IIIB halides are formed with unusually high quantum yields.

Radiative Lifetimes - A relatively straightforward technique has been developed for the approximate determination of long-lived excited state radiative lifetimes (10^{-2} to 10^{-4} seconds). This technique is

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on the kinetics of metastable states formed in a beam-gas reaction and takes advantage of the "collision induced" enhancement of fluorescence which can characterize these systems. Because radiative lifetimes in the range from 10^{-4} to 10^{-2} seconds are very difficult to measure experimentally, a straight-forward approximate method for their determination can be quite useful.

"Superhighways" for Energy Transfer Among Excited States - We have been concerned with very efficient energy transfer routes connecting the excited states of high temperature molecules and have developed techniques which allow us to discern the locations of nonequilibrium distributions caused by these energy transfers. We are dealing with energy transfer occurring at gas kinetic or faster rates. This rapid transfer results from the strong interactions and hence perturbations between the excited states of high temperature molecules. The transfer routes manifest themselves as one extends "single collision" chemiluminescent studies ($\approx 10^{-6}$ to 10^{-4} torr) to higher pressures commensurate with the operation of a typical chemical laser system (1 to 100 torr). Our focus in these studies has been in large part on metal oxidation reactions and the controlled relaxation of distributions observed under single collision conditions.

Exploding Wire Laser Studies - We are attempting to achieve lasing action in those systems which we deem promising using an exploding wire laser system developed at Los Alamos Scientific Laboratory. This system has been moved from Los Alamos to our laboratory and is currently being used to study Group IIIB metal-halogen systems.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Photoluminescence Spectroscopy with a CW Dye Laser: A Study of the Diatomic Alkaline Earth Metal Halides and Oxides
2. PRINCIPAL INVESTIGATOR: Dr. David O. Harris
Department of Chemistry
University of California
Santa Barbara, California 93106
3. INCLUSIVE DATES: 1 June 1973 - 31 December 1977
4. GRANT NUMBER: AFOSR 73-2565
5. COSTS AND FY SOURCE: \$39,575, FY73; \$40,210, FY74; \$40,353, FY75;
\$40,832, FY76
6. SENIOR RESEARCH PERSONNEL: Robert W. Field
7. JUNIOR RESEARCH PERSONNEL:

Peter J. Domaille
Timothy C. Steimle
8. PUBLICATIONS:

"Vibrational Population Distribution of Ground State BaO Formed by the Reaction Ba + O₂," Michael A. Revelli, Brian G. Wicke and David O. Harris, Chem. Phys. Lett., 39, 454 (1976).

"Vibrational Population Distributions of Ground State Barium Oxide Formed in the Ba + O₂ and Ba + N₂O Reactions," Michael A. Revelli, Brian G. Wicke and David O. Harris, J. Chem. Phys., 66, 732 (1977).

"On the Importance of Ba(³D) as the Key Reactant Leading to BaO(A-X) Chemiluminescence in the Ba + N₂O Reaction," Brian G. Wicke, Michael A. Revelli and David O. Harris, J. Chem. Phys., 63, 3120 (1975).

"Argon Ion and Dye Laser Induced MgO B¹Σ⁺ + -X¹Σ⁺ and B¹Σ⁺ - A¹Π Photoluminescence Spectra (Analysis of a³Π_i - X¹Σ⁺ + Perturbations)," Tatsuya Ikeda, Nign Bew Wong and David O. Harris, J. Mol. Spectr., 68, 452 (1977).

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"The Rotational Spectrum of the $\chi^2\Sigma^+$ State of the Ca^{35}Cl Radical Using Laser Microwave Optical Double Resonance," Peter J. Domaille, Timothy C. Steimle and David O. Harris, J. Mol. Spectr., 66, 503 (1977).

"Optical-Optical Double Resonance with Two Dye Lasers: Rotational Analysis of the $\text{E}^2\Sigma - \text{B}^2\Sigma$ System of Ca^{35}Cl ," Peter J. Domaille, Timothy C. Steimle and David O. Harris, J. Chem. Phys., 68, 4977 (1978).

"Rotational Analysis of the $\text{B}^2\Sigma^+ - \chi^2\Sigma^+$ System of SrF Using a cw Tunable Dye Laser," Timothy C. Steimle, Peter J. Domaille and David O. Harris, J. Mol. Spectr., 68, 134 (1977).

"The Rotational Spectrum of the $\chi^2\Sigma^+$ State of the SrF Radical Using Laser Microwave Optical Double Resonance," Peter J. Domaille, Timothy C. Steimle and David O. Harris, J. Mol. Spectr., 68, 146 (1977).

"Continuous Wave Dye Laser Excitation Spectroscopy $\text{CaF } \text{A}^2\Pi_r - \chi^2\Sigma^+$," Robert W. Field, David O. Harris and Takehiko Tanaka, J. Mol. Spectr., 57, 107 (1975).

"Microwave Optical Double Resonance and Reanalysis of the $\text{CaF } \text{A}^2\Pi_r - \chi^2\Sigma$ Band System," Jun Nakagawa, Peter J. Domaille, Timothy C. Steimle and David O. Harris, J. Mol. Spectr., 70, 374 (1978).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

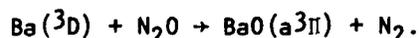
A. Spectroscopic Studies of the Barium Plus Oxidant Reaction.

There has been considerable interest in efficient chemiluminescent reactions between metal atoms and suitable oxidants as candidates for chemically pumped laser systems. This prompted a detailed study of the nature and mechanism of the reaction of Barium with N_2O , O_2 and NO_2 . In particular, it has been observed that in the reaction of $\text{Ba} + \text{N}_2\text{O} \rightarrow \text{BaO}$, fully 20 percent of all the Ba atoms reacting yield photons originating from the $\text{A}^1\Sigma$ excited state of BaO. In addition, one third of those photons arise from $v' = 1$ of the $\text{A}^1\Sigma$ state. It was therefore of interest to investigate the possibility of there being a population inversion between $\text{A}^1\Sigma(v' = 1)$ and vibrational levels of the $\text{X}^1\Sigma$ ground state of BaO under the conditions existing in the $\text{Ba} + \text{N}_2\text{O}$ flame.

Experiments were carried out in which single vibrational levels v' , of the $\text{A}^1\Sigma$ state were pumped from adjacent ground state vibrational levels using a tunable cw dye laser. By monitoring the photoluminescence intensity originating from a pumped excited state level, v' , to a third ground state level it was possible to measure the relative populations of the two adjacent ground state vibrational levels.

Repeated application of this technique yielded the relative vibrational population distribution of the ground state manifold as a function of various flame conditions. Using previously available data and our results, suggest that a population inversion may exist between $A^1\Sigma(v'=1)$ and $X^1\Sigma(v''=7)$. Our experiments and results are reported in detail in references 1 and 2.

A second area of interest was the details of the mechanism of the $Ba + N_2O$ reaction which leads to the observed high $A \rightarrow X$ chemiluminescence efficiency and why such a large proportion of the emitting molecules are in the $A^1\Sigma(v'=1)$ state. Specifically it had been proposed that metastable $BaO(a^3\Pi)$ which cannot emit to the ground state serves as a reservoir state for the reaction. Molecules trapped in this state relax vibrationally to the first few vibrational levels of the $a^3\Pi$ metastable state and are then transferred collisionally to the $A^1\Sigma$ state from which they emit. This leads to the high chemiluminescence efficiency. It had been further proposed that the $BaO(a^3\Pi)$ was initially formed via the reaction of $Ba(^3D)$ excited state atoms ($\Delta E = 1$ e.v.) present in the flame by the reaction



In order to test this hypothesis we carried out a series of experiments in which total $A^1\Sigma - X^1\Sigma$ chemiluminescent yield as a function of $Ba(^3D)$ concentration was monitored. As reported in reference 3, it was found that an increase of $Ba(^3D)$ concentration by a factor of ten to a hundred had no significant effect on chemiluminescent yield. Thus we conclude that $Ba(^3D)$ is not the key reactant leading to the observed high chemiluminescence efficiency.

B. The a^3 State of MgO

We recently completed our laser induced fluorescence study of MgO . MgO is produced by the reaction $Mg + O_2$ in an apparatus similar to that used for the study of BaO . Three lines of the Ar^+ laser have the following chance coincidences with transitions in the $MgO B^1\Sigma - X^1\Sigma$ system

476.5nm	R(26)	5-4 band	^{24}MgO
	R(49)	4-3 band	^{24}MgO
	R(70)	3-2 band	^{24}MgO
496.5nm	R(36)	2-2 band	^{26}MgO
514.5nm	P(10)	4-5 band	^{24}MgO
	R(25)	3-4 band	^{26}MgO
	R(50)	2-3 band	^{25}MgO
	R(70)	1-2 band	^{24}MgO

Photoluminescence spectra from $B^1\Sigma$ to both the $X^1\Sigma$ ground state and the $A^1\Pi$ excited state ($T_e = 3563 \text{ cm}^{-1}$) and calculated Franck-Condon factors confirm these assignments. In addition to the B-X and A-X systems, transitions were observed and assigned to the previously unobserved $a^3\Pi$ state which is iso configurational with the $A^1\Pi$ state. In the case of the 476.5 nm excitation, the 5 GHz linewidth of the Ar^+ laser produces simultaneous excitation of all three levels listed above. However, when the laser is operated single mode by insertion of an intracavity Fabry Perot etalon the spectrum is greatly simplified by reducing the number of coincidences. The laser can be scanned over its gain profile in 150 MHz steps thus exciting each of the coincidences sequentially with little overlap, and the resulting fluorescence spectrum is particularly simple. As was expected a $B^1\Sigma \rightarrow X^1\Sigma$ P-R doublet is seen, but in addition transitions to a $^3\Pi_0$ and a $^3\Pi_1$ are also observed. These normally unallowed $B^1\Sigma - a^3\Pi$ "extra" lines are made possible by specific perturbations between levels of the $X^1\Sigma$ and $a^3\Pi$ manifolds. Additional fluorescence spectra were obtained as a function of etalon setting. By comparing relative intensities of each line and noting those sets which remain constant relative to each other as the etalon is tuned, transitions originating in the $v=4$ and 5 of $B^1\Sigma$ MgO can also be uniquely assigned.

The perturbations are a sensitive probe of the positions of the energy levels of a^3 relative to those of $X^1\Sigma$. For example, the perturbation allowed extra lines of the $J'=69$ (3,3) transition to appear on either side of the main $B^1\Sigma - X^1\Sigma$ lines thus indicating that the Π_0 and Π_1 levels bracket the corresponding Σ level. Conversely, however, for the $J'=25$ (5,5) lines the extra lines both appear to the red of the main line.

Analysis of these perturbations using some sixty lines has resulted in an accurate determination of the molecular constants of the $a^3\Pi$ state.

This work is described in detail in reference 4.

C. Excitation, Microwave Laser Double Resonance and Laser-Laser Double Resonance Spectroscopy of CaCl , CaF and SrF

We have carried out an extensive program on the spectroscopy of the alkali metal halides. Despite the simplicity of these molecules, little prior work has been done due to the complexity of their spectra. The first electronic excited state of these molecules corresponds to the excitation of an ns electron to an empty np orbital on the metal resulting in two nearby molecular electronic states: $A^2\Pi$ and $B^2\Sigma$. Since the excitation involves a non-bonding electron, most of the molecular parameters in the $A^2\Pi$ and $B^2\Sigma$ states are only slightly

changed relative to the $X^2\Sigma$ ground state. Consequently, the A-X and B-X spectra occur mainly as $\Delta V=0$ transitions yielding extremely dense and overlapped spectra. Despite this complexity which prevented their study and analysis using conventional spectroscopic techniques, it has been possible to use tunable lasers to completely characterize several electronic states of several alkaline earth monohalides. Included are (1) a study of the $B^2\Sigma - X^2\Sigma$ system of CaCl (reference 5) using tunable laser excitation spectroscopy; (2) an accurate determination of the ground state constants of CaCl using laser-microwave optical double resonance (reference 6) and (3) a rotational analysis of the $E^2\Sigma - B^2\Sigma$ system of CaCl using optical-optical double resonance (reference 7). Similar studies on SrF (references 8 and 9) and on CaF (references 10 and 11) have also been carried out.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Processing Mechanisms, Structure and Morphology of High-Temperature Polymeric Alloys
2. PRINCIPAL INVESTIGATOR: Dr. Ian L. Hay
Celanese Corporation
Celanese Research Company
Box 1000
Summit, New Jersey 07901
3. INCLUSIVE DATES: 1 February 1977 - 31 January 1979
4. CONTRACT NUMBER: F49620-77-C-0046
5. COSTS AND FY SOURCE: \$29,246, FY77; \$49,681, FY78; \$18,762, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. J. R. Shaner
Dr. P. K. Sullivan

7. PUBLICATIONS:

"Processing Mechanisms, Structure and Morphology of High Temperature Polymeric Alloys Part I," I. L. Hay and J. R. Shaner, AFOSR-TR-78-0954, April 1978.

"Processing Mechanisms, Structure and Morphology of High Temperature Polymeric Alloys, Part II," I. L. Hay, J. R. Shaner and P. K. Sullivan, AFOSR-TR-78-0954, March 1979.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this program was to study the mechanisms of the processability of intractable polymers when alloyed with compatible polymers and monomers.

The processing conditions expected to optimize interactions at a molecular level between poly(bisbenzimidazobenzophenanthroline) (BBB) and polybenzimidazole (PBI) were investigated and the reaction products evolved under these conditions examined. Studies of the mechanical properties and the morphology indicate that binary interactions between BBB-BBB, PBI-PBI and BBB-PBI may all be occurring. The BBB-BBB interactions occur at temperatures greater than 500°C

but PBI-PBI and BBB-PBI interactions arise at temperatures more than 100°C lower. Mass spectroscopic studies indicate that the principal reaction products in the presence of PBI are water and phenol whereas with BBB alone only water is evolved. Moreover in the mixture of BBB-PBI, phenol is evolved at lower temperatures than is the case with PBI alone. Possible end group reactions and reactions with partially cyclized rings, consistent with the observed evolution of water and phenol, are proposed for the improved processability of BBB in the presence of PBI.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Novel Organophosphorus and Organonitrogen Derivatives and Their Use for the Synthesis of Unusual Transition Metal Complexes
2. PRINCIPAL INVESTIGATOR: Dr. R. B. King
Department of Chemistry
University of Georgia
Athens, Georgia 30602
3. INCLUSIVE DATES: 30 June 1975 to 30 September 1979
4. GRANT NUMBER: AFOSR-75-2869
5. COSTS AND FY SOURCE: \$40,000, FY75; \$40,000, FY76; \$45,000, FY77;
\$45,000, FY78
6. SENIOR RESEARCH PERSONNEL:

Dr. W. F. Masler, III	Dr. K. -N. Chen
Dr. J. Gimeno	Dr. T. J. Lotz
Dr. W. Z. M. Rhee	Dr. T. -W. Lee
Dr. S. Goel	Dr. R. N. Kapoor
7. JUNIOR RESEARCH PERSONNEL:

S. P. Diefenbach	R. M. Murray
M. Chang	K. S. Raghuveer
J. W. Bibber	H. E. Davis
8. PUBLICATIONS:

"Complexes of Trivalent Phosphorus Derivatives. XVIII. Some Complexes of Neopentylphosphines with Rhodium, Nickel, and Palladium Chlorides," R. B. King, J. C. Cloyd, Jr., M. E. Norins, and R. H. Reimann, J. Coord. Chem., 7, 23 (1977).

"Tris[methylaminobis(difluorophosphine)] metal (0) Derivatives of Chromium, Molybdenum, and Tungsten: New Volatile Carbonyl-free Zerovalent Metal Derivatives of High Thermal and Oxidative Stabilities," R. B. King and J. Gimeno, Chem. Comm., 142 (1977).

"Novel Bimetallic Products from Octacarbonyldicobalt and Methylaminobis-(difluorophosphine)," M. G. Newton, R. B. King, M. Chang, N. S. Pantaleo, and J. Gimeno, Chem. Comm., 531 (1977).

- "Novel Bimetallic Products from Iron Carbonyls and Methylaminobis (difluorophosphine): an Example of Square Pyramidal Pentacoordinate Iron(0)," M. G. Newton, R. B. King, M. Chang, and J. Gimeno, J. Amer. Chem. Soc., 99, 2802 (1977).
- "Polytertiary Phosphines and Arsines. XV. Some Polyphosphines with Terminal Dialkylamino and Alkoxy Groups," R. B. King and W. F. Masler, J. Amer. Chem. Soc., 99, 4001 (1977).
- "Organonitrogen Derivatives of Metal Carbonyls. XII. Reactions of Cyclopentadienylmetal Tricarbonyl Chlorides of Molybdenum and Tungsten with Pyrazole and Imidazole," R. B. King and K. -N. Chen, Inorg. Chem., 16, 3372 (1977).
- "Cyclopentadienylbis[methylaminobis-(difluorophosphine)]vanadium: The First Fully Substituted Cyclopentadienyltetracarbonylvanadium Derivative," R. B. King and K. -N. Chen, Inorg. Chim. Acta, 23, L19 (1977).
- "Methylaminobis-(difluorophosphine) as a Monoligate Monometallic Ligand," R. B. King, M. G. Newton, J. Gimeno, and M. Chang, Inorg. Chim. Acta, 23, L35 (1977).
- "Tetrakis[methylaminobis(difluorophosphine)] carbonyldiiron: Unsymmetrical Bonding of Methylaminobis-(difluorophosphine) to a Pair of Transition Metals Involving Phosphorus-Nitrogen Bond Cleavage," M. G. Newton, R. B. King, M. Chang, and J. Gimeno, J. Amer. Chem. Soc., 100, 326 (1978).
- "Novel Iron Complexes from Cocondensations of Iron Vapor with Amino-difluorophosphines," M. Chang, R. B. King, and M. G. Newton, J. Amer. Soc., 100, 998 (1978).
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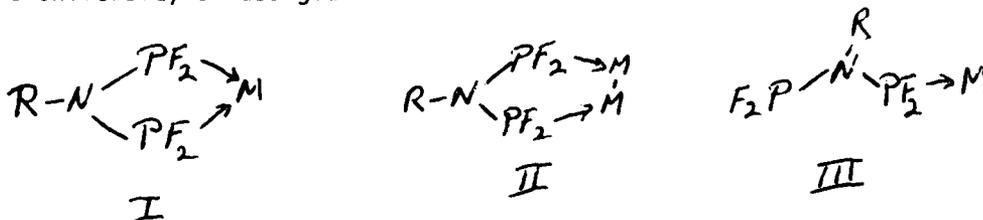
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The original objective of this basic research program was the development of new organophosphorus and organonitrogen ligands and their transition metal complex chemistry. The most significant scientific achievement during the course of this research program was the development of the transition metal chemistry of the chelating strong π -acceptor fluorophosphine ligands of the type $RN(PF_2)_2$ ($R=CH_3$ and C_6H_5). This work resulted in the discovery of materials with unexpected thermal and oxidative stability (e.g. $[CH_3N(PF_2)_2]_3Cr$) and with unusual redox properties (e.g. $[CH_3N(PF_2)_2]_3Co_2(CO)_2$). Another significant achievement arising from this research project was the development of the first general methods for the synthesis of polyphosphines containing terminal dialkylamino and/or alkoxy groups. Such polyphosphines are useful not only as ligands in transition metal chemistry but are also reactive intermediates for the synthesis of a variety of organophosphorus compounds including materials potentially useful for antioxidants and flame-resistant polymers.

The results of this work can be grouped into the following major areas:

a. Transition Metal Fluorophosphine Complexes.

Ligands of the type $RN(PF_2)_2$ have been shown to bond to transition metals in diverse ways. They can act as bidentate ligands forming four-membered chelate rings (I) or they can bridge a metal-metal bond to form five-membered chelate rings (II). Alternatively, they can function as a monodentate ligand (III) in which case the uncomplexed PF_2 group is susceptible towards solvolytic cleavage to form a coordinated CH_3NHPF_2 ligand. Furthermore, in certain cases a $CH_3N(PF_2)_2$ ligand can undergo phosphorus-nitrogen cleavage to form complexes containing separate CH_3NPF_2 and PF_2 units. Examples of all of these types of chemical bonding of $RN(PF_2)_2$ ligands have now been characterized by X-ray diffraction structure determinations in collaboration with Prof. M. G. Newton of the Chemistry Department of the University of Georgia.



Ultraviolet irradiation of the metal hexacarbonyls $M(\text{CO})_6$ ($M = \text{Cr}$, Mo , and W) with excess $\text{RN}(\text{PF}_2)_2$ ($R = \text{CH}_3$ and C_6H_5) results in complete displacement of all six carbonyl groups to give white volatile $[\text{RN}(\text{PF}_2)_2]_3M$ ($R = \text{CH}_3$ and C_6H_5 ; $M = \text{Cr}$, Mo , and W) exhibiting relatively high thermal and oxidative stabilities. Displacement of norbornadiene from $\text{C}_7\text{H}_8\text{M}(\text{CO})_4$ ($M = \text{Cr}$, Mo , and W) with $\text{RN}(\text{PF}_2)_2$ ($R = \text{CH}_3$ and C_6H_5) can give either the corresponding chelates $\text{RN}(\text{PF}_2)_2\text{M}(\text{CO})_4$ or the monodentate complexes $[\text{RN}(\text{PF}_2)_2]_2\text{M}(\text{CO})_4$ ($M = \text{Cr}$, trans isomer; $M = \text{Mo}$ and W , cis isomer) depending upon the reaction conditions. Displacement of cycloheptatriene from $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_3$ with $\text{RN}(\text{PF}_2)_2$ ($R = \text{CH}_3$ and C_6H_5) gives mer- $[\text{RN}(\text{PF}_2)_2]_2\text{Cr}(\text{CO})_3$ containing one monodentate and one bidentate $\text{RN}(\text{PF}_2)_2$ ligand as well as the binuclear complex mer- $[\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2]_3\text{Cr}_2(\text{CO})_6$. Pyrolysis and/or photolysis of some of these systems can lead to binuclear complexes of the types $[\text{RN}(\text{PF}_2)_2]_3\text{M}_2(\text{CO})_5$ ($R = \text{CH}_3$, $M = \text{Cr}$, Mo , and W ; $R = \text{C}_6\text{H}_5$, $M = \text{Mo}$), $[\text{RN}(\text{PF}_2)_2]_4\text{M}_2(\text{CO})_3$ ($R = \text{CH}_3$, $M = \text{Mo}$ and W ; $R = \text{C}_6\text{H}_5$, $M = \text{Mo}$), $[\text{CH}_3\text{N}(\text{PF}_2)_2]_5\text{M}_2\text{CO}$ ($M = \text{Mo}$ and W , and $[\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2]_5\text{Mo}_2(\text{CO})_2$. The complexes $[\text{RN}(\text{PF}_2)_2]_3\text{M}_2(\text{CO})_5$ and $[\text{RN}(\text{PF}_2)_2]_4\text{M}_2(\text{CO})_3$ are shown by X-ray crystallography and infrared spectroscopy to contain bridging carbonyl groups, a rare structural feature for Cr , Mo , and W carbonyl derivatives.

Reactions of iron carbonyls with $\text{RN}(\text{PF}_2)_2$ ligands give a variety of products depending upon the reaction conditions. Mononuclear products include monodentate $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Fe}(\text{CO})_4$, $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Fe}(\text{CO})_2$ containing one monodentate and one bidentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand, and $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{FeCO}$ containing two bidentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands. Binuclear products include the complete metal-metal bonded series of formal $\text{Fe}_2(\text{CO})_9$ substitution products $[\text{CH}_3\text{N}(\text{PF}_2)_2]_n\text{Fe}_2(\text{CO})_{9-2n}$ ($n = 1, 2, 3$, and 4). However, X-ray diffraction of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}_2\text{CO}$ indicates an unprecedented structure where the P-N bond of one of the $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands has been cleaved to form separate PF_2 and CH_3NPF_2 units. Cocondensation of iron vapor with $\text{CH}_3\text{N}(\text{PF}_2)_2$ gives $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}$ shown by X-ray diffraction to have a structure containing three monodentate and one bidentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands. Reaction of $[\text{C}_6\text{H}_5\text{CH}=\text{CHC}(\text{O})\text{CH}_3]\text{Fe}(\text{CO})_3$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ involves the coordinated benzalacetone ligand in an unexpected manner to give a product shown by X-ray diffraction to be the diene-iron complex $[\text{C}_6\text{H}_5\text{CHC}(\text{CH}_3)=\text{C}(\text{OPF}_2)\text{N}(\text{CH}_3)\text{PF}_2]\text{Fe}(\text{CO})(\text{PF}_2)_2\text{NCH}_3$.

The cobalt chemistry of $\text{RN}(\text{PF}_2)_2$ ligands is dominated by a variety of stable derivatives containing $[\text{RN}(\text{PF}_2)_2]_3\text{Co}_2$ units in which a cobalt-cobalt bond is bridged by three $\text{RN}(\text{PF}_2)_2$ ligands. For example, reaction of $\text{Co}_2(\text{CO})_8$ with $\text{RN}(\text{PF}_2)_2$ ($R = \text{CH}_3$ and C_6H_5) at room temperatures results in rapid CO evolution to form the purple complexes $[\text{RN}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ ($R = \text{CH}_3$ and C_6H_5). The terminal CO groups in these complexes can be replaced by a variety of other ligands including tertiary phosphines, phosphites, isocyanides, and fluorophosphines. The $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2$ system in $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2(\text{CO})_2$ survives bromination to brown $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Co}_2\text{Br}_4$ as well as stepwise chemically and electrochemically reversible reduction to a green radical anion and a yellow dianion.

Reactions of $\text{Ni}(\text{CO})_4$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ give the binuclear complexes $[\text{CH}_3\text{N}(\text{PF}_2)_2]_6\text{Ni}_2$, $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Ni}_2(\text{CO})_2$, or $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Ni}_2(\text{CO})_3$ or a coordination polymer $\{[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Ni}\}_n$ depending upon the reaction conditions. Mass spectrometry data indicate that the coordination polymer sublimates in vacuum as a dimer $\{[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Ni}\}_2$.

A variety of interesting complexes have been obtained by various reactions of cyclopentadienylmetal carbonyls with $\text{CH}_3\text{N}(\text{PF}_2)_2$. Ultraviolet irradiation of $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ results in the pairwise displacement of CO groups to form successively $\text{C}_5\text{H}_5\text{V}(\text{CO})_2(\text{PF}_2)_2\text{NCH}_3$ and $\text{C}_5\text{H}_5\text{V}[\text{PF}_2]_2\text{NCH}_3$. The latter compound is the first known example of a fully substituted derivative of $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$. Other reactions of cyclopentadienyl-metal carbonyls with $\text{CH}_3\text{N}(\text{PF}_2)_2$ give $\text{C}_5\text{H}_5\text{M}(\text{CO})_2[(\text{PF}_2)_2\text{NCH}_3]\text{Cl}$ (M = Mo and W), $\text{C}_5\text{H}_5\text{M}[(\text{PF}_2)_2\text{NCH}_3]_2\text{Cl}$ (M = Mo and W), $\text{C}_5\text{H}_5\text{Mo}(\text{CO})(\text{NO})(\text{PF}_2)_2\text{NCH}_3$, $\text{C}_5\text{H}_5\text{Mn}(\text{CO})(\text{PF}_2)_2\text{NCH}_3$, $\text{C}_5\text{H}_5\text{Mn}[(\text{PF}_2)_2\text{NCH}_3]_2$, $\text{C}_5\text{H}_5\text{Fe}(\text{CO})(\text{PF}_2)_2\text{NCH}_3\text{Cl}$, and $\text{C}_5\text{H}_5\text{Fe}[(\text{PF}_2)_2\text{NCH}_3]_2\text{Cl}$ containing various combinations of monodentate and bidentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands which can be distinguished by careful examination of their proton and carbon-13 n.m.r. spectra. Ultraviolet irradiation of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ with $\text{CH}_3\text{N}(\text{PF}_2)_2$ results in pairwise displacement of CO groups to form successively $[\text{C}_5\text{H}_5\text{FeCO}]_2(\text{PF}_2)_2\text{NCH}_3$ and $[\text{C}_5\text{H}_5\text{Fe}(\text{PF}_2)_2\text{NCH}_3]_2$. A structure determination on the latter complex by X-ray crystallography indicates rupture of the iron-iron bond and phosphorus-nitrogen bond cleavage of one of the $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands to form separate PF_2 and CH_3NPF_2 units, each of which bridges the pair of iron atoms. The bridging CH_3NPF_2 unit is of particular interest since it is bonded to one iron through its phosphorus and to the other iron through its nitrogen; the latter is the first example of a transition metal-nitrogen bond in amino-fluorophosphine coordination chemistry. The fluorophosphines $\text{RN}(\text{PF}_2)_2$ (R = CH_3 and C_6H_5) undergo facile addition to the metal-metal triple bonds in the pentamethylcyclopentadienyl derivatives $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_2]_2$ (M = Mo and W) to form the corresponding $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_2](\text{PF}_2)_2\text{NCH}_3$ derivatives apparently containing a metal-metal single bond bridged by the $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand.

b. Polyphosphines Containing Terminal Dialkylamino and Alkoxy Groups and their Metal Complexes.

Several polyphosphines containing terminal dialkylamino groups have been prepared. Thus additions of the secondary phosphines R_2PH (R = CH_3 and C_6H_5) to $[(\text{CH}_3)_2\text{N}]_2\text{PCH}=\text{CH}_2$ catalyzed by KH give the corresponding diphosphines $\text{R}_2\text{PCH}_2\text{CH}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$. The base-catalyzed additions of the primary phosphines RPH_2 (R = CH_3 and C_6H_5) to $[(\text{CH}_3)_2\text{N}]_2\text{PCH}=\text{CH}_2$ can be controlled to give either the 1:1 adduct diphosphines $\text{RP}(\text{H})\text{CH}_2\text{CH}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ or the 1:2 adduct triphosphines $\text{RP}[\text{CH}_2\text{CH}_2\text{P}[\text{N}(\text{CH}_3)_2]_2]_2$ depending mainly upon the mole ratio of the reactants. Reaction of KPH_2

Rhodium, nickel, and palladium chloride complexes containing various monodentate neopentylphosphines have been prepared. Attempted addition reactions of hexafluoroacetone or hexafluorobutanedione to $(CF_3)_2Pn(CO)_5$ and $(C_6F_5)_2PFe(CO)_2C_5H_5$ failed. Reactions of pyrazone and imidazole with $C_5H_5M(CO)_3Cl$ ($M = Mo$ and W) lead to both ionic complexes of the type $[C_5H_5M(CO)_2L_2]Cl$ and non-ionic complexes of the type $C_5H_5M(CO)_2LCI$ ($L =$ pyrazole and imidazole), which interconvert very readily in the case of the pyrazole derivatives. Attempts to prepare polypyrazolylborates with tert-butyl, trifluoromethyl, and cyano substituents were unsuccessful. Octahedral metal carbonyl complexes of the types $LM(CO)_5$, $cis-L_2M(CO)_4$, and $fac-L_3M(CO)_3$ have been prepared from both enantiomers of the optically active isocyanide $C_6H_5CH(CH_3)NC$.

AFOSR Program Manager: Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Structure and Properties of Glasses
2. PRINCIPAL INVESTIGATOR: Dr. John D. Mackenzie
Materials Department
University of California
Los Angeles, CA 90024
3. INCLUSIVE DATES: 1 September 1974 - 30 September 1978
4. GRANT NUMBER: AFOSR-75-2764
5. COSTS AND FY SOURCE: \$28,280, FY75; \$44,840, FY76; \$55,913,
FY77; \$44,805, FY78
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8. PUBLICATIONS:

"Development of Glasses for Some New Applications," J. D. Mackenzie,
Proc. Tenth Inter. Cong. on Glass, 4, 71-81 (1974).

"Preparation of Low Dielectric Constant Glasses," F. Chen, B. Dunn
and J. D. Mackenzie, J. Non-Crystalline Solids, 16, 313-314 (1974).

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J. K. Clifton, J. V. Masi and J. D. Mackenzie, Appl. Phys. Letters,
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- "The Electrical Properties of Thin Films of TiN_x and TiC_x ," P. J. P. deMaayer and J. D. Mackenzie, Z. Furer Naturfors. 36a, 1661-1666 (1976).
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"Iron Recovery and Glass Formation from Copper Slag," T. Horiuchi, C. H. Chung and J. D. Mackenzie, Proc. 6th Mineral Waste Symp., Chicago, Ill. May 2-3 (1978).

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Glasses are solidified liquids without long-range order. It is usually difficult to obtain structural information by direct tools such as X-ray diffraction. The relationship between properties and chemical composition is thus difficult to obtain in the absence of structural information. The objectives of this research are to obtain structural information and indirect information from the measured results of some properties. From such structural information and knowledge of chemical composition, it was planned that predictions can be made of properties of some oxide glasses.

In this project, theoretical considerations have led to the development of an equation which permitted the calculation of thermal expansion from a knowledge of chemical composition. Many new glasses of high expansion coefficients were subsequently prepared. The chemical durability of these glasses was significantly improved by ion-exchange of the glasses in fused salt. It was discovered that phase separation in some indicate glasses could result in practically zero expansion coefficients.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Structure and Properties of Glasses
2. PRINCIPAL INVESTIGATOR: Dr. John D. Mackenzie
Materials Department
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3. INCLUSIVE DATES: 1 October 1978 - 30 September 1979
4. GRANT NUMBER: AFOSR-79-0019
5. COSTS AND FY SOURCE: \$56,075, FY79
6. SENIOR RESEARCH PERSONNEL: Dr. T. Yoshio
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8. PUBLICATIONS:

"Improvement of Chemical Durability of High Expansion Phosphate Glasses by Ion-Exchange, K. Matusita and J. D. Mackenzie, J. Matls. Sci., 14, 1508-1509 (1979).

"Fundamental Condition for Glass Formation in Fluoride Systems," C. M. Baldwin and J. D. Mackenzie, J. Am. Ceram. Soc., 62, 537-38 (1979).

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"Ionic Transport and Defect Structure of Vitreous Beryllium Fluoride,"
C. M. Baldwin and J. D. Mackenzie, J. Non-Crystalline Solids,
accepted for publication.

"Infrared Absorption and Structure of Chlorophosphate Glasses,"
R. M. Almeida and J. D. Mackenzie, J. Non-Crystalline Solids,
accepted for publication.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The broad objectives of this research are to obtain a greater understanding of the relationships between structure, chemical composition and properties of glasses. From such understanding it was hoped that new glasses of controllable and predictable properties would be prepared.

During this period, it was first predicted and subsequently confirmed that the elastic modulus of oxide glasses was affected by ion-exchange because of the variation of the "unoccupied space" within the glassy network. The elastic modulus of some silicate glasses was significantly increased by ion-exchange in fused salts. Water entrapped in beryllium fluoride glasses can have a large effect on ionic conductivity despite the fact that fluorine ions are the carriers of current in these glasses. A theory involving a new concept of "defects" in fluoride glasses was satisfactory in explaining the role of water. New composite glasses based on porous silica glass and polymethyl methacrylate with superior optical transmission and high mechanical strengths have been prepared.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Time-Temperature Studies of High Temperature Deterioration Phenomena in Lubricant Systems: Synthetic Ester Lubricants
2. PRINCIPAL INVESTIGATOR: Dr. Lee R. Mahoney
Fuels and Lubricants Department
Ford Motor Company
Dearborn, Michigan 48121
3. INCLUSIVE DATES: 1 April 1976 - 30 September 1979
4. CONTRACT NUMBER: F44620-76-C-0097
5. COSTS AND FY SOURCE: \$80,000, FY76; \$80,000, FY77; \$86,000, FY78; \$86,500, FY79

Government funded 75% of the cost pursuant to applicable cost sharing provisions.

6. SENIOR RESEARCH PERSONNEL:

Dr. Stefan Korcek
Dr. Pierre A. Willermet
Dr. Edwin J. Hamilton, Jr.
Dr. Mikio Zinbo
Dr. Joseph M. Norbeck

7. JUNIOR RESEARCH PERSONNEL:

Ronald K. Jensen
Larry A. Scheich
Shihadeh Kandah

8. PUBLICATIONS AND PRESENTATIONS:

"A Kinetic Study of the Autoxidation of Pentaerythritol Tetraheptanoate at 180 and 200°C," E. J. Hamilton, Jr., S. Korcek, and L. R. Mahoney, 174th National Meeting of the Am. Chem. Soc., Phys. 10, Chicago, Ill., August 1977.

"Kinetics and Mechanism of the Autoxidation of Pentaerythrityl Tetraheptanoate at 180 to 220°C," E. J. Hamilton, Jr., S. Korcek, L. R. Mahoney, and M. Zinbo, Int. J. Chem. Kinet., in press.

"Lubricant Degradation and Wear. IV. The Effect of Oxidation on the Wear Behavior of Pentaerythrityl Tetraheptanoate," P. A. Willermet, L. R. Mahoney, and S. Kandah, to be presented at the 1980 ASME/ASLE Lubrication Conference, San Francisco, California, August 18-21, 1980.

"Kinetics and Mechanism of 4,4'-Dioctyldiphenylamine Inhibited Autoxidation at 160 to 220°C," R. K. Jensen, S. Korcek, L. R. Mahoney, L. A. Scheich, and M. Zinbo, manuscript in preparation for publication.

"Mechanism of 4,4'-Methylenebis(2,6-di-tert-butylphenol) Inhibited Autoxidations at 180 to 220°C," R. K. Jensen, S. Korcek, L. R. Mahoney, and M. Zinbo, manuscript in preparation for publication.

"Effects of Structure on the Thermooxidative Stability of Synthetic Ester Lubricants: Theory and Predictive Method Development," L. R. Mahoney, S. Korcek, and J. M. Norbeck, manuscript in preparation for publication.

"Time-Temperature Studies of High Temperature Deterioration Phenomena in Lubricant Systems: Synthetic Ester Lubricants," L. R. Mahoney, Final Technical Report

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to obtain basic information on lubricant deterioration and metal corrosion phenomena occurring in oxidative environments at high temperatures.

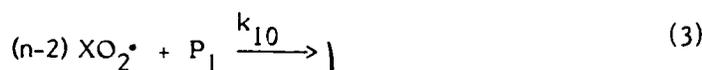
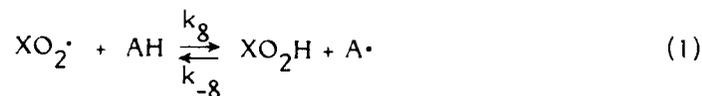
A kinetic and mechanistic study of the autoxidation of liquid pentaerythrityl tetraheptanoate, PETH, in a stirred flow reactor at 180 to 220°C was completed. The results are consistent with the occurrence of a chain reaction scheme similar to that proposed for n-hexadecane autoxidation. This scheme includes the formation of monohydroperoxides by the intermolecular abstraction reaction, formation of α , γ - and α , δ -dihydroperoxides and hydroperoxyketones by intramolecular peroxy radical abstraction reactions, bimolecular termination reaction of peroxy radicals, reaction, and rapid conversion of α , γ -hydroperoxyketones to cleavage acids and methylketones, reaction.

Comparisons of various rate parameters for the n-hexadecane and PETH systems reveal that the values of k_7 and $(k_3/H\text{-atom})/(2k_6)^{1/2}$ are within experimental uncertainties identical for the two systems at 180°C.

Laboratory studies showed that small degrees of autoxidation produce large increases in metal wear when PETH functions as a boundary

lubricant. The results indicate that monoesters of dicarboxylic acids produced in reaction are the products which in conjunction with hydroperoxides result in the increased wear.

We find that upon the introduction of an antioxidant, AH, the radical termination reactions are replaced by the termination reaction sequences,



} non radical products



where P_1 and P_2 are antioxidant active intermediate products of the reactions of the initial antioxidant radical A and n is the total number of $\text{XO}_2\cdot$ radicals consumed by the reactions of a molecule of AH and its reactive products.

The results for the 4,4'-dioctyldiphenylamine inhibited autoxidation of PETH at 180 to 220°C are consistent with the occurrence of reaction sequence (1) through (3) where $k_{-8}(\text{XOOH}) \gg k_9(\text{XO}_2\cdot)$ and \underline{n} is very large, ca. 19. This large value of \underline{n} requires that reactions (2) and (3) be cyclic processes involving the consumption and then the regeneration of species such as nitroso radicals and hydroxylamine products of $\text{A}\cdot$.

The results for the 4,4'-methylenebis(2,6-di-tert-butylphenol) inhibited autoxidation of PETH at 180 to 220°C are consistent with the occurrence of reaction scheme (1) - (3) where $k_9(\text{XO}_2\cdot)$ and $k_{9'}(\text{A}\cdot) \gg k_{-8}(\text{XOOH})$ and \underline{n} is equal to ca. 4.0. The product of

reaction (2') has been shown to be the quinone methide, QM. From the consumption of AH and the growth and the decay of QM a general rate equation for the disappearance of AH has been derived.

Based upon the results of these inhibited autoxidation studies a method for establishing the relationships between structure and thermoxidative stability of synthetic ester lubricants has been developed. Kinetic equations have been derived for the autoxidation of ester systems inhibited by antioxidants for which $k_9(XO_2\cdot) \gg k_8(XOOH)$ and numerical procedures have been developed for the solutions of these equations. The solutions yield values of the ratios of the inhibition periods for ester systems as a function of the values of $k_8/(k_3/H\text{-atom})$, \bar{n} and the relative contribution of intramolecular and intermolecular abstraction reactions in the inhibited ester autoxidations. Utilizing values of $k_4/k_2(RH)$ and $k_4^*/k_3(RH)$ observed in the autoxidation of PETH, values of \bar{n} equal to 2.0, and $k_8/(k_3/H\text{-atom})$ equal to 2.5×10^3 , the ratios of the inhibition periods calculated by the procedure are found to be in excellent agreement with the experimental ratios for the n-C₅ through n-C₈ pentaerythrityl alkanoates containing 1 weight per cent N-phenyl- α -naphthylamine at 232°C.

AFOSR Program Manager: Lorelei A. Krebs, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Ion Photofragment Spectroscopy - Potential Surfaces of Molecular Ions
2. PRINCIPAL INVESTIGATOR: Dr. John T. Moseley
Molecular Physics Laboratory
SRI International
Menlo Park, CA 94025
3. INCLUSIVE DATES: 17 May 1976 - 16 May 1979
4. CONTRACT NUMBER: F44620-76-C-0095
5. COSTS AND FY SOURCE: \$29,000, FY76; \$67,000, FY77; \$70,000, FY78;
\$43,000, FY79

6. SENIOR RESEARCH PERSONNEL:

Dr. P. C. Cosby	Dr. B. Huber
Dr. R. P. Saxon	Dr. R. Abouaf
Dr. T. M. Miller	Dr. M. Tadjeddine
Dr. L. C. Lee	Dr. J.-B. Ozenne
Dr. G. P. Smith	Professor J. Durup
Dr. J. R. Peterson	Dr. H. Helm

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Laser-Ion Coaxial Beams Spectrometer", B. A. Huber, T. M. Miller, P. C. Cosby, H. D. Zeman, R. L. Leon, J. T. Moseley, and J. R. Peterson, Rev. Sci. Instr. 48, 1306 (1977).

"Photofragment Spectroscopy and Potential Curves of Ar_2^+ ", J. T. Moseley, R. P. Saxon, B. A. Huber, P. C. Cosby, R. Abouaf, and M. Tadjeddine, J. Chem. Phys. 67, 1659 (1977).

"Photodissociation Spectroscopy of O_3^- ", P. C. Cosby, J. T. Moseley, J. R. Peterson, and J. H. Ling, J. Chem. Phys. 69, 2771 (1978)

"Photofragment Spectroscopy and Potential Curves of Kr_2^+ ", R. Abouaf, B. Huber, P. C. Cosby, R. P. Saxon, and J. T. Moseley, J. Chem. Phys. 68, 2406 (1978).

"The Dissociation Energy of $O_2(X^3\Sigma_g^-)$ ", D. L. Albritton, J. T. Moseley, P. C. Cosby, and M. Tadjeddine, J. Mol. Spec. **70**, 326 (1978).

"Photodissociation Cross Sections of Ne_2^+ , Ar_2^+ , Kr_2^+ , and Xe_2^+ from 3500 to 5400 Å", L. C. Lee and G. P. Smith, Phys. Rev. A. (in press).

"High Resolution Photofragment Spectroscopy of the $O_2^+(b^4\Sigma^-, v'=3,4,5 \leftarrow a^4\Pi_u, v'=3,4,5)$ First Negative System Using Coaxial Dye-Laser and Velocity-Tuned Ion Beams," P. C. Cosby, J.-B. Ozenne, J. T. Moseley, and D. L. Albritton, J. Mol. Spec. (in press).

"Observation of Predissociated Levels of CH^+ ", P. C. Cosby, H. Helm and J. T. Moseley, Astrophys. J. (in press).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Techniques of ion photofragment spectroscopy have been used to investigate the structure and dissociations of molecular ions. For this research, a unique laser-ion coaxial beams spectrometer was constructed, allowing substantially improved sensitivity and resolution. The rare gas dimer ions were studied in detail, resulting in the determination of potential curves, absorption and photodissociation cross sections, and photofragment angular distributions for these ions. Effects from spin-orbit coupling were found to be very important. The predissociation of the positive and negative ozone ions were investigated to obtain structural information about these ions. Very high resolution spectroscopy of the quartet states of the positive oxygen ion allowed a substantial improvement in these potential curves, as well as an improved determination of the bond dissociation energy of neutral oxygen. Photofragment spectroscopy of the positive ion of CH led to the observation of two predissociations, one in the singlet and one in the triplet system. Similar measurements on the positive ion of methyl iodide led to the resolution of rotational and fine structure levels in the previously observed predissociation of this ion.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Basic Studies Relating to the Synthesis of 1,1-Dimethylhydrazine by Chloramination
2. PRINCIPAL INVESTIGATOR: Dr. William E. McQuistion
Propellant Sciences Department
Naval Surface Weapons Center
Silver Spring, Maryland 20910
3. INCLUSIVE DATES: 1 September 1975 - 30 September 1978
4. CONTRACT NUMBER: MIPR-76-007; MIPR-7T-0002; MIPR-77-0002;
MIPP-78-0008
5. COSTS AND FY SOURCE: \$32,557, FY76; \$9,934, FY7T; \$39,981, FY77;
\$20,000, FY78
6. SENIOR RESEARCH PERSONNEL:

Dr. R. E. Bowen
Dr. G. A. Carpenter
Dr. G. B. Wilmot

7. PUBLICATIONS:

"Basic Studies Relating to the Synthesis of 1,1-Dimethylhydrazine by Chloramination," W. E. McQuistion, R. E. Bowen, G. A. Carpenter and G. B. Wilmot, Final Technical Report.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Because of health hazards associated with the previous method for the manufacture of the important liquid rocket fuel component, 1,1-dimethylhydrazine (UDMH), studies were carried out to determine the kinetics of formation of UDMH by an alternative process, the chloramination of dimethylamine. The kinetics of undesirable side reactions which lower UDMH yields in the chloramination method were also investigated. The reaction between chloramine (NH_2Cl) and dimethylamine gives UDMH. Chloramine can react with the UDMH formed to give a variety of subsequent products, chiefly formaldehyde dimethylhydrazone. A stopped flow reaction system was assembled and used to measure the rate of formation of UDMH in anhydrous organic solvents (chiefly chloroform) in the temperature range $15^\circ\text{-}30^\circ\text{C}$. Reaction rates and an activation energy of 9.8 kcal/mole were derived

from these measurements. Bench-scale and modeling experiments showed that the reaction rate for the formation of the hydrazone is about 600 times that for the formation of UDMH at 0°C. The second order kinetics model for these consecutive reactions indicated and experiment showed that the concentration of UDMH quickly reaches a steady-state value while the yield of the hydrazone steadily increases with chloramine addition. The large-scale production of UDMH in anhydrous organic solvents by chloramination of dimethylamine does not appear feasible at practical temperatures because of the low ratios (<.3) of UDMH to hydrazone obtained in these experiments.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Photodissociation and Photodetachment of Atmospheric Negative Ions

2. PRINCIPAL INVESTIGATORS: Dr. J. T. Moseley
Dr. L. C. Lee
Molecular Physics Laboratory
SRI International
Menlo Park, CA 94025

3. INCLUSIVE DATES: 15 August 1978 - 14 August 1979

4. CONTRACT NUMBER: F49620-78-C-0119

5. COSTS AND FY SOURCE: \$73,320, FY79

6. SENIOR RESEARCH PERSONNEL:

Dr. P. C. Cosby
Dr. R. V. Hodges

Dr. G. P. Smith
Dr. J. R. Peterson

7. PUBLICATIONS:

"Photodissociation and Photodetachment of Molecular Negative Ions. VI. Ions in $O_2/CH_4/H_2O$ Mixtures from 3500 to 8600 Å," L. C. Lee and G. P. Smith, J. Chem. Phys., 70, 1727 (1979).

"Photodissociation and Photodetachment of Molecular Negative Ions. VII. Ions Formed in $CO_2/O_2/H_2O$ Mixtures, 3500-5300 Å," G. P. Smith, L. C. Lee, and J. T. Moseley, J. Chem. Phys. (in press).

"Photodissociation and Photodetachment of Molecular Negative Ions. VIII. Nitrogen Oxides and Hydrates, 3500 - 8250 Å," G. P. Smith, L. C. Lee, and P. C. Cosby, J. Chem. Phys. (in press).

"Photodissociation and Photodetachment of Cl_2^- , ClO^- , Cl_3^- , and $BrCl_2^-$," L. C. Lee, G. P. Smith, J. T. Moseley, P. C. Cosby, and J. A. Guest, J. Chem. Phys., 70, 3237 (1979).

"Photodissociation and Photodetachment of Molecular Negative Ions. IX. Atmospheric Ions at 2484 and 3511 Å," R. V. Hodges, L. C. Lee, and J. T. Moseley, Submitted to J. Chem. Phys.

"Photodissociation Spectroscopy of O_3^- and $O_3^- \cdot H_2O$. 4170-4700 Å," G. P. Smith and L. C. Lee, J. Chem. Phys., 71, 2323 (1979).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Any process that affects the electron and ion densities in the atmosphere is very important for defense purposes because these densities directly affect radio and radar transmission. Ion and electron charge densities routinely vary as a result of natural phenomena, such as sunrise and auroral events, and can be markedly changed by a nuclear burst or a chemical release. Complex models of the atmospheric reactions that control the electron and ion densities have been developed to predict the effectiveness of communications and missile detection following these events. These models require laboratory determinations of the ion-molecule reaction rates and of the photodetachment and photodissociation cross sections that control the ion and electron populations.

It was in recognition of this need that we began research in April 1973 to study the ion-molecule reaction rates and photodetachment and photodissociation cross sections for negative ions of atmospheric importance, using a unique drift tube mass spectrometer and laser facility of our design and construction. In this funding period, photodetachment and photodissociation cross section measurements have been made for a wide variety of negative ions considered to be of atmospheric importance at wavelengths of 2484, 3500, (3507 and 3569 combined), 4067, and 4131 Å. The ions for which cross sections were measured include O^- , OH^- , O_2^- , O_3^- , O_4^- , CO_3^- , HCO_3^- , CO_4^- , NO_2^- , NO_3^- , Cl_2^- , ClO_2^- , Cl_3^- , and $BrCl_2^-$, as well as hydrates of many of these ions. The photodissociation of CO_3^- in the region of the threshold near 6550Å was reinvestigated in detail, because of the present controversy concerning the bond energy of this ion. These measurements most strongly confirmed our previous conclusion that the bond energy of this ion is less than 1.9 eV. All measurements were made using a drift tube mass spectrometer photodestruction apparatus and with a krypton ion laser or a rare gas halogen laser.

Before our research began, it was only possible to account for the photodetachment of O^- in the atmospheric models; photodissociation was not considered at all. At the end of the current contract, we have enough information to account for photodestruction of nearly all of the ions considered to be important, covering the wavelength range from 2484 to 8600 Å. In addition, we have learned about the structure and excited states of these ions. Many of the photodestruction processes we have studied appear to be important in determining the ion and electron densities in the atmosphere.

AFOSR Program Manager: Capt. Russell A. Armstrong

COMPLETED PROJECT SUMMARY

1. TITLE: Electrochemistry of Solutes in Chloroaluminate Melts and the Development of Related Electrochemical Methodology
2. PRINCIPAL INVESTIGATORS: Dr. Robert Osteryoung
Dr. Janet Osteryoung
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523
3. INCLUSIVE DATES: 1 April 1976 - 30 June 1979
4. GRANT NUMBER: AFOSR-76-2978
5. COSTS AND FY SOURCE: \$50,000, FY76; \$80,000, FY77; \$18,000, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. Graham Cheek
Dr. Robert Gale
Dr. Bernard Gilbert
Dr. David Koran

Dr. Hogne Linga
Dr. Jeffrey Phillips
Dr. James Robinson
Dr. Thomas Santa Cruz

8. PUBLICATIONS:

"Molybdenum Chemistry in NaCl-AlCl_3 Melts at 175°C ," J. Phillips and R. A. Osteryoung, J. Electrochem. Soc., 124, 1405 (1977).

"The Acid-Base Chemistry of Oxide and Chalcogenides in Sodium Tetrachloroaluminate Melts at 175°C ," J. Robinson, B. Gilbert and R. A. Osteryoung, Inorg. Chem., 16, 3040 (1977).

"Ligand-Oxidation in Iron Diimine Complexes. III. Electrochemical Oxidation of tris-(glyoxalbis(methylimine)) Iron (II)," H. Li Chum, T. Rabockai, J. Phillips and R. A. Osteryoung, Inorg. Chem., 16, 1812 (1977).

"The Electrochemical Behavior of Metal Carbonyls in a Mixture of a Room Temperature Molten Salt and Benzene," H. Li Chum, D. Koran and R. A. Osteryoung, J. Organometallic Chem., 140, 349 (1977).

"Photochemistry of Iron(II) Diimine Complexes in a Room Temperature Molten Salt," H. Li Chum, D. Koran and R. A. Osteryoung, J. Am. Chem. Soc., 100, 310 (1978).

"Electrochemical Studies of Selenium and Selenium Compounds in Molten Sodium Tetrachloroaluminate Melts," J. Robinson and R. A. Osteryoung, J. Electrochem. Soc., 125, 1454 (1978).

"Electrochemical Studies on Nickel Electrodes in Molten Sodium Tetrachloroaluminates," B. Gilbert and R. A. Osteryoung, J. Amer. Chem. Soc., 100, 2725 (1978).

"Acid-Base Dependent Redox Chemistry in Molten Chloroaluminates," G. Mamantov and R. A. Osteryoung, in CHARACTERIZATION OF SOLUTES IN NON-AQUEOUS SOLUTIONS," pg. 225-250, G. Mamantov, ed., Plenum Publishing Co. (1977).

"Raman Spectra of Molten Aluminum Chloride: 1 Butyl Pyridinium Chloride Systems at Ambient Temperature," R. J. Gale, B. Gilbert and R. A. Osteryoung, Inorg. Chem., 17, 2728 (1978).

"The Electrochemical Behavior of Te(IV) in Sodium Tetrachloroaluminates," J. Robinson and R. A. Osteryoung, J. Electrochem. Soc., 125, 1784 (1978).

"Potentiometric Investigation of Dialuminum Heptachloride Formation in Aluminum Chloride-1-Butylpyridinium Chloride Mixtures," R. J. Gale and R. A. Osteryoung, Inorg. Chem., 18, 1603 (1979).

"¹H and ¹³C Nuclear Magnetic Resonance Spectroscopy Studies of Aluminum Halide - Alkylpyridinium Halide Molten Salts and Their Benzene Solutions," J. Robinson, R. C. Bugle, H. L. Chum, D. Koran and R. A. Osteryoung, J. Am. Chem. Soc., 101, 3776 (1979).

"The Electrochemical and Spectroscopic Behavior of Some Aromatic Hydrocarbons in the Room Temperature Molten Salt System AlCl₃:n-butylpyridinium Chloride," J. Robinson and R. A. Osteryoung, J. Amer. Chem. Soc., 101, 323 (1979).

"The Electrochemical Behavior of Aluminum in the Low Temperature Molten Salt System n-Butylpyridinium Chloride: Aluminum Chloride and Mixtures of this Molten Salt with Benzene," J. Robinson and R. A. Osteryoung, J. Electrochem. Soc., in press.

"Electrochemical Studies in a Room Temperature Molten Salt," R. A. Osteryoung, R. J. Gale, J. Robinson, R. Bugle and B. Gilbert, in PROCEEDINGS OF THE SECOND INTERNATIONAL CONFERENCE ON MOLTEN SALTS, J. Braunstein, ed., The Electrochemical Society, in press.

"Electrochemical Studies in a Room Temperature Aluminum Halide Containing Melt," H. L. Chum and R. A. Osteryoung, in IONIC LIQUIDS, D. Inman and D. Lovering, editors, Plenum Press, in press.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Research carried out under this grant had, as its primary goal, the investigation of molten haloaluminates as solvent systems for the study of electrochemical reactions. The particular interest has been in the fact that systems, such as the molten tetrachloroaluminates, show significant acid-base dependent behavior which is reflected in solute electrochemistry.

In the $\text{NaCl}:\text{AlCl}_3$ system (sodium tetrachloroaluminate), the acid-base chemistry of oxides and chalcogenides was investigated. The electrochemistry of Mo, Se and Te was investigated; Mo was studied in the basic melt (excess NaCl) while Se and Te were investigated as a function of melt acidity and a variety of acidity dependent electrochemical reactions were uncovered. The electrochemistry of Ni(II) was also investigated, and it was found that NiCl_2 was insoluble in the neutral and basic melt. At 175°C the melt becomes saturated with NaCl at about 1% excess. Although not subject to detailed investigation, it was found that oxygen reduction in this melt could be catalyzed by the presence of metal cations, such as Cu(I) and Mo(V).

A new "room temperature" molten salt, N-Butylpyridinium chloride (BuPyCl)-aluminum chloride, was discovered. The 1:1 mole ratio mixture of $\text{BuPyCl}:\text{AlCl}_3$ is liquid at 27°C , and the mole ratio may be varied from 1:0.6 to 1:2 at essentially room temperature, thus permitting significant variation in acidity. Raman spectroscopic studies were carried out and the dominant solvent equilibrium, $2\text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$ was potentiometrically as $< 3.8 \cdot 10^{-13}$ on the mole fraction scale, the limitation being imposed because the BuPy^+ species is reduced by an Al indicator electrode in the basic melt, thus rendering precise determination of this constant difficult. This melt is miscible with benzene and other organic solvents and nmr studies indicated that the benzene undergoes no specific interaction with the melt, serving as a simple diluent. Determination of the dominant equilibrium referred to above in a 50-50 volume percent mixture of melt plus benzene gave a value for the equilibrium constant essentially identical to that for the pure melt. This again indicates the absence of any specific interaction of the melt with the benzene. A number of physical properties - conductivity, and viscosity, in particular - are improved upon addition of benzene.

The Raman, potentiometry and other physical studies indicated that the 1:1 melt is essentially $\text{BuPy}^+ + \text{AlCl}_4^-$, while the 2:1 $\text{AlCl}_3:\text{BuPyCl}$ system can be regarded as $\text{BuPy}^+ + \text{Al}_2\text{Cl}_7^-$. The equilibrium,

$\text{AlCl}_3 + \text{AlCl}_4^- = \text{Al}_2\text{Cl}_7^-$ lies much further to the right than in the corresponding alkali halide-aluminum halide systems, even when the temperature difference of these systems is taken into account.

The electrochemistry of a number of aromatic polynuclear hydrocarbons was studied across the acidity range. All were shown to undergo a one-electron oxidation to the radical cation that was independent on melt acidity and, compared to ferrocene, oxidized at the same relative potential as in acetonitrile. At high acidity, certain of the hydrocarbons appeared to participate in acid-base chemistry with the melt, and it was postulated that an aluminum chloride analog of a carbonium ion was formed. Some of the more easily oxidized hydrocarbons were spontaneously oxidized by the most acid melt mixture.

In related work, the electrochemistry of a number of metal carbonyls was investigated in another room temperature melt, a 2:1 mixture of aluminum chloride and ethylpyridinium bromide. Attempts to study the electrochemistry of iron diimine complexes failed, since it was found that the Fe(II) complexes underwent photochemical conversion to the Fe(III) complex.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Viscosity of Chloroaluminate Melts
2. PRINCIPAL INVESTIGATOR: Dr. Harald A. Øye
Institute of Inorganic Chemistry
University of Trondheim
7034 Trondheim NTH 9, Norway
3. INCLUSIVE DATES: 1 January 1977 - 31 December 1978
4. GRANT NUMBER: AFOSR-77-3198
5. COSTS AND FY SOURCE: \$22,084, FY77; \$26,276, FY78
6. SENIOR RESEARCH PERSONNEL:

Dr. Knut Tørklep

Dr. Wolfgang Brockner

7. JUNIOR RESEARCH PERSONNEL:

Helge Rørvik
Jan Havdahl
Esther Urdahl

Henning Meyer Johansen
Tharald Tharaldsen

8. PUBLICATIONS:

"Viscosity of Aluminum Chloride and Acidic Sodium Chloroaluminate Melts," W. Brockner, K. Tørklep, H. A. Øye, Ber. Bunsenger. Phys. Chem., 83 (1979).

"An Absolute Oscillatington Cyclinder Viscometer for High Temperatures," K. Tørklep and H. A. Øye, submitted to J. Phys. E. Sci. Instrument.

"Viscosity of Chloroaluminate Melts," Harald A. Øye, Final Report, AFOSR-TR-79-0597.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The aim of the project was to obtain reliable viscosity data for mixtures between LiCl-NaCl-AlCl_3 with $0.50 \leq X_{\text{AlCl}_3} \leq 1.00$ and combine the data with previous spectroscopic studies in order to gain further insight of the structures of these melts. The technical implication of the study is the use of these melt mixtures in the development of thermal and secondary batteries.

Viscosity data for molten salts has been notoriously unreliable. An automated oscillation viscometer was developed with no need for calibration. This viscometer gives viscosity with an estimated standard deviation of 0.2% when the utmost care is applied. More routine measurements give a standard deviation of 0.5-1%. The work has resulted in viscosity values for NaCl which will be accepted as the new National Bureau of Standard value. The previous NBS value was up to 50% higher.

The adaption of the developed techniques to the present studies needed the use of a closed container in which the liquid was contained. The mathematical solutions for determination of viscosity from the damping of the oscillations have been obtained and it has also been possible to correct for the formed meniscus due to wetting of the liquid in the upper part of the container. The overall standard deviation in measurements is estimated to 0.5-0.6%.

Pure AlCl_3 , the binary mixtures $\text{AlCl}_3\text{-LiCl}$, $\text{AlCl}_3\text{-NaCl}$ and ternary mixtures of $\text{AlCl}_3\text{-LiCl-NaCl}$ have been studied for $0.5 \leq X_{\text{AlCl}_3} \leq 1$. The actual compositions measured are given in Fig. 1. The temperature range is between 100 and 300°C dependent on vapor pressure and liquidus temperature.

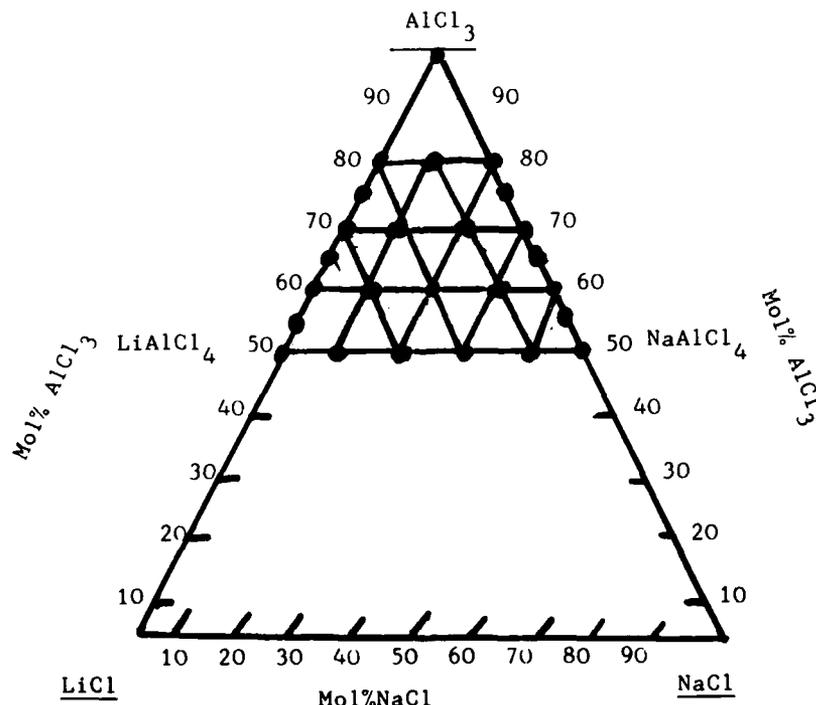


Figure 1 Diagram of compositions for which viscosity determinations were performed.

The results for pure AlCl_3 and the AlCl_3 - NaCl system have been published.

It has been possible to rationalize the data in terms of the existence of the melt species AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$ and Al_2Cl_6 assuming an Arrhenius temperature dependence and the Arrhenius mixing rule being valid:

$$\text{Species viscosity: } \eta_i = A_i \exp(B_i/T)$$

$$\text{Total viscosity: } \ln \eta = \sum X_i \ln \eta_i$$

The model gave a total fit of 0.4%.

Provisional calculations for the AlCl_3 - LiCl system show that a similar model as that for AlCl_3 - NaCl will give a satisfactory description of the data with a total fit of 0.3%.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Syntheses of Phosphotriazines for Potential High Temperature Fluids Applications
2. PRINCIPAL INVESTIGATOR: Dr. K. L. Paciorek
Ultrasystems, Inc.
2400 Michelson Drive
Irvine, CA 92715
3. INCLUSIVE DATES: 1 March 1976 - 28 February 1979
4. CONTRACT NUMBER: F44620-76-C-0065
5. COSTS AND FY SOURCE: \$23,333, FY76; \$40,000, FY77; \$40,000, FY78;
\$16,667, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. T. I. Ito
Dr. J. Kaufman
Dr. R. H. Kratzer
Dr. J. H. Nakahara

7. PUBLICATIONS:

"Phospha-s-triazines. I. Synthesis and Properties of Mono(diarylphospha)-s-triazines," R. H. Kratzer, K. J. L. Paciorek, J. Kaufman, and T. I. Ito, J. Fluorine Chem., 10, 231 (1977).

"Phospha-s-triazines. II. Mass Spectra of Mono(diarylphospha)-s-triazines," K. J. L. Paciorek, J. H. Nakahara, and R. H. Kratzer, J. Fluorine Chem., 11, 537 (1978).

"Phospha-s-triazines. III. Syntheses and Properties of 1,3-Bis(diarylphospha)-5-perfluoroaliphatic-2,4,6-triazines," R. H. Kratzer, K. J. L. Paciorek, J. Kaufman, T. I. Ito, and J. H. Nakahara, J. Fluorine Chem., 13, 189 (1979)

"Phospha-s-triazines. IV. Degradation Studies of 1-Diarylphospha-3,5-bis(perfluoroaliphatic)-2,4,6-triazines and 1,3-Bis(diarylphospha)-5-perfluoroaliphatic-2,4,6-triazines, R. H. Kratzer, K. J. L. Paciorek, J. Kaufman, T. I. Ito, and J. H. Nakahara, J. Fluorine Chem., 13, 199 (1979)

"Phospha-s-triazines. V. Synthesis of Dumbbell Compounds,"
R. H. Kratzer, K. J. L. Paciorek, J. Kaufman, T. I. Ito, and
J. H. Nakahara, to be submitted to the Journal of Fluorine Chemistry.

"Diphosphatetraazacyclooctatetraenes. I. Synthesis and Properties,"
R. H. Kratzer, K. J. L. Paciorek, J. Kaufman, T. I. Ito, and J. H.
Nakahara, to be submitted to the Journal of Fluorine Chemistry.

"Syntheses of Phosphatriazines for Potential High Temperature Fluids
Applications," K. L. Paciorek, J. Kaufman, J. H. Nakahara, T. I.
Ito, and R. H. Kratzer, Final Technical Report.

8. PATENT DISCLOSURES:

"Monophospha-s-triazines," AF Invention No. 12,317

"Diphospha-s-triazines," AF Invention No. 13,252

"Lubricant Composition," AF Invention No. 13,411

"Dumbbell Phospha-s-triazines," in preparation

"Diphosphatetraazacyclooctatetraenes," in preparation

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The synthesis of a series of heterocycles containing phosphorus, carbon and nitrogen ring atoms was undertaken with the ultimate aim of developing materials incorporating the low melting characteristics of the fluorinated triazines with the lubricating and corrosion inhibiting properties of phosphorus containing compounds. A series of six and eight membered heterocycles was synthesized. The specific classes of compounds prepared were monophospha-s-triazines, diphospha-s-triazines, and diphosphatetraazacyclooctatetraenes. The presence of perfluoroalkylether groups on the carbon ring atoms rendered the resulting compounds liquids at room temperature; substitution by perfluoroalkyl groups invariably led to solids. Both the mono- and diphospha-s-triazines were found to be effective anti-corrosion additives for perfluoroalkylether type fluids.

The monophospha-s-triazines, namely 1-diphenylphospha-3,5-bis (perfluoro-n-heptyl)-2,4,6-triazine, 1-diphenylphospha-3,5-bis [C₃F₇-[OCF(CF₃)CF₂]_xOCF(CF₃)]-2,4,6-triazine (x = 1 and 2) and the pentafluorophenyl-substituted analogues were prepared, in yields of 50-75%, from the respective imidoylamidines and trichlorophosphoranes. The physical properties of the corresponding phenyl and pentafluorophenyl monophospha-s-triazines did not differ significantly. On electron impact, the ion R₂PN₂C⁺ (R = C₆H₅ or C₆F₅) constituted the base peak.

The diphospha-s-triazines, namely 1,3-bis(diphenylphospha)-5-perfluoro-n-heptyl-2,4,6-triazine and 1,3-bis(diphenylphospha)-5-perfluoro-alkylether-2,4,6-triazines, $[(C_6H_5)_2PN]_2[C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_3)CN]$ ($x = 1$ and 2) were synthesized in yields of 30-65% by interaction of imido-tetraphenyl-diphosphinic acid trichloride and the respective amidines.

The above synthetic approaches were successfully extended to the formation of dumbbell compounds.

Thermal and thermal oxidative stability evaluations were performed on mono- and diphospha-s-triazines at 235 and 316°C using sealed Pyrex ampoules. The specific compounds studied were: 1-diphenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine, 1-diphenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazines, their respective pentafluorophenyl analogues, 1,3-bis(diphenylphospha)-5-perfluoro-n-heptyl-2,4,6-triazine and 1,3-bis-(diphenylphospha)-5-perfluoro-alkylether-2,4,6-triazine. All the compounds wherein phenyl groups were present on the phosphorus exhibited good thermal stability up to 316°C; the analogous pentafluorophenyl substituted materials were degraded extensively at these temperatures. The oxidative stability of both the mono- and diphospha-s-triazines was excellent at 235°C, but at 316°C some degradation was observed. This was more pronounced in compounds containing the perfluoroalkyl moiety on carbon than in the perfluoroalkylether substituted members of the series.

The symmetrical diphosphatetraazacyclooctatetraenes were obtained from the interaction of perfluoroalkyletheramidines and trichlorophosphoranes. Using this procedure, a mixture of products was afforded. The unsymmetrical isomers were prepared in excellent yields, (>80%), from perfluoroalkyletherimidoylamidines and imido-tetraphenyl-diphosphinic acid trichloride. The specific representatives of the eight membered heterocycles thus far synthesized and characterized are: 1,5-bis(diphenylphospha)-3,7-bis($C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_3)$)-2,4,6,8-tetraazacyclooctatetraene ($x = 0$ and 1) and 1,3-bis(diphenylphospha)-5,7-bis($C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_3)$)-2,4,6,8-tetraazacyclooctatetraene ($x = 0$ and 1).

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Studies of HnFn Oligomeric Species
2. PRINCIPAL INVESTIGATOR: Dr. Richard L. Redington
Department of Chemistry
Texas Tech University
Lubbock, Texas 79409
3. INCLUSIVE DATES: 1 June 1978 - 31 May 1979
4. GRANT NUMBER: AFOSR 78-3616
5. COSTS AND FY SOURCE: \$10,000, FY78
6. SENIOR RESEARCH PERSONNEL: Delphia F. Hamill
7. JUNIOR RESEARCH PERSONNEL: None
8. PUBLICATIONS:

"Infrared Matrix-Isolation Studies of HnFn Oligomers," R. L. Redington and D. F. Hamill, In Preparation.

"Nonideal Gas Model for HF Vapor," R. L. Redington, In Preparation.

"Gaussian Basis Studies of HnFn Oligomers," D. F. Hamill and R. L. Redington, In Preparation.

"Studies of H_nF_n Oligomeric Species," R. L. Redington, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Infrared matrix-isolation spectra of HF and HF/H₂O mixtures suspended in solid argon have been obtained in the range 400-4000cm⁻¹. Bands attributed to HF and to HF-H₂O oligomers were observed. HF stretching modes were assigned to dimer, chain trimer, cyclic tetramer, and cyclic hexamer of HF. Some of the FH...F angle deformation modes were observed for these molecules. The oligomers are formed during matrix deposition and the chain trimers appear to be matrix stabilized in a double substitution site in argon. Application of a non-ideal gas model to the literature vapor phase data on HF suggests that the dimer and the hexamer are the dominant vapor phase oligomers, with the hexamer most important near saturation vapor pressures. The tetramer is the next most important vapor phase oligomer, but it contributes

only weakly to the vapor phase properties. Minimal basis set STO-3G computations on chain and cyclic HF trimer and tetramer molecules suggest the marked increase in stability that arises on catenation or (unstrained) cyclization of HF systems.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Studies of Ionization Processes
2. PRINCIPAL INVESTIGATOR: Dr. Erhard W. Rothe
Research Institute for
Engineering Sciences
College of Engineering
Wayne State University
Detroit, Michigan 48202
3. INCLUSIVE DATES: 1 August 1975 - 30 September 1978
4. GRANT NO: AFOSR 75-2770
5. COSTS AND FY SOURCE: \$46,833, FY76; \$54,719, FY77; \$57,091, FY78
6. SENIOR RESEARCH PERSONNEL:

Professor Gene P. Reck
Professor Pieter K. Rol
Dr. Bhagwan P. Mathur
7. JUNIOR RESEARCH PERSONNEL:

Dhruba Sinha
Gregory Wells
Kanwal Mahajan
Yoram Hirsch

Sheila McEntire
Patricia Bodner
Charles Messner
Fern Bean
8. PUBLICATIONS:

"Ionizing Collisions of Cesium with Cl₂, Br₂ and I₂," S. Y. Tang, C. B. Leffert, E. W. Rothe and G. P. Reck, J. Chem. Phys., 62, 134 (1975).

"Measurement of Electron Affinities of O₃ and SO₂ and SO₃ by Collisional Ionization," S. Y. Tang, E. W. Rothe and G. P. Reck, J. Chem. Phys., 62, 3829 (1975).

"Branching Ratios in Charge Exchange Collisions," E. W. Rothe, S. Y. Tang and G. P. Reck, Ninth International Conference on the Physics of Electronic and Atomic Collisions, pg. 373 (University of Washington Press, Seattle, 1975).

"Negative Gaseous Ions from Nitric Acid," B. P. Mathur, E. W. Rothe, S. Y. Tang, K. Mahajan and G. P. Reck, J. Chem. Phys., 64, 1247 (1976).

"Negative Ion Formation in Halocarbons by Charge Exchange with Cesium," S. Y. Tang, B. P. Mathur, E. W. Rothe and G. P. Reck; J. Chem. Phys., 64, 1270 (1976).

"Negative Ions from Phosphorus Halides due to Cesium Charge Exchange," B. P. Mathur, E. W. Rothe, S. Y. Tang and G. P. Reck, J. Chem. Phys., 65, 565 (1976).

"Chem-ionization in Thermal Energy Collisions of K_2 and Cs_2 with Halogen Molecules," E. W. Rothe, B. P. Mathur and G. P. Reck, J. Chem. Phys., 65, 2912 (1976).

"Chem-ionization Reactions of Alkali Dimers with Halogen Molecules," G. P. Reck, B. P. Mathur and E. W. Rothe, J. Chem. Phys., 66, 3847 (1977).

"Ionization Reactions of Metal Hexafluorides with Alkali Atoms and Dimers," B. P. Mathur, E. W. Rothe and G. P. Reck, J. Chem. Phys., 67, 377 (1977).

"Near-Threshold Ionization of Excited $Na(3^2P)$ by Collisions with O_2 and SO_2 ," E. W. Rothe, B. P. Mathur and G. P. Reck, Chem. Phys. Letters, 51, 71 (1977).

"Chem-ionization from Excited $Na(3^2P)$ Collision with Simple Molecules," G. P. Reck, E. W. Rothe and B. P. Mathur, Tenth International Conference on the Physics of Electronic and Atomic Collisions, Vol. 2, p. 1152 (Commissariat a L'Energie Atomique, Paris, 1977).

"Thermal energy Chem-ionization of Alkali dimers by Molecules," E. W. Rothe, B. P. Mathur and G. P. Reck, Tenth International Conference on the Physics of Electronic and Atomic Collisions, Vol. 2, p. 1152, (Commissariat a L'Energie Atomique, Paris, 1977).

"Isotope Fractionation in Two-Step Photoionization of Li_2 ," E. W. Rothe, B. P. Mathur and G. P. Reck, Chem. Phys. Letters, 53, 74 (1978).

"Two-Photon Ionization of Na_2 by an Ar^+ Laser," B. P. Mathur, E. W. Rothe and G. P. Reck, J. Chem. Phys., 68, 2518 (1978).

"Two-Photon Ionization of Li_2 : Isotopic Separation and Determination of $IP(Li_2)$ and $De(Li_2)$," B. P. Mathur, E. W. Rothe, G. P. Reck and A. J. Lightman, Chem. Phys. Letters, 56, 336 (1978).

"Calculated Transitions in Li_2 Isotopes at Argon Laser Frequencies," A. J. Lightman and B. P. Mathur, J. Chem. Phys., 69, 2262 (1978).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main objective of this research program was to determine the role of energy in chemical reactivity. In order to do this we have examined the effect of translational, electronic and vibrational-rotational energy on ionization process as this is the simplest type of chemical change.

Advances in chemical dynamics are not usually achieved by a single experiment but by a blend of information using a variety of techniques. The experiments supported under this grant were all performed via various combinations of molecular beam and laser techniques in order to more fully exploit the advantages of each.

The three main categories of experiment were:

A. Lasers were used to produce and characterize atoms in specific electronic states or molecules in specific electronic vibrational and/or rotational states. We performed two photon ionization experiments on alkali dimers and observed ionization from specific vibrational and rotational states. We also prepared Na(3p) and used it to promote the collisional ionization of O₂ and SO₂. In both these experiments, energy for ionization was produced wholly or partially from photons. It is expected that two photon ionization may be used to characterize the products of chemical reactions while electronically excited atomic states will be useful in further understanding chemical reactivity.

B. In addition, we continued our well-established program for determining the electron affinities and bond strengths for negative molecular ions. An understanding of complex chemical systems in which energy deposition and flow are important, such as in plasma, atmospheric chemistry, combustion, flames and lasers, involves the knowledge of the energetics of ionic species as well as their reactions with neutral species. These reactions have energy-thresholds which lie where the molecular energies predict; i.e., the products do not contain excess kinetic or internal energy, in contrast to behavior frequently observed with photon or electron impact. Accordingly, this approach may be used to measure such molecular parameters as bond energies in neutrals or in negative ions, and to measure electron affinities in atoms, molecules and radicals. This research program has been active in developing the relativity complex experiments and computer codes that are required to obtain very precise energies. The results are summarized in Table I.

Another application of these techniques is to a study of the detailed dynamics of a particular process. An analysis of the chemi-ionization of the freons by Cs using simple surprisal theory reveals that the process is direct rather than statistical.

C. In addition to the work described above in which ion pairs were formed via the collision of molecules with several electron volts of initial kinetic energy, we also performed measurements in which all the ionization energy was produced by chemical change.

The prototype reaction was that of an alkali dimer with a halogen. A crossed beam apparatus was used to characterize ionic products of thermal energy collisions of alkali dimers M_2 with homonuclear halogens X_2 and with $I\text{Br}$ and ICl . All possible alkali-halogen combinations were studied, except Rb_2 with ICl and IBr . The predominant reaction path leading to ions was found to be



when these reactions are exoergic. Reaction via the alternative paths



and



was observed when (1) is endoergic.

For Li_2 and Na_2 , path (1) is energetically forbidden (except with F_2), but paths (2) and (3) are allowed and were found to occur. Some experiments were done with the scientifically interesting UF_6 (electron affinity=6eV). The energetics which may be determined from the observed dimer reaction are shown in Table 1.

Table 1. Summary of molecular energetics determined by alkali atom impact and dimer reactions:

Molecule	E.A. (eV)	Dissociation Energy (eV)
MoF_6	<4.5	
MoF_5	<3.3	
WF_6	<4.9	$D(\text{WF}_5-\text{F}) < 5.0$
UF_6	<4.3	
UF_5	<1.9	
HNO_3	0.57	$D(\text{NO}_3^--\text{H}) 1.28$ $D(\text{NO}_2^--\text{OH}) 0.4$

Molecule	E.A. (eV)	Dissociation Energy (eV)
PCl ₃	0.8	D(PCl ₂ -Cl) 3.3
POCl ₃	1.4	D(POCl ₂ -Cl) 3.5
PBr ₃	1.6	D(PBr ₂ -Br) 2.6
PCl ₂ Br	1.5	
PBr ₂ Cl	1.6	
POCl ₂	3.8	
CO ₂	-1.1 > >-2.1	
O ₃	2.14	
SO ₂	1.14	
SO ₃	≥1.70	
Cl ₂	2.5	
Br ₂	2.5	
I ₂	2.5	
CF ₃ I	1.4	D(Cf ₃ -I) 2.05 D(CF ₃ -I ⁻) 0.38

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Power Spectral Performance of a cw Chemical Laser

2. PRINCIPAL INVESTIGATOR: Dr. Lee H. Sentman
Aeronautical and Astronautical
Engineering Department
University of Illinois
Urbana, IL 61801

3. INCLUSIVE DATES: 15 May 1978 to 14 May 1979

4. GRANT NUMBER: AFOSR-78-3669

5. COSTS AND FY SOURCE: \$52,746, FY78

6. SENIOR RESEARCH PERSONNEL:

W. Brandkamp
Dr. W. Rushmore

7. JUNIOR RESEARCH PERSONNEL:

P. Bradbury
L. Lang

8. PRESENTATIONS AND PUBLICATIONS:

"A Simplified Rotational Nonequilibrium Model - Some Results,"
L. H. Sentman and W. Rushmore, presented at the Sixth Annual Tri-
Service Chemical Laser Symposium, AFWL, Kirtland AFB, NM, August 28-30,
1979.

"An Efficient Rotational Nonequilibrium Model of a CW Chemical
Laser," L. H. Sentman and W. Brandkamp, Final Report, AAE TR 79-5,
UILU Eng 79-0505, University of Illinois, Urbana, IL, July 1979.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this investigation was to develop a computationally efficient, rotational nonequilibrium model of a cw chemical laser which will provide quantitative predictions of the power and power spectral distribution of the laser. For computational efficiency, the number of dependent variables must be kept to a minimum. Based on experience with the qualitative, but computationally efficient, rotational nonequilibrium model developed by Sentman, the approach

used in this study was to include the essential chemical kinetics - the pumping reactions, major deactivation reactions and rotational relaxation reactions - , and to include the fluid dynamic effects of mixing by inputting the pressure, temperature, velocity, mass flow rate remaining in the primary, mass flow rate remaining in the secondary and the length of the active media as functions of x which are obtained from one of the available quasi-2D, 2D or 3D fluid dynamic, rotational equilibrium, chemical kinetic laser models such as Blaze II, Lamp, Apache, etc. This approach was motivated by the fact that changes in chemical kinetics, which significantly affect the power spectral performance, in most cases, have only a minor effect on the flow field in which the kinetics takes place. Thus, the fluid dynamics provides the environment in which the kinetics occurs.

To ensure the general applicability of the kinetics model and of the polynomial fits for the fluid variables, the model evolved from detailed comparisons with the Blaze II code for two different cases, an Aerospace arc driven HF power spectral experiment which employed a slow mixing nozzle, and the Bell Aerospace Textron CL XI lasing lines experiment, which employed a fast mixing nozzle. Detailed comparisons of the species profiles for H, H₂, F, F₂ and HF(v), $v=0-3$, power, power spectral distribution and lasing zone length were made. In addition to the cold pumping reaction, major collisional deactivators and rotational relaxation, it was found that the hot pumping reaction, F-atom wall recombination and multiquantum deactivations all have a significant effect on laser performance and must be included in the model. The use of sparse matrix techniques resulted in the quite reasonable run times of 100 to 200 sec on the CYBER 175. This efficient, rotational nonequilibrium kinetics model was coupled to the AFWL physical optics strip resonator code.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Studies of New Chemical Analysis Techniques
2. PRINCIPAL INVESTIGATOR: Dr. Robert E. Sievers
Department of Chemistry
University of Colorado
Boulder, Colorado 80309
3. INCLUSIVE DATES: 1 September 1975 - 30 September 1979
4. CONTRACT NUMBER: F44620-76-C-0031
5. COSTS AND FY SOURCE: \$316,000, FY76; \$33,000, FY77; \$150,000, FY77; \$100,000, FY78; \$60,000, FY79

6. SENIOR ENLISTED PERSONNEL:

Dr. Robert Barkley	Dr. Donald Denney
Dr. Louis Jambor	Dr. Gerda Lange
Dr. Larry Field	Dr. James Duncan
Dr. George Hess	Dr. Toshihiko Hanai
Dr. James Navratil	

7. JUNIOR RESEARCH PERSONNEL

M. Wizner	K. Brooks
R. Hutte	J. Tesch
T. Bettes	A. Nitka
J. Stanley	W. Evans
J. Harder	R. Jelinek
W. Rehg	

8. PUBLICATIONS:

"Analysis for Beryllium in Ambient Air Particulates by Gas Chromatography," W. D. Ross, J. L. Pyle, and R. E. Sievers, Environmental Sci. and Tech., 11, 467 (1977).

"Determination of Chromium in Human Blood Serum by Gas Chromatography with a Microwave-Excited Emission Detector," M. S. Black and R. E. Sievers, Anal. Chem., 48, 1972 (1976).

"Microdetermination of Nitrates and Nitrites in Saliva, Blood, Water and Suspended Particulates in Air by Gas Chromatography," J. W. Tesch, W. R. Rehg, and R. E. Sievers, J. Chromatography, 126, 743 (1976).

"Improvements in Gas Chromatography Columns Formed by In Situ Polymerization," T. M. Chen, G. G. Hess, and R. E. Sievers, J. Chromatography, 134, 170 (1977).

"Open-pore Polyurethane Columns for Collection and Pre-concentration of Polynuclear Aromatic Hydrocarbons from Water," J. D. Navratil, R. E. Sievers, and H. F. Walton, Anal. Chem., 49, 2260 (1977).

"Gas Chromatographic Technique for Compound Class Analysis of Jet Engine Exhaust," M. S. Black, W. R. Rehg, R. E. Sievers, and J. J. Brooks, J. Chromatography, 142, 809 (1977).

"Chemical Separations with Open-Pore Polyurethane," J. D. Navratil and R. E. Sievers, American Laboratory, 9, 38 (1977).

"Electron Capture Gas Chromatographic Determination of Nitrates and Nitrites in Biological and Environmental Samples," J. W. Tesch, Ph.D. Thesis, University of Colorado, 1977.

"Volatile Metal Complexes," R. E. Sievers and J. Sadlowski, Science, 201, 217 (1978).

"Gas Chromatographic Injector Attachment for the Direct Insertion and Removal of a Porous Polymer Sorption Trap," H. Peterson, G. A. Eiceman, L. R. Field, and R. E. Sievers, Anal. Chem., 50, 2152 (1978).

"Structures of Europium Complexes and Implications in Lanthanide NMR Shift Reagent Chemistry," J. A. Cunningham and R. E. Sievers, Inorg. Chem., accepted for publication (1979).

"Selective Collection and Measurement of Particulate Nitrate, Gaseous Nitric Acid, and Nitrogen Dioxide in Ambient Air," J. Tesch and R. E. Sievers, submitted (1979).

"Lanthanide Chelates as Antiknock Additives," R. L. Tischer, K. J. Eisentraut, K. Scheller, R. E. Sievers, R. C. Bausman, and P. R. Blum, Rev. of Petroleum Chemistry, in press (1979).

"Selective Electron-Capture Sensitization," R. E. Sievers, M. D. Phillips, R. M. Barkley, M. A. Wizner, M. J. Bollinger, and R. S. Hutte, J. Chromatography, in press (1979).

"Derivatization Technique for Analysis of Molybdenum and Aluminum by Atomic Absorption Spectrophotometry," J. S. Stanley, L. G. Jambor, and R. E. Sievers, in preparation.

"Atomic Absorption Spectrophotometric Characterization of Aluminum β -Diketonates," J. S. Stanley, M. S. Thesis, University of Colorado, in preparation.

"Studies of New Chemical Analysis Techniques," R. E. Sievers, Final Technical Report.

9. REPORT OF OBJECTIVES AND ACCOMPLISHMENTS:

New chemical analysis techniques have been studied in three separate, but often interrelated areas. Volatile metal chelates have been synthesized and studied with a view towards improving the sensitivity of quantitative analysis for molybdenum, chromium and aluminum, separating enantiomeric isomers, and developing selective sorbent materials. Chromatographic systems have been fabricated and studied in order to evaluate the performance of innovative separation and detector schemes. Various environmental studies have been made to develop analyses for several species, including polynuclear aromatic hydrocarbons (PAH), nitrogen oxides, and several anionic species.

Several monomeric, Mo (VI) β -diketonates have been synthesized and studied to assess their potential in making more sensitive atomic absorption measurements of Mo in an $N_2O-C_2H_2$ flame. Molybdenum complexes of 2,2,6,6,-tetramethyl-3,5-heptanedione (Hthd), 3-(trifluoromethylene)-d-camphor (Hfacam), and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (Hfod), for example, show enhanced sensitivity in a $N_2O-C_2H_2$ flame over ammonium phosphomolybdate. When *n*-butylacetate is the solvent a 2-fold enhancement is found and the detection limit (1% absorption) is 0.065 $\mu\text{g/mL}$. This enhancement is in addition to the enhancement observed when changing to an organic solvent from water. Similar, but smaller enhancements are observed in analogous experiments with Al and Cr chelates.

A lanthanide metal chelate, tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) europium (III), $\text{Eu}(\text{fod})_3$, was used as a pre-chromatographic column which is specific for oxygenated compounds. The metal chelate was sorbed onto porous silica and used in a subtractive technique to remove oxygen containing interferences in a gas chromatographic separation. The technique also has been used to remove solvent methanol from a sample, yielding a chromatogram free of a solvent peak. This work also demonstrates the possibility of thermally desorbing compounds from this metal chelate sorbent, resulting in highly class-specific analyses.

Separation of optically active isomers have been attempted using chiral lanthanide chelates. Glass capillary columns were deactivated with 3-aminopropyltriethoxysilane folled by diketene. This procedure is intended to cover the glass surface with β -ketoamide functional groups. A chiral complex, such as $\text{Eu}(\text{facam})_3$ could then become bonded to the glass surface via a ligand exchange reaction with the modified glass surface. To date, however, no successful separations of optical isomers have been attained with columns prepared in this way.

Enhanced electron capture detector sensitivity for certain compounds is possible when N_2O is added to N_2 carrier gas. This sensitization is selective for compounds which can undergo ion-molecule reactions with O^- and NO^- that are generated in situ in the detector when N_2O is present. Enhanced response by Selective Electron Capture Sensitization (SECS) has been observed for methane, ethane, *n*-propane, *n*-butane, *n*-pentane, *n*-hexane, benzene, ethanol, methylisobutylketane, hydrogen, and carbon dioxide. Several hydrocarbons are detectable at the picogram level. With the SECS detector, a 5000-fold increase in response is found for CO_2 , a 10-fold increase for methane, and a 40-fold increase for hydrogen.

Open-pore polyurethane (OPP) chromatographic media have been extended in two ways. Improved gas chromatographic column behavior has been observed with respect to peak shape and temperature stability. A column prepared using a hydroxyl to isocyanate functional group ratio of approximately 2:1 yields good separation and symmetrical peaks for polar compounds, including alcohols. OPP columns coated with Carbowax 20M show improved temperature stability in the 150°C to 225°C range and have been used for separation of the herbicides methyl-2, 4-D (methyl 2,4-dichlorophenoxyacetate) and methyl Fenac (methyl 2,3,6-trichlorophenylacetate).

Pre-concentration columns of OPP have been tested for ion-exchange properties, solvent compatibilities, and ability to preconcentrate polynuclear aromatic hydrocarbons from water. Pyrene recovery is nearly 100% when 1 L of solution containing 1 μ g of pyrene is passed through a 0.3 x 5 cm column and eluted with 5 mL of methanol.

A gas chromatographic injector attachment has been developed and fabricated for use with samples that are concentrated on porous polymer sorbents. The device allows insertion, heating, and removal of a polymer sorbent trap from a chromatograph injection port in a convenient manner.

Preliminary studies have been made to determine the feasibility of using microwave energy as a selective thermal heater for various stationary phases that could be used in gas chromatographic separations. A series of selected chromatographic liquid phases were subjected to microwave excitation; the results of these experiments indicate that the various phases are heated roughly in proportion to their polarity.

A method for the analysis of nitrates and nitrites has been developed for use with a wide variety of samples, including human saliva, blood, drinking water and airborne particulates. Aqueous nitrate ion is first converted to nitrobenzene in the presence of a catalyst.

Nitrobenzene is then quantified by electron capture gas chromatography. Appropriate sample pretreatment allows a similar determination to be made for nitrite ion and other oxides of nitrogen. Nitrite ion in blood or saliva can be quantified at the 0.1 ppm (w/w) level using approximately a 0.05 mL (one drop) sample. Sample collection parameters and appropriate modifications of this technique have been determined to allow collection and measurement of particulate nitrate, gaseous nitric acid, and nitrogen dioxide in ambient air. An appropriate series of filter media affords a pre-separation of these species. More recent work has shown that a Teflon particulate filter is an important improvement over a glass fiber filter because Teflon does not collect nitric acid.

Jet engine exhaust analyses have been performed which allow determination of compound classes. A simple gas chromatographic technique utilizing two analytical columns has been developed for the determination of saturated, olefinic, and combined oxygenated-aromatic fractions of jet engine exhaust which is collected on a dual sorbent trap containing Tenax GC and Carbosieve B. Experimental results have been obtained with synthetic exhaust hydrocarbon mixtures and jet combustor exhaust samples.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Evaporation and Dispersion of Hazardous Materials from Accidental Spills
2. PRINCIPAL INVESTIGATOR: Dr. Charles Springer
Department of Chemical Engineering
University of Arkansas
Fayetteville, Arkansas 72701
3. INCLUSIVE DATES: 15 May 1978 - 14 May 1979
4. GRANT NUMBER: AFOSR-78-3559
5. COSTS AND FY SOURCE: \$21,447, FY78 (\$10,000 Mini Grant; \$11,447 MIPR from CEEDO)
6. PUBLICATION:
"Evaporation and Dispersion of Hazardous Materials," Charles Springer, Final Technical Report
7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This work was undertaken in order to develop a state-of-the art predictive model for the evaporation and dispersion of hazardous liquids, especially hydrazine family fuels and propellants, which might be accidentally spilled.

All of the several model elements were assembled and combined in a FORTRAN computer program which will compute evaporation rates and limits of the hazardous region; that is, the maximum distance away from the centerline where a hazard would exist as well as the maximum distance down wind that a hazard would exist. Depending upon the input data supplied, the program will also predict the amount of water that would be required for sufficient dilution to eliminate the hazard, the effects of changing variables (as for example, the effects of changes in wind speed, or in air temperature or in atmospheric stability), and the effect of the passage of time (up to twenty-four hours) if weather conditions are updated hourly. In the latter case, allowances are made for composition changes in the remaining pool because of preferential evaporation of components, possible absorption of water from the atmosphere, and absorption of (and reaction with) carbon dioxide from the atmosphere.

A number of computations were made in order to determine the effects of changes in the several input parameters. The results of these were presented in the form of correction factors which can be used to correct from certain "base cases," and thus provide for rapid field estimation when needed.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: New Perfluoropolymer-forming Reactions
2. PRINCIPAL INVESTIGATOR: Dr. Madeline S. Toy
Science Applications, Inc.
1257 Tasman Drive
Sunnyvale, CA 94086
3. INCLUSIVE DATES: 1 October 1975 - 31 March 1979
4. CONTRACT NUMBER: F44620-76-C-0027
5. COSTS AND FY SOURCE: \$48,446, FY76; \$49,783, FY77; \$49,761, FY78;
\$24,824, FY79
6. SENIOR RESEARCH PERSONNEL: R. S. Stringham
7. PUBLICATIONS:
 - "Electrophilic Additions Involving Fluoronium Ions. II. The Addition of Fluoroxy Groups to Perfluoroaromatic Compounds," M. S. Toy and R. S. Stringham, J. Fluorine Chem., 5, 31 (1975).
 - "Photochemical Reactions of Fluoroxyperfluoroalkanes with Perfluorocycloolefins," M. S. Toy and R. S. Stringham, J. Fluorine Chem., 5, 481 (1975).
 - "Photochemical Reactions of Perfluorodialkyl Peroxides with Perfluorocycloolefins," M. S. Toy and R. S. Stringham, J. Fluorine Chem., 7, 229 (1976).
 - "Addition Reaction of Tetrafluorohydrazine to Perfluoro-t-butyl Hypofluorite," M. S. Toy and R. S. Stringham, J. Fluorine Chem., 7, 229 (1976).
 - "NMR Studies on Microstructures of Polyperfluorobutadiene," M. S. Toy and R. S. Stringham, J. Polymer Sci., B, 14, 717 (1976).
 - "NMR Studies of Some Perfluorocarbocyclic Ethers and Polyethers," M. S. Toy and R. S. Stringham, Am. Chem. Soc. Polymer Preprints, 18 (2), 438 (1977).

"Copolymerization Reactions of 'Dewar' Hexafluorobenzene," M. S. Toy and R. S. Stringham, Am. Chem. Soc. Polymer Preprints, 19 (1), 534 (1978)

"Fluorine-19 and Carbon-13 NMR Spectra of Polyperfluorobutadiene," M. S. Toy and R. S. Stringham, Chapter 1 in APPLICATIONS OF POLYMER SPECTROSCOPY, edited by E. G. Brame, Academic Press (1978).

"Some Perfluorocarbocyclic Ethers and Polyethers from Hexafluorobenzene," M. S. Toy and R. S. Stringham, J. Polymer Sci., A-1, 16, 2781 (1978).

"Some New Perfluoroethers and Copolymers from 'Dewar' Hexafluorobenzene," M. S. Toy and R. S. Stringham, J. Fluorine Chem., 13, 23 (1979).

"Thermal Isomerization of a Perfluorobicyclo[2.2.0]hexene Derivative," M. S. Toy and R. S. Stringham, J. Fluorine Chem., May 1979.

"Thermal Isomerization of Perfluorobicyclo[2.2.0]hexene Oxides," M. S. Toy and R. S. Stringham, submitted to J. Org. Chem.

"Copolymerization of Pentafluoropyridine," M. S. Toy and R. S. Stringham, Am. Chem. Soc. Polymer Preprints, 20 (1), in press (1979); accepted to J. Polymer Sci., B.

"The Polymerization of Octafluoronaphthalene," M. S. Toy and R. S. Stringham, will be submitted to Am. Chem. Soc. Polymer Preprints, Sept., 1979.

"New Perfluoropolymer-forming Reactions," M. S. Toy, Final Technical Report.

8. PATENT APPLICATIONS:

"Method of Preparation of Perfluoroethers," M. S. Toy and R. S. Stringham, AF Invention No. 11,991 (Feb 1977).

"Method for Preparation of Bis(perfluoro-t-butyl) Peroxide," M. S. Toy and R. S. Stringham, AF Invention No. 11,996 (Feb 1977).

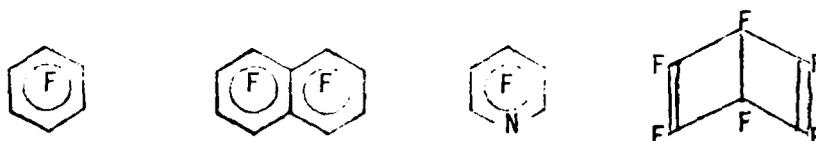
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to establish polymer-forming reactions that could be utilized to synthesize perfluoropolymers with elastomeric properties over a broad temperature range. The principal lines of research activity pursued included studies of (1) the

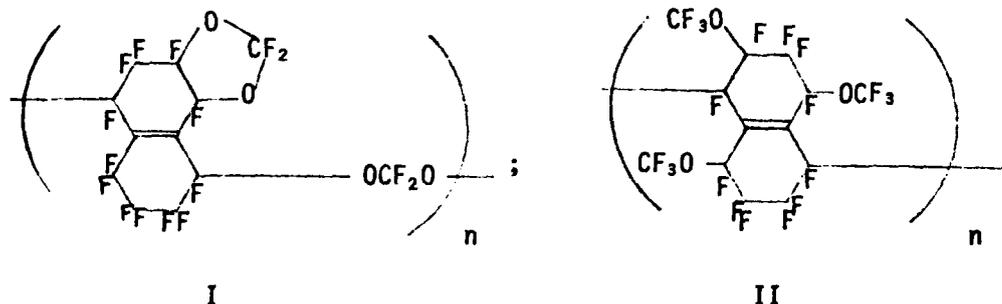
nature of oxygen-to-fluorine bond dissociations and additions, (2) new perfluoropolymer-forming reactions, and (3) synthesis of certain monomers and monomer-precursors.

Homolysis and heterolysis of the covalent O-F bond of tertiary fluoroxyperfluoroalkane are described. The electrophilicity of fluoroxyperfluoroalkanes shows the following decreasing order: $(CF_3)_3COF > CF_3OF > CF_2(OF)_2$.

The copolymerizability of $CF_2(OF)_2$ was established with perfluoroaromatic, perfluoro-N-heteroaromatic and para-bonded perfluoroaromatic. The examples included the following:

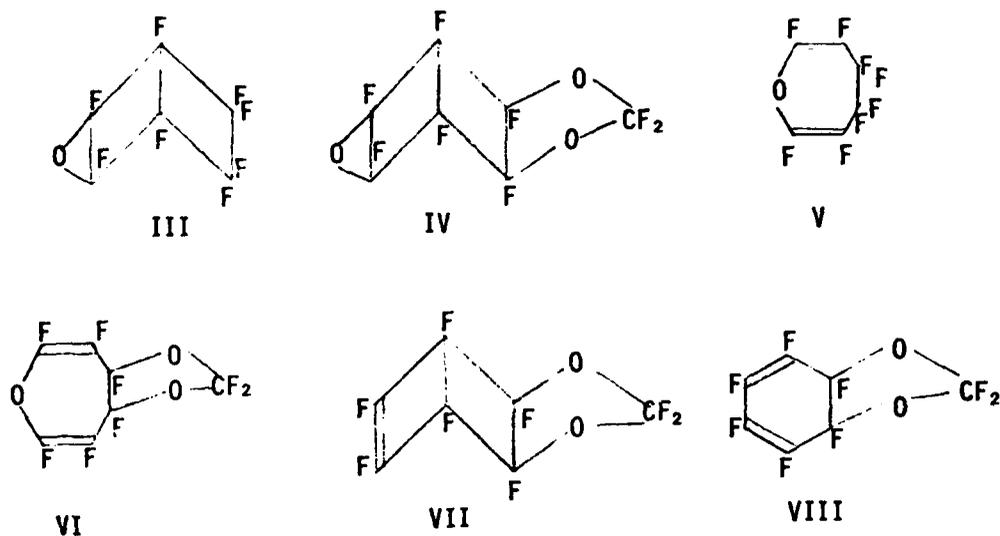


These comonomers were interposed by stable- OCF_2O -linking groups, but did not form simple alternate copolymers. Fluorination and pendant perfluoro-1,3-dioxolane ring formation occurred simultaneously during copolymerization. Homopolymerizability of perfluoroaromatics was also established by CF_3OF through aromatic nuclear-addition reactions. The homopolymerization of hexafluorobenzene and octafluoronaphthalene happened concurrently with fluorination and pendant trifluoromethoxy group additions to the aromatic rings. The octafluoronaphthalene copolymer(I) and homopolymer(II) at about 1:3 mole ratio of $C_{10}F_8$ to CF_3OF or $CF_2(OF)_2$ showed unsaturation between the carbons common to both rings, e.g.

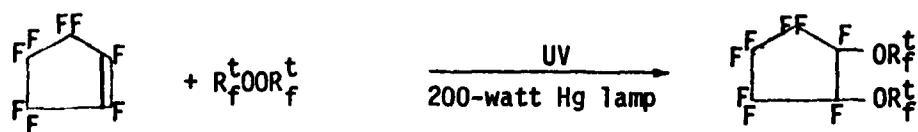


The perfluoropolyethers (I, II) were low melting solids (m.p. $<100^\circ C$) and soluble in hexafluorobenzene and perfluoro-2-butyltetrahydrofuran (FC-75).

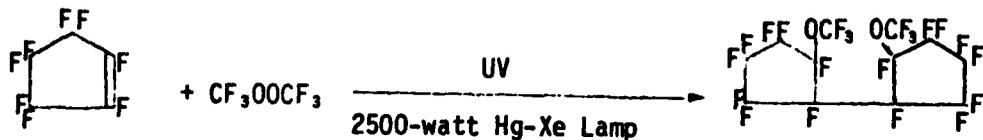
Unimolecular isomerization was identified for perfluorobicyclo [2.2.0] hexene oxides (III, IV) to 1,6-epoxyperfluoro-1,5-dienes (V, VI) respectively and a perfluorobicyclo[2.2.0]hexene (VII) to perfluorocyclohexa-1,3-diene (VIII). Homopolymerizability of the latter was established.



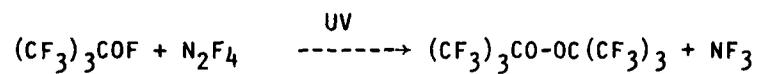
In the new synthesis category the discoveries included synthesizing (1) vicinal perfluorodi-*t*-butoxycycloalkanes by low temperature photolysis of $(CF_3)_3CO-OC(CF_3)_3$ and perfluorocycloalkenes, e.g.,



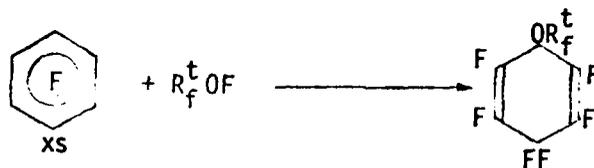
(2) 2,2'-perfluorodimethoxycycloalkyls by photolysis of CF_3OOCF_3 and perfluorocycloalkenes, e.g.,



(3) bis(perfluoro-t-butyl) peroxide by photolysis of $(CF_3)_3COF$ and N_2F_4 , e.g.,



(4) new perfluoroethers via aromatic nuclear-addition reactions, e.g.,



From the preparative viewpoint the last example provides a convenient method for the synthesis of many new perfluorocarbocyclic ethers, polyethers and ether-containing intermediates.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Kinetic Aspects of Gas Phase Metal Atom Oxidation Reactions
2. PRINCIPAL INVESTIGATOR: Dr. John Wiesenfeld
Department of Chemistry
Cornell University
Baker Laboratory
Ithaca, New York 14853
3. INCLUSIVE DATES: 1 June 1976 - 31 May 1979
4. GRANT NUMBER: AFOSR 76-3039
5. COSTS AND FY SOURCE: \$28,650, FY76; \$35,359, FY77; \$37,000, FY78
6. SENIOR RESEARCH PERSONNEL:

Sherwin Amimoto
Peter Whitkop

7. JUNIOR RESEARCH PERSONNEL: Maria Josephine Yuen

8. PUBLICATIONS:

"Kinetic Study of the Reaction $\text{Sn} + \text{N}_2\text{O} \rightarrow \text{SnO} + \text{N}_2$," J. R. Wiesenfeld and M. J. Yuen, Chem. Phys. Lett., **42**, 293 (1976).

"Effect of Diabatic Correlations on the Oxidation of N_2O and CO_2 by O Atoms," J. R. Wiesenfeld, Chem. Phys. Lett., **45**, 384 (1977).

"Kinetic Studies of Tin and Germanium Atom Oxidation in the Gas Phase," J. R. Wiesenfeld and M. J. Yuen, J. Phys. Chem., **82**, 1225 (1978).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The oxidation of Ge and Sn by various gases including N_2O has been studied by flash photolysis at room temperature and the kinetics determined. The rate of $\text{Sn} + \text{N}_2\text{O}$ is probably too slow to permit construction of a chemical laser based on this reaction. A new set of techniques involving laser pumping of alkaline earth atoms is also described which will permit the study of the kinetic behavior of their low-lying excited levels in bimolecular collisions.

AFOSR Program Manager: Russell A. Armstrong, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Atomic and Molecular Gas Phase Spectrometry
2. PRINCIPAL INVESTIGATOR: Dr. James D. Winefordner
Department of Chemistry
University of Florida
Gainesville, FL 32611
3. INCLUSIVE DATES: 1 September 1975 - 30 September 1979
4. CONTRACT NUMBER: F44620-76-C-0005
5. COSTS AND FY SOURCE: \$100,000, FY76; \$110,000, FY77; \$125,000,
FY78; \$125,000, FY79
6. SENIOR RESEARCH PERSONNEL:

Dr. Radu Mavrodineanu	Dr. Howard Latz
Dr. Piet Walters	Dr. Nicolo Omenetto
Dr. Robert Michel	Dr. Al Massoumi
Dr. Christian Favez	Dr. Jean Michel Mermet
Dr. David Johnson	Dr. Kitao Fujiwara
Dr. Alan Ullman	Dr. Roger Reeves
Dr. Hiroki Haraguchi	
7. JUNIOR RESEARCH PERSONNEL:

Benjamin Smith	Frank Ottinger
Stephan Weeks	Raymond Cooney
Jerry Messman	James Bower
John Fitzgerald	Sief Nikdel
Lucas Hart	Ricky Bateh
Bruce Pollard	Terry Tuell
Marlana Blackburn	David Bolton
Glenn Boutilier	Melanie Elder
C. Chen	John Horvath
Thomas Chester	Sam Bayer
William Fowler	Edward Lai
8. PUBLICATIONS:

"Interference of Magnesium by Trace Concomitants in Flame Atomic Absorption Spectrometry," C. Chen and J. D. Winefordner, Can. J. Spectrosc., 20, 87 (1975).

"Some Considerations on the Microwave Electrodeless Discharge Plasma Diagnostics in Argon, Helium or Nitrogen Atmospheres," R. Avni and J. D. Winefordner, Spectrochim. Acta B, 30B, 281 (1975).

"A Comparison of Signal-to-Noise Ratios for Single Channel Methods (Sequential and Multiplex) vs Multichannel Methods in Optical Spectroscopy," J. D. Winefordner, R. Avni, T. L. Chester, J. J. Fitzgerald, L. P. Hart, D. J. Johnson, and P. W. Plankey, Spectrochim. Acta 31B, 1-19 (1976).

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"Atomic Fluorescence Spectrometry with an Eimac Continuum Excitation Source and a Graphite Filament Atomizer," P. S. Chuang and J. D. Winefordner, Appl. Spectrosc., 29, 412 (1975).

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"Atomic Fluorescence Spectrometry with a Premixed Argon/Oxygen/Acetylene Flame," D. J. Johnson and J. D. Winefordner, Anal. Chem., 48, 341 (1976).

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"The Analytical Capabilities of the Selectively Modulated Interferometric Dispersive Spectrometer (SEMIDS)," T. L. Chester and J. D. Winefordner, Anal. Chem., 49, 113 (1977).

"Flame Diagnostics: Local Temperature Profiles and Atomic Fluorescence Intensity Profiles in Air-Acetylene Flames," H. Haraguchi and J. D. Winefordner, Appl. Spectrosc., 31, 195 (1977).

"Temperature Profiles of Air-Hydrogen Flames Measured by Two-Line Atomic Fluorescence Method," H. Haraguchi and J. D. Winefordner, Appl. Spectrosc., 31, 330 (1977).

"Comparison of Pulsed Source with CW Source Excitation in Atomic and Molecular Luminescence Spectrometry via Signal-to-Noise Ratio Calculations," G. D. Boutilier, J. D. Bradshaw, S. J. Weeks, and J. D. Winefordner, Appl. Spectrosc., 31, 307 (1977).

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"The Atomic Fluorescence of Sodium under Continuous Wave Laser Excitation," B. Smith, J. D. Winefordner, and N. Omenetto, J. Appl. Physics, 48, 2687 (1977).

"A Review and Tutorial Discussion of Noise and Signal-to-Noise Ratios in Analytical Spectrometry," C. Th. J. Alkemade, W. Snelleman, G. D. Boutilier, B. D. Pillard, J. D. Winefordner, T. L. Chester, and N. Omenetto, Spectrochim. Acta B, Vol. 33B, 383 (1978), PART I.

"A Review and Tutorial Discussion of Noise and Signal-to-Noise Ratios in Analytical Spectrometry - Part II," C. Th. J. Alkemade, W. Snelleman, G. D. Boutilier, B. D. Pollard, J. D. Winefordner, T. L. Chester, and N. Omenetto, Spectrochim. Acta B, Vol. 33B, 401 (1978).

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"Atomic Absorption Inhibition Release Titration as a Method for Studying of Releasing and Inhibition Effects," D. Stojanovic, J. Bradshaw, and J. D. Winefordner, Anal. Chim. Acta, 96, 45 (1978).

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"Improvement of the Detection Limits in Laser-Excited Atomic Fluorescence Flame Spectrometry," S. J. Weeks, H. Haraguchi, and J. D. Winefordner, Anal. Chem., 50, 360 (1978).

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"Steady State Atomic Fluorescence Radiance Expressions for Continuum Excitation," G. D. Boutilier, M. B. Blackburn, J. M. Mermet, S. J. Weeks, H. Haraguchi, J. D. Winefordner, and N. Omenetto, Appl. Optics, 17, 2291 (1978)

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"A Review and Tutorial Discussion of Signal-to-Noise Ratios in Analytical Spectrometry - III, Multiplicative Noises," C. Th. J. Alkemade, W. Snelleman, G. D. Boutilier, and J. D. Winefordner, Spectro. Chim. Acta B., submitted.

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research completed during the past four years can be generally divided into combustion diagnostics and analytical gas phase atomic and molecular spectrometry. Significant advances have been made in both areas. New and improved techniques to spatially and temporally measure flame gas temperatures and species have been and are being developed. These techniques are all based upon fluorescence detection. Earlier studies involved the use of a conventional xenon arc lamp source, whereas recent studies involve the use of a pulsed, high peak power tunable dye lasers. By measuring the ratio of two fluorescence transitions (in a probe, such as indium) excited with two different wavelengths, the flame temperature can be measured with a precision and accuracy better than 50 K. The two main temperature techniques developed depend upon either the linear relationship between fluorescence and the excitation flux on the approach to saturation of the fluorescence with high excitation fluxes. The measurement of total species concentrations in flames and fluorescence quantum efficiencies is readily performed by

measurement of the absolute fluorescence flux reaching a calibrated detector as a function of absolute laser flux. A rather simple graphical method allows both species concentration and species fluorescence quantum efficiencies to be measured. Using these approaches, both flame temperature and species concentration spatial profiles in a variety of laboratory flames (acetylene/air, acetylene/ N_2O , H_2 /air, H_2/O_2 /Ar, etc.) have been measured.

Analytical gas phase spectrometric studies have spanned a considerable breadth. Theoretical calculations of signal-to-noise ratio have been made to obtain: approaches to the optimization of spectral measurement systems (linear spectral scan spectrometers vs sequential slow scan spectrometers vs multiple detector spectrometers vs multiplex spectrometers, such as Hadamard Transform and Fourier Transform); approaches to the optimization of conventional and time resolution of luminescent components (cw source-cw detection, pulsed source-gated detection with no time resolution, and pulsed source-gated detection with time resolution); approaches to the optimization of atomic and molecular analytical methods (absorption vs emission vs fluorescence vs Raman and the use of optogalvanic and optoacoustic detection as well as the use of non-linear methods involving more than one photon processes); and finally approaches to the optimization and use of image detectors (vidicons, SIT, ISIT, diode arrays, etc.) over photomultiplier detectors for optical spectroscopy.

Experimental analytical gas phase spectrometric studies have involved: the development and refinement of pulsed (and cw) tunable dye laser excitation of atoms produced by spraying aerosols into combustion flames, furnaces, and inductively coupled plasmas; the development and refinement of an EIMAC xenon arc source-flame-slew scan atomic fluorescence spectrometer for multielement analysis in real samples, such as engine oils, biological materials, etc.; the development and refinement of an innovative source for atomic fluorescence flame spectrometry, namely the use of an ICP source which has the benefits of both a continuum source in terms of wavelength selectivity and line sources in terms of intense narrow line output; and development of chemiluminescence produced above a furnace (into which samples are nebulized) as an analytical method. By means of these approaches, considerable selectivity (near specificity in several cases) is obtained with detection limits in the picograms per milliliter in most cases and with precisions (%RSD) of the order of 5% or better. The above techniques have been applied to the selective measurement of ultratrace elements in real samples, such as elements in river water and the selective measurement of trace elements in samples with complex matrices, such as zinc in copper alloys, trace elements in orange juice, and trace elements in fly ash.

Other analytical and diagnostical studies performed include: a comparison of wavelength vs amplitude modulation in optical spectroscopy; use of a continuum source, resonance monochromator for atomic absorption flame spectrometry; identification of the molecular fluorescence components of unseeded and seeded flames; identification of the major spectral noise peaks in flame emission and fluorescence spectrometry; a tutorial and definitive report on additive and multiplicative noises in optical emission and fluorescence spectrometry; an evaluation of commercial RF-electrodeless discharge lamps and the design of an experimental approach to prepare and evaluate microwave electrodeless discharge lamps for atomic fluorescence flame spectrometry; and an evaluation of several multiplex (including the Hadamard spectrometer) approaches and image devices for multiple element measurements in atomic emission and fluorescence spectrometry.

In summary, the past four years have been fruitful in the development of combustion diagnostical approaches which will have considerable use in evaluating large flames (as in combustors) and in developing selective, sensitive approaches to trace element measurements.

AFOSR Program Manager: Denton W. Elliott

BACK COVER

The technique of Z contrast using the scanning transmission electron microscope has been proven feasible for the study of microstructure in polymers by Professor Donald Uhlmann and Dr. John B. Vander Sand of the Massachusetts Institute of Technology (AFOSR-77-3226). It has been shown possible with this technique to characterize structural features in polymers by carrying out ultramicrotomy, followed by staining with uranyl acetate and viewing in the scanning transmission electron microscope in the Z contrast mode. Here the bright field image is combined with the annular dark field image to produce an image with greatly increased contrast.

Results using this technique have indicated structural inhomogeneities in both amine-cured and anhydride-cured epoxies, as well as in polyimides. This is shown in the photo for an epon 812 epoxy resin cured with NMA, DDSA and BPMA at 80°C for four hours. The sizes of the inhomogeneities seen in the epoxy resins are similar to those inferred from small angle X-ray scattering studies of the same polymers, i.e., in the range of 50-200 Å. These heterogeneities are regions of different crosslink density, whose now-confirmed presence has important implications for the behavior of the materials in high performance applications. The light areas represent regions of high crosslink density; the dark regions represent regions of low crosslink density. Without the use of uranyl acetate as a staining agent, the microstructure appears homogeneous. This technique offers outstanding promise for investigating the morphology and microstructure of polymers.

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