AFOSR 68-2810

CHEMISTRY

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AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Office of Aerospace Research ★ United States Air Force
Fiscal Year 1968

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THE COVER

Beginning on page 3 an account is given of a novel system of photographic imaging based on photopolymerization. This development of the Hughes Research Laboratories was assisted by research contributions of Dr. J. David Margerum under AFOSR sponsorship. The Hughes system is characterized by an extremely short time span -- a fraction of a second -- between image exposure and display. It is believed adaptable for "real time" information display, even three-dimensionally. In a recent submission to Applied Physics Letters, D. H. Close, A. D. Jacobsen, J. D. Margerum, R. G. Brault, and F.J. McClung report application of the Hughes system in "Hologram Recording on Photopolymer Materials." The cover illustration was printed from a hologram of a resolution chart made with the photopolymer. We regard the design to be quite eye-catching.

AFOSR 68-2810
January 1969

14th Annual Chemistry Program Review

Fiscal Year 1968

Dr. William L. Ruigh, Scientific Editor

Dr. Donald L. Ball, Managing Editor

DIRECTORATE OF CHEMICAL SCIENCES
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
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DEPARTMENT OF THE AIR FORCE
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (OAR)
ARLINGTON, VIRGINIA 22209

31 January 1969

TO: Members of the Chemistry Evaluation Panel for the
Directorate of Chemical Sciences (AFOSR)

Members of Congress bitterly complain--and rightfully so in my opinion as far as the Chemical and Engineering News (C&EN) of the American Chemical Society (ACS) is concerned--because federally appropriated funds are not cited as being an important element in the productivity of scientific research in the U.S.A.

There are at least three important elements in most productive research efforts: (1) the principal investigator and his ideas, (2) the research environment and facilities made available to him by his institution, and (3) additional restraints, funds, equipment and/or facilities.

The taxpayers and the Congress which earmarks the taxpayers' money for research are concerned with the source of funds, as well as the payoff of socially desirable ends. This concern is emphasized by the dwindling/shrinking tax dollars for research. The ACS, our own professional society, allows its voice (C&EN) to the public (the taxpayers) to ignore this vital, elemental self-interest of chemistry, the concern of Congress and the taxpayers.

Most issues of (C&EN) contain stories of research accomplishments in chemistry which would be impossible without generous support of one and sometimes two agencies* utilizing federal funds and/or facilities. The researcher is often quite vocal and appreciative of the outside support which (C&EN) refuses to acknowledge even though the reporter may have promised to do so when getting the story.

This letter is an appeal to the panel members to join me in strongly urging researchers in chemistry to seek other suitable outlets for the stories about their research accomplishments until there is a change in this short-sighted (C&EN) policy which I consider stupid as well as personally abhorrent.

In the meantime, this book is our report to you of how we have used your advice and the taxpayers' dollars.

Again thanking you for your devoted assistance,

AMOS G. HORNEY
Director of Chemical Sciences

*Occasionally an investigator pools numerous supports and it might be awkward in telling the story to acknowledge other than "several federal and private agencies assisted the institution and the investigator in making this research possible."

AFOSR

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FY 1968

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MISSION

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

The Directorate obtains and maintains for the Air Force a diversified program of chemical research through support of scientists in promising original endeavors of their own choosing. 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 aids the Air Force in its maintenance of technological superiority.

ACKNOWLEDGMENTS

Besides the technical staff many others assisted in preparing this review. The Directorate is particularly grateful to Dr. Sam R. Hoover and Prof. George S. Hammond, who granted permission to include their writings in the Appendix. Special thanks are due Mrs. Mary Koval for her many hours devoted to typing the manuscript. Noteworthy assistance in preparing drafts and final copy came from Mrs. Elizabeth Lewis and Mrs. Wanda Climenhaga. The editors and authors are grateful also to Mrs. Amos Horney for the arduous task of proofreading. The preparation of the notably striking cover was by Mr. Charles P. Shealy, Presentations Division, Office of Information, OAR.

CONTENTS

INTRODUCTION

The Webster definition of science (from the latin root meaning knowledge) is firstly "the possession of knowledge as distinguished from ignorance" and secondly it is a branch of systemetized knowledge. Chemistry is defined as a "science that deals with the composition, structure and properties of substances and of the transformations that they undergo." Webster further divides this branch of science into the two classical branches of inorganic and organic chemistry. This classification was actually made obsolete by Wöhler's discovery of the transformation of ammonium cyanate into urea in 1828, one hundred and forty years ago. This and other classifications of chemistry have been widely accepted, used and are still embedded in the research and teaching structures of most university departments of chemistry.

The present inadequate classifications of the basic science of chemistry are particularly unsatisfactory in the choice, administration and "selling" of chemistry whether the sale is to a university dean, a secretary of the Department of Defense or the general public as personified in the average congressman and budget bureau administrator. In an effort to overcome these difficulties, the basic research sponsored by the Directorate of Chemical Sciences, AFOSR, has now been reclassified according to five new categories:

(1) Chemical Instrumentation and Techniques

(2) Chemical Structure and Properties

(3) Chemical Energetics

(4) Theoretical Chemistry

(5) Chemical Synthesis and Dynamics

The nature and content of these categories will be illustrated in the pages to follow. Each will be defined and examples of recent significant developments will be given. With these highlights we hope to convey some understanding of the unique characters of our chemistry program including its relation to the current needs and future interests of the Air Force.

CHEMICAL INSTRUMENTATION AND TECHNIQUES

By Denton W. Elliott

Chemistry depends upon the gathering of data and information about what is going on in atoms and molecules. The objective is to assess these data and information, and arrive at conclusions on the fundamental principles involved in the various ways in which these components of matter can combine, rearrange, or react. A considerable amount of analytical data from observations of chemical systems is needed to accomplish this. The application of physical methods to measure selected properties is extremely important. Analytical instruments are the key in measuring such properties.

Due to improved methods of sensing, processing and display of data, the entire family of optical spectrometers, from I.R. to U.V. has moved into the chemical laboratory, and has become almost indispensable. The same can be said for resonance spectroscopy and various diffraction techniques. Other forms of instrumentation that have carved or are carving their niche in the chemical research picture, and have endeared themselves to our program, are mass spectrometry, Mossbauer Effect, molecular beam, and rapid-scan spectroscopy.

The following accounts are just a sampling of the dividends from researches in our instrumental and techniques program.

HIGH-STABILITY PHOTOMETER UTILIZING OPTICAL FEEDBACK

The application of chemical kinetics to solve new or difficult problems of analysis has lagged behind the development of other new analytical methods. The success of any method is dependent on the reliability of its measuring system. So it was with Dr. Harry L. Pardue and his group at Purdue University. In recent work with reaction rate measurements they encountered a critical need for photometric precision beyond that obtainable from available instrumentation. They found that the rate of photometric drift in their instrument approached the rate of signal change from the reaction being studied. They knew of several recent developments that were directed at providing improved photometric reliability, but they did not meet the requirements which were imposed by their experiments. The results obtained by the other groups did not permit an evaluation of the long-term stability of the system, or of the photometric reliability obtainable without signal averaging. Consequently, Dr. Pardue and his group have primarily concerned themselves with the long-term stability achievable using an optical feedback system, as wel as the instrumental parameters contributing to this stability. They have developed a photometer system having ultra-high stability over extended periods of time.

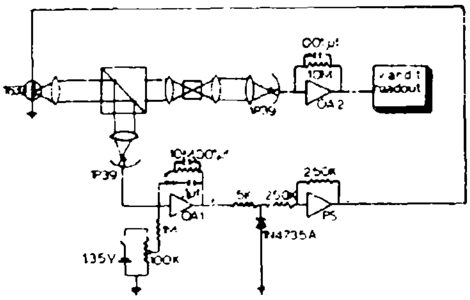


Figure 1. Schematic diagram of high-stability photometer

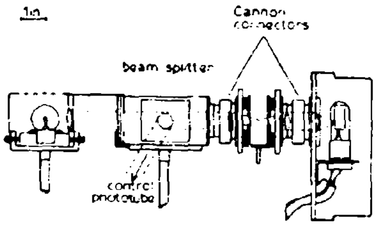


Figure 2. Optical system of photometer

Figures 1 and 2 denote schematic representations of the photometer with its optical system. A beam splitter directs one portion of the radiant energy through the sample compartment to a sample phototube and a second portion of the beam to a control phototube. The output from the control phototube is amplified, and the amplified signal is used to drive a programmable power supply. The programmable power supply drives the radiant energy source. Any variation in the energy source results in a change in the control phototube output, which in turn causes the power supply to change in a direction and by the proper amount, to compensate for the change.

Potassium dichromate was used to test the reliability of photometric measurements on a system at equilibrium. For an evaluation of the utility of the photometer for kinetic measurements, the iodine-catalyzed cerium (IV)-arsenic (III) reaction was used. This reaction is used routinely for the determination of traces of iodide in biological materials. The results have shown that the photometer exhibits long-term stability within two-hundreths per cent transmission (0.02%), over periods of several hours. The reproducibility of measurements made over periods up to one hour is within 0.01%T. The applicability of the system for the study of moderately slow kinetics has been well demonstrated.

Reference:

"High-Stability Photometer Utilizing Optical Feedback," H.L. Pardue and P. Rodriguez, Anal. Chem., 39, 901 (1967).

TRAPPING THE LIGHT FANTASTIC

At the Hughes Research Laboratories in Malibu, California, Dr. David Margerum and his associates, under an AFOSR contract, have been investigating the inhibition, initiation, and propagation of dye-sensitized polymerization reactions. These particular reactions are of much interest to novel photographic processing. Concurrently with this fundamental research being performed by Dr. Margerum, the research laboratory was in the process of developing a photopolymerization system for photographic imaging which could be utilized in large screen information displays. A system was required which was as close as possible to a "real time" display. The time between recording and display must be as short as possible. They made satisfactory progress as far as the mechanical aspects of the system were concerned, but became stymied in the photopolymerization process. They could accomplish the initiation of the photopolymerization events which produces the image, but they lacked a means of stopping the process at the proper time. It was at this point that the basic research results of Dr. Margerum's work came to the rescue. This work involved the discovery that the ultraviolet photochemical formation of aci-anions in the monomer-dye-catlyst solutions could be used to decolorize the dyes and inhibit the photopolymerization. This was the inhibitor they needed to stop the processing in their photopolymerization system. Figure 1 demonstrates diagrammatically how the system works.

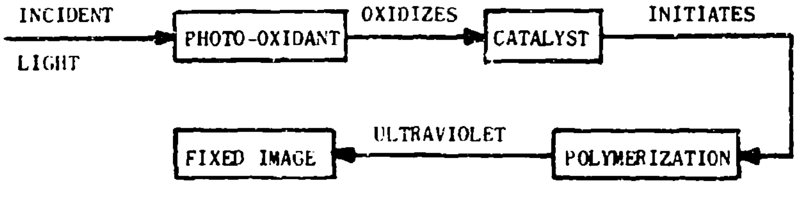


Fig. 1.

To start the chain of polymerization events, light raises the dye molecules to an excited state, thereby producing a stronger oxidizing agent than in the ground state. This species oxidizes the catalyst to a free radical polymerization of barium acrylate. The newly formed polymer precipitates as colloidal particles that scatter light, producing an image. UV light in the manner mentioned above, deactivates the unexposed solution with the help of a second photochemical system, thereby fixing the image.

Hughes has now developed the foregoing system to the extent that they can take a picture, complete the photopolymerization process, and project the image in less than a half second.

These photopolymer systems have many potential military applications, such as in tactical display systems, large screen display systems, synthetic array radar processing, rapid data storage and readout process. Future applications might also include their use as intermediate recording media for scanning cw lasers in display systems. Also it could be used as a pulsed laser, holographic recording medium with immediate display of optically fixed holograms. (See cover).

It is quite pertinent to point out that the foregoing accomplishments might not have been achieved if it had not been for certain fundamental research that was "sparked" by AFOSR support over twelve years ago. This was the work of Dr. Oster at Brooklyn Polytechnic Institute and of Technical Operations, Inc., in which was initiated some of the original basic research on the acrylic monomer and on the photosensitive dyes that initiate the reaction.

References:

"Acid-Base Characteristics of Photochromism," Final Technical Report, Contract AF 49(638)-1264, AFOSR 68-0345, AD 665 426.

"Photopolymerization Systems Come of Age," Chemical and Engineering News, 46, No. 10, 46 (March 4, 1968).

"Hologram Recording on Photopolymer Materials," D. H. Close, A. D. Jacobson, J. D. Margerum, R. G. Brault, and F. J. McClung, submitted to Applied Physics Letters.

OSCILLATING DETECTION

Absorption spectroscopy often involves trying to measure weak absorptions of a medium by detecting small changes in the intensity of the components of the irradiating light. In addition, the signal generated by the detector when exposed to the light from the spectrograph exhibits small fluctuations with time, which is commonly known as instrument noise. These fluctuations will be dutifully recorded by the recorder. Therefore, if the absorption signals in the spectral curve are only as large in magnitude as the fluctuations characteristic of noise, then this method of detection is not capable of accurately measuring such weak absorptions. A more sensitive detector must be used.

Professor G. W. Robinson and his group at the California Institute of Technology, under AFOSR sponsorship, have overcome this problem to some extent by developing a frequency modulated spectrometer capable of detecting extremely weak absorptions. To better understand how they have been able to add more sensitivity to the detection system, it will help to describe what happens to light upon entering a typical spectrograph. An illustration is shown in Figure 1.

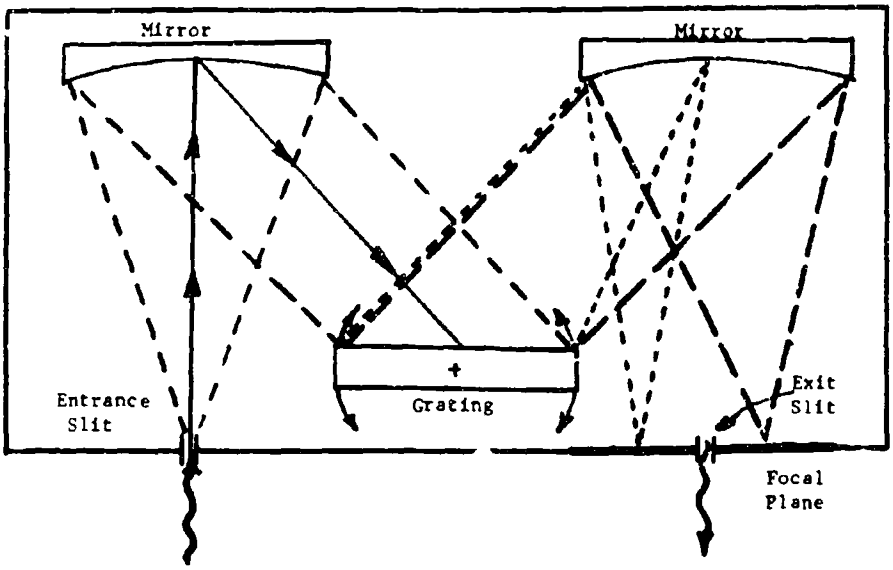


Fig. 1. A diagram of the optics within a spectrograph.

Light diverges from the entrance slit and is reflected by the left mirror into the grating, at which point the components of the light are diffracted into different directions, the direction depending upon the wavelength of each component. The end result is that different wavelengths of light finally converge at different points in the focal plane preceding the exit slit. The only light that emerges from the exit slit is the component that converges directly in front of the slit.

Suppose, however, instead of an exit slit, a detector with the same dimensions, i. e., 5 to 500 microns wide and 0.5 cm high, is positioned where the exit slit should be (see Fig. 2). The same absorption spectrum would be obtained, since the rotation of the grating would sweep the different components of light across the face of the detector, which in turn would record the intensity for each component wavelength.

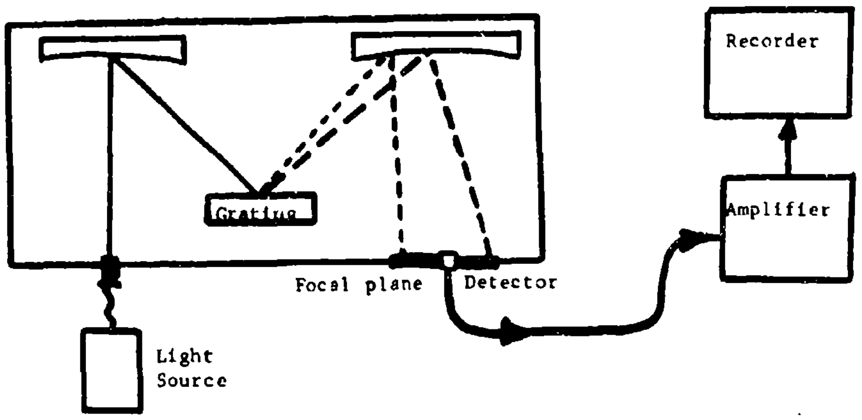


Fig. . A spectrograph with a detector situated in the position of an exit slit.

Now consider what the signal from the detector will be if the detector is moved back and forth in the focal plane of the spectrograph with harmonic motion, as in a pendulum. To aid in understanding what happens, consider the absorption curve drawn in Fig. 3a.

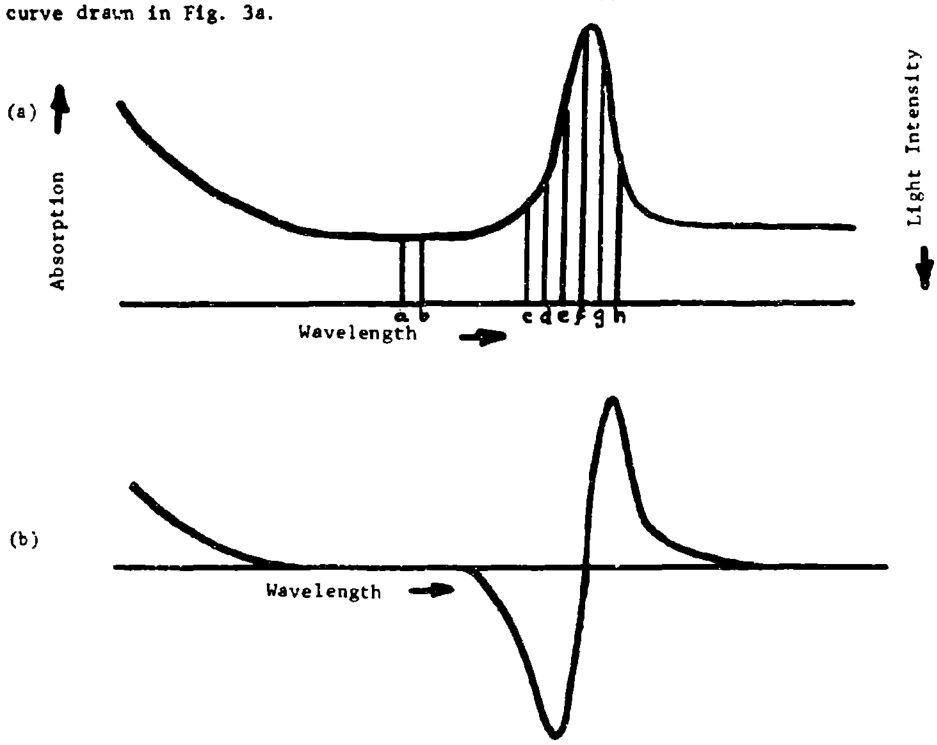


Fig. 3. An arbitrary absorption curve; The same absorption curve as observed by an oscillating detector and lock-in amplifier.

As described above, this pattern would be recorded if the detector was stationary and the grating was rotated, sweeping the component wavelengths before the detector. The same pattern could be recorded if the grating was moved across the focal plane, measuring the intensity as it swept through the point of convergence of each component wavelength. With this in mind, suppose the detector oscillates in the focal plane. Between the points corresponding to wavelengths a and b in the spectrum, the detector does not see any change in intensity of the light. However, the signal at c is greater than at d (the intensity of light at c is greater, meaning that the absorption of light at c is less), so that oscillations between wavelengths c and d will produce a corresponding oscillation in the detection signal. For oscillation between wavelengths d and e, the change in signal is even more noticeable. The maximum variation in the signal is observed when the detector is oscillating between the points in the focal plane corresponding to the wavelengths e and f. Then as the oscillations move to a position between f and g, the change in signal reduces to zero. Progressing further along the absorption curve, the changes in the signal with oscillation of the detector are described as above, but now with a change in sign, i. e., as the detector sweeps from left to right (from g to h), the detector signal increases rather than decreases, as occurs above for a similar sweep of the detector.

If there existed an amplifier that was sensitive to and could measure the magnitude and sign of the change in detector signal over the range of each oscillation, then the absorption pattern for the curve illustrated in Fig. 3(a) would appear as a lock-in amplifier (equipped with rectifier filters and phase-sensitive detection).

For whatever oscillation frequency characterizes the harmonic motion of the detector back and forth in the focal plane, the same frequency is associated with the alternating signal that is produced at the detector and transmitted to the amplifier. If the lock-in amplifier is tuned to this particular frequency, much like a radio tuned to the frequency of a radio station, then only the alternating signal that oscillates at this frequency is received and amplified by the amplifier. Other signals that exhibit a different frequency or exhibit no oscillating behavior at all, such as stray light picked up by the detector or instrument noise, are filtered out by the amplifier and are not amplified. Herein lies the advantage of such a detection technique. Observation of weak absorptions with this technique results in an amplified absorption signal while the instrument noise of the system is suppressed. A measurement with considerable sensitivity of weak absorption properties of materials is thereby provided.

Drs. Kohler and Dubin of the Caltech group have checked out the instrument on a series of solutions and have detected optical densities in the neighborhood of 0.002 with a signal-to-noise ratio of 50:1. These results indicate indicate that it may be possible to detect optical densities as low as 10^{-6}.

In addition to the increased sensitivity of this development, the unique feature exists in the fact that the detector moves. There are several advantages to having the detector move: the variable amplitude of the instrument is easily achieved, the frequency of modulation may be varied to optimize the system for any desired signals, and the need for an exit slit is elminated.

This instrument, due to its reduction in weight by eliminating the rotating section and motor, has the potential of being useful as an ultralightweight satellite spectroscope. A patent application is being processed.

CHEMICAL STRUCTURE AND PROPERTIES

By Dr. William L. Ruigh

This section spans that area of chemistry from the sub-microscopic arrangement of electrons in the various energy states of an atom to the visible phase differences in an alloy. It ranges from an analysis of the trace composition of transistor materials measured in parts per billion to the effects of grain size and shape on the strength of metals. The central core of this area is the structural arrangement of atoms and molecules in space as gases, liquids, glasses or solids and crystals. It includes also the effect of such structures and changes in structure in the properties of the substances or materials. A knowledge of the nature of bonds between atoms and molecules and their arrangement in space is an essential part of this section. Although the emphasis is on static configurations, the effect of structure on the kinetics and dynamics of structural change and the effect of structural changes on the properties of materials are essential theoretical elements in our knowledge.

The relevance of this basic factual and theoretical knowledge to the mission of the Air Force lies in constant and never ending requirements for new and improved materials to meet the extreme demands of the assigned Air Force missions.

THE RELEVANCE OF BASIC POLYMER RESEARCH TO THE AIR FORCE

The study of molecular configuration is the core of the present limited AFOSR polymer program. It is appropriate to provide a historical review of this program particularly in view of recent spectacular developments on high strength graphite fibers in Britain. The structural properties of these fibers depend upon the molecular configuration of the starting polymer which is subsequently graphitized by heat.

In the annual Chemistry Program Review for FY65 there appeared a review of the SRC Polymer Program by Drs. Amos G. Horney and Anthony J. Matuszko. In this article were described the research of Dr. Paul J. Flory on the spatial configuration of chain molecules, Dr. Peter Debye on Molecular Interactions of Polymers as measured by visible light and x-ray scattering, and, finally, Dr. Richard Stein on crystal orientation and structure and change induced in polymers as induced by stress observed by the "dynamic birefringence" of the polymer film.

For FY 1966 Dr. Matuszko reviewed the work of Dr. D. J. Cram on the asymmetric induction of stereospecific polymers and that of Dr. Frank Mayo on mild oxidations common to hydrocarbon chain polymers. A grant to Dr. A. V. Tobolsky which expired in FY 1966 was not reviewed but resulted in a number of papers on the mechanism of both radical and ionic polymerization, a general treatment of equilibrium copolymerization, and the structure and transitions of helical macromolecules in the solid state.

It may be noted that the main emphasis of this limited AFOSR program in macromolecules has been on the physical chemistry of polymers with some additional work on the more theoretical aspects of certain reaction mechanisms and catalysts useful in polymer synthesis. Only one effort has been directed at the synthesis of a specific polymer system since, historically the Polymer Branch of the Materials Laboratory at Wright-Patterson Air Force Base, Ohio, has had primary responsibility for an in-house and contractual program aimed at synthesis of new and improved organic and inorganic polymers designed to meet the extreme requirements of the Air Force. With pressing day to day demands for these new materials less emphasis could be directed at long-term fundamental efforts, particularily in the area of the physical chemistry of polymers.

The Directorate of Chemical Sciences from its inception has directed its efforts to fill this need of the Air Force for long term basic research in the stereochemistry and physical chemistry of macromolecules. By fortunate circumstances, the world's foremost authority in this area, Dr. Paul J. Flory, then at Cornell University, was selected by Dr. Horney as the first chairman of the AFOSR Chemistry Review Panel and he continued with the panel for its first seven years. With Dr. Flory's advice a strong basic program was built up in this area.

The rising costs of research and the budgetary plateau of the SRC budget has resulted in a substantial cut back in this limited program and since the FY 65 review only one new effort has been added. In FY 68, Dr. F. Karasz, formerly of General Electric and now at the University of Massachusetts, was given a grant to continue his research on the calorimetry and thermodynamics of organic polymers. This new effort and the single large one under Prof. Flory at Stanford constitute the entire AFOSR program.

The single effort retained is, however, a shining jewel in the SRC crown. The project at Stanford University is directed by Dr. Flory and was funded by AFOSR for the first time in October 1961. Dr. Flory's program has been immensely productive and on his latest grant period from February 1964 to October 1968 has had fifty-three papers published in major journals. Each paper is a significant accomplishment but, in view of the lengthy recent review in a previous issue, it will be sufficient to state that this work on the physical chemistry of polymers can be subdivided into two main areas: first the structure and stereochemical configurations of polymeric chains and, second, the thermodynamic treatment of the equilibrium properties of solutions.

The practical importance of a theoretical basic knowledge of polymer configuration on the explanation and prediction of polymer properties is illustrated in the title of a lecture given by Dr. Flory at the occasion of the Goodyear Medal Address at Cleveland in April 1968. The title was "Molecular Interpretation of Rubber Elasticity." Dr. Flory's contributions are well known in this area. He has just been awarded the Peter Debye Award in Physical Chemistry based on his work on macromolecules.

Knowledge of the molecular configuration of polymers has led to one of the most spectacular achievements in the aviation industry in recent years. As noted above this is the development of a very high strength graphite fibre from the carbonization of certain specially configured organic polymers by the Royal Aircraft Establishment, at Farnsworth, England, and the Rolls Royce Company and two other British companies.

At present great secrecy surrounds the production processes for the "Hyfil" graphite fibres now being produced by the three British companies for the preparation of composite materials. It is suspected the present most favored starting polymer is a specially processed polyacrylonitrile. It is known that the molecular conformation of the original polymer has a great influence on the subsequent strength and properties of the final carbon fiber.

The Rolls Royce success with composite graphite fibre compressor blades has enabled the company to design jet engines such as the RB168 for vertical take off experimental planes and the RB211 engine for the Lockheed L-1011 "Air bus." An early problem with the composite blades was ingestion damage in tropical rainstorms. Eltis, the Rolls Royce director of engineering, claims the present nickel plated "Hyfil" compressor blade has overcome these difficulties and will resist the impact of a four pound bird.

Although the present "Hyfil" costs are high, the British have a large program on the engineering and structural use of the carbon composites from application in satellite materials to the fabrication of composite honeycomb air wing panels. A series of articles in "Aviation Week" in October 1968 discussed these recent developments both here and in England.

Although the details remain largely secret still, it is certain that a basic knowledge of the molecular configuration of polymers and their modification by physical treatment has contributed greatly to this break-through in materials. Much of this basic knowledge of polymer structure and configuration is due to the universally acknowledged research contributions of Dr. Flory in this field.

PULSED LINEAR ACCELERATOR USED IN NEUTRON DIFFRACTION
(Prepared by LtCol L. D. Whipple)

Air Force men and systems are operating in increasingly extreme environmental conditions. It is necessary to provide scientific data acquired in these extreme conditions to understand the structural and related property changes that occur and to develop new materials capable of withstanding these extreme conditions of pressure, temperature, radioactivity, and toxicity.

Dr. J. S. Kasper of the General Electric Research and Development Center, Schenectady, New York, under sponsorship of the Directorate of Chemical Sciences, AFOSR, is conducting a program directed toward structural characterization of various materials produced by high pressure and toward identification of changes with pressure in the structural characteristics of some materials that do not undergo phase transitions under pressure. He is using both x-ray and neutron diffraction techniques in these studies. One of the significant accomplishments has been the development of a new neutron diffraction technique using a pulsed linear accelerator. The use of neutrons in diffraction studies provides the potential of investigating a greater variety of materials than is possible with x-rays. For example there is less absorption by heavy elements. There is the capability of locating hydrogen atoms. In addition there is the capability of locating other light elements such as B, C, N, and O in the presence of heavy elements. Of specific interest in Dr. Kasper's studies, neutron diffraction can be used to distinguish between neighboring elements in the periodic table. For example, the scattering power of x-rays is insufficient to determine specific site occupancy of the different atoms in InSb. Also, direct determination of magnetic structure is possible using neutron diffraction techniques.

As with x-ray diffraction, the use of neutron diffraction for work at conditions of extreme environments such as high pressure, high temperature, high radioactivity or high toxicity is restricted because of limitations imposed by the necessity for large amounts of shielding or heavy structural materials surrounding the specimen. These limitations are not as severe for the new method for obtaining neutron diffraction patterns from polycrystalline specimens developed by Dr. Kasper in conjunction with Mr. M. J. Moore of the General Electric Research and Development Center and Dr. J. H. Menzel of Rensselaer Polytechnic Institute.

The new method has the potential of being less expensive, faster, and less complex in comparison with other neutron diffraction techniques. The equipment includes a pulsed linear accelerator (LINAC) for a neutron source and a time-of-flight (TOF) detection system. Although the TOF system has been used previously, this is the first application in conjunction with a LINAC. Also, there has been no reported previous use of accelerator neutron sources in neutron diffraction studies of polycrystalline specimens.

Using the pulsing characteristic of the LINAC eliminates the need for an elaborate, expensive ($50,000 to $60,000) chopper which is required when a steady state reactor is used as a neutron source. In addition, the use of a chopper results in a relatively high loss of neutron flux. Thus, without the chopper the new method has the potential of being a faster technique for obtaining diffraction patterns.

The new method also uses a fixed detector instead of a moving detector. This simplifies the construction of the specimen container and thus reduces the limitations imposed by the extreme environment requirements for heavy shielding and structural materials around the specimen.

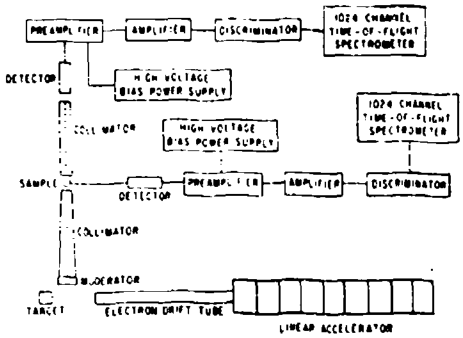


Fig. 1 Block diagram of the pulsed LINAC neutron diffraction system

Figure 1 is a block diagram of the LINAC diffraction system used. The LINAC electron pulse is impinged upon a water cooled tantalum target which produces a very high flux of gamma rays. A (γ, n) reaction in the target gives high energy neutrons with an isotropic distribution. The moderator covers as large a solid angle as possible, assuming the target is a point source of electrons. A 70 inch long collimator directs the beam of neutrons from the moderator on to the cylinder containing the sample. The cylinder was shielded by a can of B_4C with three small ports: one for the entering beam. one for the diffracted beam and one for the beam monitor detector. The diffracted beam detectors were at 90° to the incident beam. The detector counters were placed at an angle so as to intercept the largest possible arc of the diffraction one. The entire sample-detector system was contained in a block house with 24 inch thick concrete walls.

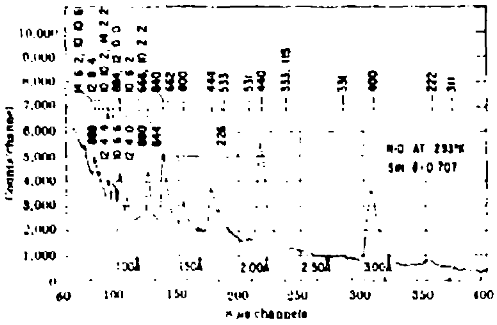


Fig. 2. The raw data for NiO which were collected furing a 4 h LINAC run, plotted as counts/channel against 8 μs channels.

Initial experimentation using a NiO specimen resulted in a satisfactory diffraction pattern obtained in 4 hours with the main features of the pattern discernible in the first two minutes of operation. This indicates that the flux of usable neutrons was relatively high. The LINAC operating conditions were: 45meV electron energy, 500μA average current, 235 pulses/s repetition rate and 4.5μs electron pulse width. The average power of the electron beam hitting the target was 22,500W. The raw data collected during the 4 hour run are shown in Figure 2. The accuracy of the determination of interplanar spacings (d values) and the lattice parameter is limited by the accuracy of the measurement of the flight path. The measurements of d were checked for internal consistency with the result that an accuracy of 0.3% was indicated for lattice parameter determinations. This is a modest degree of accuracy but adequate for indexing most structures that are not of great complexity.

This first short experiment demonstrates that it is possible to do neutron diffraction studies with a pulsed LINAC and that this method is an attractive alternative to more conventional methods. Dr. Kasper's previous work in elucidating the polymorphic forms of boron are of particular significance to the Air Force because of current interest in boron and graphite reinforced composite materials. Development and use of new techniques such as the pulsed LINAC neutron diffraction method will greatly enhance the fundamental knowledge of the structure of compounds containing light elements such as boron and carbon.

Reference:

"Pulsed LINAC Neutrons Diffraction," M. J. Moore, J. S. Kasper, and J. H. Menzel, Nature, 219, 849 (1968).

CHEMICAL ENERGETICS

By Dr. Donald L. Ball

The category chemical energetics encompasses studies of the rates, mechanisms, and equilibria of chemical reactions. Of interest, therefore, are microscopic as well as macroscopic processes. Emphasis is placed on detailed descriptions of the transfer and redistribution of energy accompanying all the component reaction steps leading to overall chemical change. Analysis is made in terms of the various states of molecular and/or atomic excitation (translational, vibronic, rotational, and electronic) and the alterations produced by radiative processes, collisions and other non-radiative processes.

It is convenient to subdivide the subject of energetics into three smaller units. Principally macroscopic processes are included as Thermodynamics. Emphasis is given to calorimetric determinations of bond energies and measurement of activity coefficients and equilibrium constants by assorted methods. Two categories of kinetic investigations emphasize microscopic processes; these are entitled Photochemistry, Radiation Chemistry, and Sonochemistry and Thermal Reactions and Molecular Collision Dynamics. The latter includes specialized investigations of high speed kinetics, catalysis, molecular beams, and shock waves. Some overlap is unavoidable between the content of the two kinetic categories.

Researches in chemical energetics find applications in energy conversion devices, novel photographic processes, radiation damage control, and improved utilization of fuels, propellants, and explosives. Also of interest are the chemical reactions characteristic of the upper atmosphere; the energetic, though dilute, species present interact significantly with rocket exhausts as well as the surfaces of space vehicles.

In the pages to follow, three kinetic investigations have been selected to illustrate the content of this project area. Although in each case the approach is different, a similarity in objectives may be seen. Each seeks to unravel the details of microscopic chemical events.

CHEMILUMINESCENCE - FLAMES AND AIRGLOWS

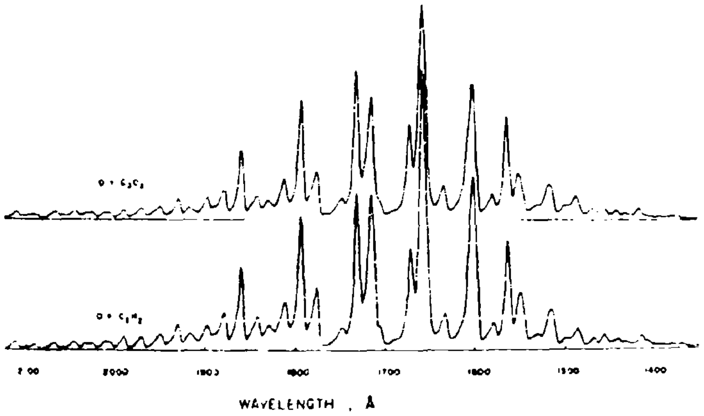
The chemical process of combustion is accomplished by a complex sequence of competitive and consecutive individual chemical reactions. Unscrambling even part of this totality of events, and identifying individual steps in the overall process, is a difficult task. It is, however, a necessary one in order to understand and optimally control and utilize the processes involved. One leader in efforts to derive order from this chaos is Professor K. D. Bayes, University of California, Los Angeles. Reaction intermediates have been identified by the characteristic, observable frequencies of light emitted by flame reactions--in other words, by chemiluminescence. Relevance to the Air Force mission includes the obvious contributions of these studies to propulsion and also the detection of rocket vehicles through the characteristic chemiluminescence of the exhaust. However, an unusual and unpredicted application of Professor Bayes basic research has been found in the interpretation of a phenomenon recently observed in the atmosphere of Venus. A reasonable chemical basis has been provided for the origin of the night airglow observed by the U. S. space probe Mariner V. The connection between these two widely separated sets of events will be revealed in the remarks to follow.

Professor Bayes has observed notably similar patterns of chemiluminescence (in the vacuum ultraviolet) to accompany the reactions of atomic oxygen with a variety of reducing agents (or fuels). The latter include acetylene, carbon suboxide (C_3O_2), ketene, 2-butyne, and propadiene. It is natural to conjecture that the same source reaction step was responsible in all instances for light energy emitted. The chemical species involved could not be hydrocarbon molecules or radicals since in one case (C_3O_2) no hydrogen was present.[1] The most reasonable choice, based on the analysis of the bond energies available, has proven to be

$$O + C_2O \rightarrow CO\ (\text{excited}) + CO\ (\text{ground state})$$

$$CO\ (\text{excited}) \rightarrow CO\ (\text{ground state}) + h\nu$$

The energy available in the electronically excited CO molecule, which is converted to the emitted light, is reasonably expected to add up to the required amount (about 9 electron volts). The species C_2O is known to occur in similar flames. Quantum mechanical calculations by Professor Bayes have revealed the stability of this radical, predicted a linear configuration (C-C-O), and indicated the special electronic character of the ground state and low lying excited states.[2] The occurrence of several of the latter excited states is responsible for the observed band of emitted frequencies instead of just a single one. In the Figure the observed ultraviolet emission for both the oxygen/carbon suboxide and the oxygen/acetylene flames are compared. They are revealed to be, indeed, remarkably similar.



A similar ultraviolet emission was observed as well by instruments aboard Mariner V during its fly-by of Venus.[3] Just before passing across the dark limb of the Venus atmosphere, u. v. probes noted a signal within the wavelength region 1350 to 2200 Angstroms. Since the Venus atmosphere is mostly CO_2, small amounts of atomic oxygen and C_2O are expected in the upper levels of the atmosphere due to electron and ion bombardment of CO_2, as well as photodissociation during the day. It is known that the irradiation of both CO and CO_2 produces carbon suboxide polymer $(C_3O_2)_n$, almost certainly via the C_2O radical. Based on this analysis, Professor Bayes has concluded that the same reaction cited above (postulated for atomic oxygen flames) is probably responsible for the Venus airglow. Further evaluation of this interpretation is hoped for in future, more detailed observations in space.

References:

1. "The CO Chemiluminescence from Flames," K. H. Becker and K. D. Bayes, J. Chem. Phys., 48, 653 (1968).

2. "The Photolysis of Carbon Suboxide. II Effect of Added Oxygen," J Am. Chem. Soc., 85, 1730 (1963).

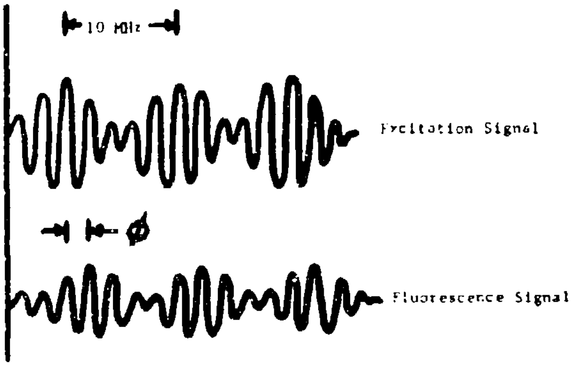
3. "Ultraviolet Emissions Observed near Venus from Mariner V," Barth, earce, Kelly, Wallace, and Fastie, Science, 158, 1675 (29 Dec 1967).

LIFETIME SPECTROMETRY AND MOLECULAR COLLISIONS

In the present section our attention will be transferred from luminescence to fluorescence. Specifically we will consider measurements of fluorescent lifetimes -- the time delay between absorption and emission of a photon by a molecule. A remarkable amount of quantitative information on complex inter- and intramolecular energy transfer processes is being gleaned in this manner in the laboratory of Prof. Edward W. Schlag, Northwestern University. Prof. Schlag has at his disposal what he calls a laboratory clock for the direct timing of collisional processes. In the remarks to follow, his remarkably sensitive and fruitful technique will be outlined and the relation demonstrated between measured fluorescence and molecular collisions, radiative and non-radiative processes.

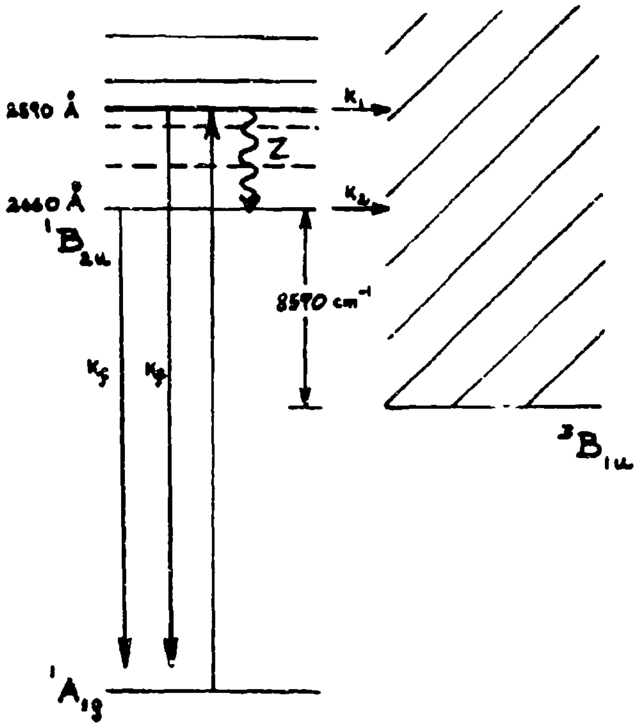
Thus far data have been provided for two systems. The first was β-naphthylamine dispersed in propylene as a heat bath; the second was pure benzene. Direct timing of fluorescence was performed with a phase fluorimeter. This instrument measures the phase lag of a fluorescent signal relative to an intensity modulated light beam. The appropriate wave length of light as well as the appropriate modulation frequency (ω) is dependent on the chemical system under study. With benzene the former was 2600 Å; the latter 10 MHz (megahertz or 10^6 cycles per second). The phase angle is the times observable which relates, via a mechanism, back to the microscopic rate constants involved. A rationale will be given now to demonstrate the connection. More detailed descriptions are available elsewhere (J. Chem. Phys. 47, 1860 (1967); Proceedings of the International Conference on Molecular Luminescence, Loyola University, Chicago, Aug 20-23, 1968, Benjamin, In Press).

In a very schematic way the experimental observation is given below.



The modulated input (or excitation) signal is compared with the output or fluorescence signal. The latter is shown displaced slightly relative to the former; this is the phase shift ϕ. There is, in other words, an observable quantity which can be quantitatively related to the very brief time delay between photon absorption and photon emission.

The relevant energy levels for benzene are given in the illustration below:



For the excited singlet labeled $^1B_{2u}$ the vibrational "fine structure" (or manifold) is indicated. The absorption of the excitation radiation (2600Å) by the ground state ($^1A_{1g}$) provides a molecule excited vibrationally as well as electronically. This is a conseequence of what is referred to as the Franck-Condon Principle. The nuclei retain essentially the same relative positions and momenta before and after the very rapid electronic excitation. These values afterwards are appropriate for an excited vibronic state whereas they were appropriate for a vibronic ground state before. The various quantized vibrational levels contribute the so called manifold. In the case of benzene, however, only two levels will be considered here.

Having described the diagram somewhat, let us consider now what can happen to a molecule after being pumped into the top vibronic level (indicated at 2590Å). A probable occurance, except at very low pressure, is relaxation to the ground vibronic level as the result of molecular collision. This event is labeled on the figure with "Z," the collision frequency. Another possibility is the radiationless inter-system crossing--(to the triplet* state $^3B_{1u}$ labelled k_1 for the excited vibronic state, k_2 for the ground state. These k's are, in fact, the associated rate constants. There is also the possibility of fracture of a molecule into simpler ones. This possibility is the subject of the next section on recent researches of B. S. Rabinovitch, but it will not be considered further at present. The final possible event is the observable one in the research of Prof. Schlag. It is a radiative fluorescence with a rate constant k_f, shown for each of two states in the figure. The observed phase shift (with the phase fluorimeter) is the composite result of all these possibilities.

We can consider the observed fluorescence intensity to be proportional to the actual concentration of molecules in the excited singlet $^1B_{2u}$. Therefore, the peak intensity -- defining the shift in phase ϕ relative to the excitation intensity peak--occurs when the density of states is highest. Following the initiation of each modulated pulse of excitation energy the density of molecules $^1B_{2u}$ can begin to rise. It must be remembered, however, that the state $^1B_{2u}$ is simultaneously depleted due to the factors mentioned above. The rate at which depletion occurs, as far as present interests are concerned, is determined by $k_1 + k_f$.

Because of the sensitivity of technique, ϕ can be determined in the "collisionless" region of pressure. Here, of course, the intensity of fluorescence is also the smallest. In this region, where the pressure is effectively zero, $\cot\phi = (k_f + k_1)/\omega$. In this pressure region the lifetime (defined by $k_f + k_1$) is that of the vibronically excited molecule formed directly on excitation. Vibrational relaxation had not time to occur. In the high pressure limit, the lifetime is that of the vibronic ground state ($k_f + k_2$). Here the expression for $\cot\phi$ is more complicated.

Because benzene is not an efficient absorber, the original phase fluorimeter (used with β-naphthylamine) was adequate for only preliminary observations. A new, improved model is now in process of construction. It was demonstrated, however, that it was possible to observe a lifetime from benzene when it is populated with 2600 Å radiation, the first strong absorption line in the spectrum. From the pressure dependence, high and low pressure lifetimes were obtained by extrapolation. The extrapolated high pressure value of 80 nsec. (10^{-9} sec = 1 nanosecond) represents the lifetime of the vibrationless ground state of the $^1B_{2u}$ manifold. The low pressure value of 1.3 nsec. is obtained with less precision due to high scattered light; additional work is in progress. The ground state lifetime is in good agreement with the observed quantum yield for this state.

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*For an excellent summary of the nature of the triplet state, the reader is referred to a recent paper by another AFOSR investigator, Prof. N. J. Turro (J. Chem. Ed., 46, 2 (1969)). The brief definition provided is -- "A triplet is a paramagnetic even-electron species which possesses three distinct but energetically similar electronic states as a result of the magnetic interaction of two unpaired electron spins."

It might be pointed out that the observed lifetimes, at low and high pressure, τ_1 and τ_2, are the reciprocals of $(k_1 + k_f)$ and $(k_2 + k_f)$, respectively. Since it is reasonable to assume that k_f is about the same in both cases, the decrease in lifetime at high energy is due to the increased probability intersystem crossing to the triplet $^3B_{1u}$. It is noteworthy that the entire subject of probabilities and rates for radiationless transition is the subject of present theoretical and experimental efforts by another AFOSR sponsored investigator, Prof. Stuart A. Rice of the University of Chicago.

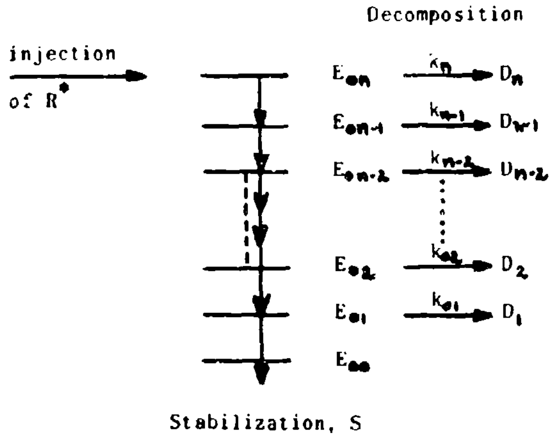
The present section will be appropriately closed by summarizing Prof. Schlag's overall objectives, as he gave them in a recent renewal proposal to AFOSR. Progress in their attainment has been given above.

> "Information in this collisionless region gives direct measurements for rates of intersystems crossings, unimolecular decomposition and fluorescence emission from molecular states defined by a monochromatic experiment. Once these processes are understood one can proceed to the second phase, which is the addition of small amounts of added gas to observe the absolute values obtained by comparison with a laboratory clock, hence one obtains unambiguous values for the inelastic collision cross-sections for large polyatomic molecules. This part of the work supplements other scattering studies, such as molecular beams, in which it is often difficult to study such large molecules, particularly for selected vibronic states."

COMPETITIVE CHEMICAL REACTION SPECTROSCOPY

The subject of molecular collisions and accompanying energy transfer is of explicit concern to Prof. B. S. Rabinovitch at the University of Washington, Seattle. He has described his interests as "the field of collisional deactivation of highly vibrationally excited polyatomic molecules; in short, the 'cooling' of hot molecules."

It is best to begin by outlining the subject briefly with a simplified diagram of excited vibronic states.



What is shown is effectively an "energy cascade," the details of which are our prime concern. Molecules, or radicals, are injected at the top of the diagram -- or the highest level of vibrational excitation -- by "chemical activation." Of course, a variety of other approaches to the top exist; photochemical activation is the example which comes first to mind. With chemical activation the energy level E_n is populated by the very act of producing the activated molecule directly by means of a chemical reaction.

What can happen next? Two possibilities must be considered. First, the molecule can collide with other molecules, transfer some energy, and, thus, fall down the cascade. The details of this process form the goal of the subject researches. In other words, how much energy is lost on the average per collision, $\langle \Delta E \rangle$, what is the probability, P_{ij} , of falling from state j to state i ? The other possibility is a unimolecule decomposition (or isomerization) of the species from each energy level which it occupies in turn. The rate constants for these processes are designated, k_j; the products of decomposition are D_j; and the associated threshold energy levels are E_{0j} . As long as a level equal to, or greater than E_{0j} is occupied, product D_j can form. Below E_{0j} it cannot. Ultimately stabilization occurs when the species falls below E_0, and, as shown in the diagram, stabilization occurs. The bottom of the cascade is reached.

A number of models exist to describe the details of the process by which activated molecules lose energy. With the strong collision model a single collision is enough for complete stabilization. This is certainly the easiest approach. However, with the simple "step-ladder" model, energy is lost in a series of equal steps. Multiple collisions are required for stabilization but the same amount of energy is lost with each. Reference to the energy diagram should reveal the rather obvious origin of this model's name. Extensions in theory consider the possibility of distributions in step sizes. The exponential model will be the last considered although still others could be given. In this case the assumption is made that collision encounter times, i.e., collision complex lifetimes, are randomly distributed and that the amount of energy transferred (or number of quanta) is directly proportional to the encounter time.

It is found in practice that different models of the process of energy transfer apply, depending on the nature of the 'hot' molecule as well as the nature of what it collides with (i.e., the bath molecule). This will be illustrated with a single example, the activated hexyl-3 radical.

Basing analysis on descriptions of the sort given above, Professor Rabinovitch has shown that the precise graphical relation of the product ratio $D_1 : D_2 \cdots D_n$ on collision frequency, ω , (or pressure) will reveal which model for energy transfer applies. High pressure data can be made to yield detailed information on transition probabilities, P_{ij} , and such information is independent of collision cross-section. The latter quantity is difficult to come by. The overall method, which is a significant innovation in experimental method, has been designated competitive chemical reaction spectroscopy (CCRS). Professor Rabinovitch admits the title to be, perhaps, somewhat flamboyant; it is nonetheless appropriately descriptive.

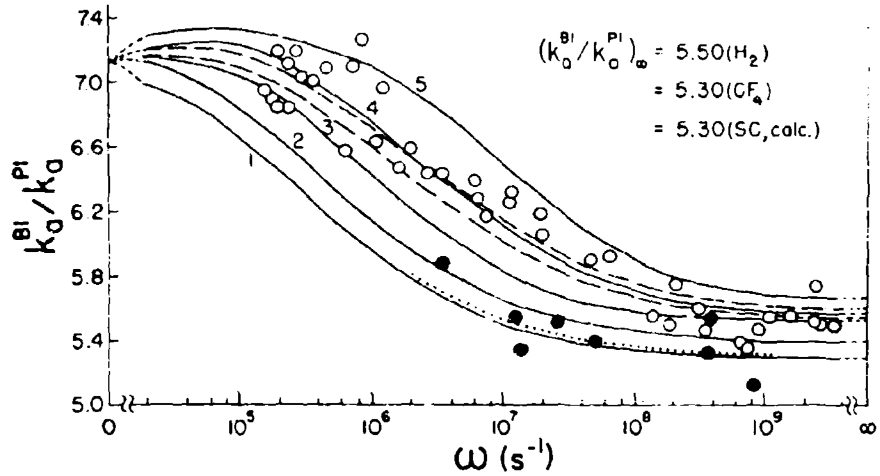
The most detailed application of CCRS has been with the hexyl-3 radical (Canadian Journal of Chemistry, 46,341 (1968)). This radical decomposes to two sets of products as shown below (in comparison with stabilization, S).

$$3\text{-}{}^{\bullet}C_6H_{13}^{*} \xrightarrow{\omega} 3\text{-}{}^{\bullet}C_6H_{13} \qquad S$$

$$\xrightarrow{k_a^{BI}} 1\text{-}C_4H_8 + {}^{\bullet}C_2H_5 \qquad D_b$$

$$\xrightarrow{k_a^{PI}} 1\text{-}C_5H_{10} + {}^{\bullet}CH_3 \qquad D_p$$

The plot which follows reveals the dependence of the rate ratio on collision frequency. Two bath molecules were used; the experimental points with hydrogen are given with open circles; those with 91%CF_4 + 9%H_2 are given by filled circles. The theoretical lines are numbered. Curve 1 is the strong collision model (SC); curves 2,3,4, and 5 represent the stepladder model (SL) with $\langle \Delta E \rangle$, in turn, 1500, 800, 400, and 200 cm^{-1}. The dotted curve is for a bath mixture which simulates the CF_4 system in composition and is 83% SC and 17% SL (400 cm^{-1}).



As was expected, the average rate ratios increase as the pressure and collision rate approaches zero. Also, in the limit of no collisions all of the models must give the same product ratio. At the other limit of $\omega = \infty$, the data can be fitted to a average value for the energy transferred per collision, $\langle \Delta E \rangle$, depending on the model. For the present system, the best fit for H_2 is $\langle \Delta E \rangle \cong \langle \Delta E \rangle \cong$ 1.2 kcal. ; for CF_4, $\langle \Delta E \rangle >$ 4.6 kcal. and the strong collision value, ($\gtrsim$ 10 kcal.) is approached.

The hexyl-3 system, however, is far from being the optimum one for study because only two reactions occur and the competitive critical thresholds for bond rupture, E_{01} and E_{02}, differ by only a few kcal.. The results with still other systems will reveal energy transfer processes in even more detail. Competitive chemical reaction spectroscopy is expected to advance significantly understanding of the microscopic events fundamental to overall chemical reactions.

THEORETICAL CHEMISTRY

by Dr. Donald L. Ball

Researches in this subject area possess as goals the explanation, correlation, and prediction of chemical behavior. Since the evolution of chemical science is based on the coupled advances of theory and experiment, theoretical chemistry is a vital component of all the program areas. It logically assists each of the other categories in their contributions to applied needs. However, direct use of theoretical analysis does occur in the evaluation of processes and materials for projected operations under conditions where experimental information is inadequate and difficult to obtain.

Program content includes major efforts in the quantum mechanical computation of chemical and physical properties. A balanced program is maintained incorporating ab initio ("from scratch") methods and semi-empirical methods. Although the former approach is perhaps more 'rigorous' (no experimental data is employed), it is restricted to comparatively small molecules. On the other hand, by including a very limited amount of experimental data, the latter approach can render tractable very complex molecular systems.

Other theoretical efforts seek to improve the capabilities of kinetic theory and statistical mechanics. Particular application is seen in furthering the understanding of the liquid state. Another important goal lies in unraveling the details of energy transfer processes. These processes are often of very short duration involving radiative and non-radiative processes. Here, advances in experimental techniques for rapid, detailed, and sensitive measurements have made more and more exacting challenges to theory. However, the converse has been true also.

For the purposes of the 14th Annual Chemistry Program Review, our attention will be limited to efforts in quantum chemistry. These efforts, each with unique viewpoints, will be described.

ORGANIC CHEMICAL PHYSICS

The present section will summarize the objectives and some recent results of a research program by Prof. Michael J. S. Dewar of the University of Texas. This AFOSR sponsored effort bears the title "Organic Chemical Physics." This term was selected because of the particular emphasis of the research, namely, the use of chemical techniques to develop the physical theory of organic molecules. In a remarkably diverse program, experimental as well as theoretical studies are included.

In preparation for a recent Air Force briefing on the nature of the research sponsored by the Directorate of Chemical Sciences, Prof. Dewar provided us with a succinct review of his efforts. The document contains at least some of the flavor of a truly remarkable research program. It is certainly worthy of consideration by a wider audience than was originally intended. However, it should be remembered that it was a specialized audience for which the words were chosen and emphasis was given to brevity. The words that follow are Prof. Dewar's.

"Our object is to devise some general quantum mechanical treatment of molecules, accurate enough to be of practical value to chemists. Such a treatment must be able to provide estimates of heats of formation and molecular geometries with "chemical" accuracy (± 1 kcal/mole, ± 0.02Å and must be applicable to molecules of all kinds (including transition states), and of reasonable size (at least 25 atoms). Prior to our work, such an endeavor would have seemed ridiculously optimistic, and indeed no one else seems as yet to have made any serious attempt in this direction; neverthless we seem to be well on the way to success. Of course any such treatment must inevitably be semi-empirical in nature; for a priori calculations of this degree of accuracy are as yet limited to the very simplest diatomic molecules (e.g. He_2^+ of LiH).

"Our first approach was based on the Hückel σ,π approximation and consequently limited to conjugated molecules; here the contributions of σ bonds to the total heat of atomization is written as a sum of bond energies and compression energies, while the π binding energy is calculated theoretically. Figure 1 shows a plot of the observed heats of formation of a number of conjugated and aromatic hydrocarbons, and heteroconjugated compounds of nitrogen and oxygen, against the calculated values; the line in the figure is the theoretical line of unit slope on which the points should in theory lie; as will be seen, they do, the deviations in all cases being less than the possible limits of experimental error in the thermochemical measurements. (In several cases, one dot on the slide represents two or more almost coincident points.) This procedure also gives very good estimates of bond lengths, and apparently even of force constants.

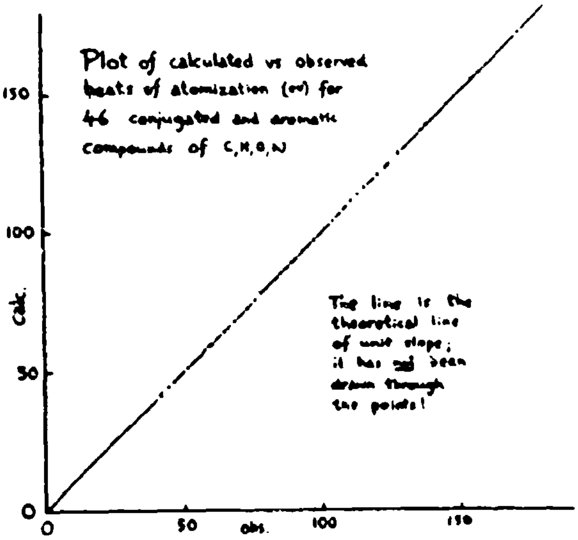


Fig. 1.

"The second approach is much more general; in this all the valence electrons are included, both σ and π. As yet we have not been able to get correct estimates of bond lengths; if, however, we assume standard geometries for molecules, we can usually calculate their heats of formation to within ± 3 kcal/mole. This is true for molecules of all kinds formed from carbon, hydrogen, nitrogen, and oxygen, even compounds containing small rings; our treatment thus accounts quantitatively for strain energies. Figure 2 illustrates these remarks. Here the deviations have been amplified twentyfold in comparison with Figure 1, by plotting standard heats of formation in kcal/mole rather than total bond energies in ev. The errors are more than one hundred times smaller than those given by other published treatments; indeed, the latter would lie so far off the line that they would not appear on the slide at all.

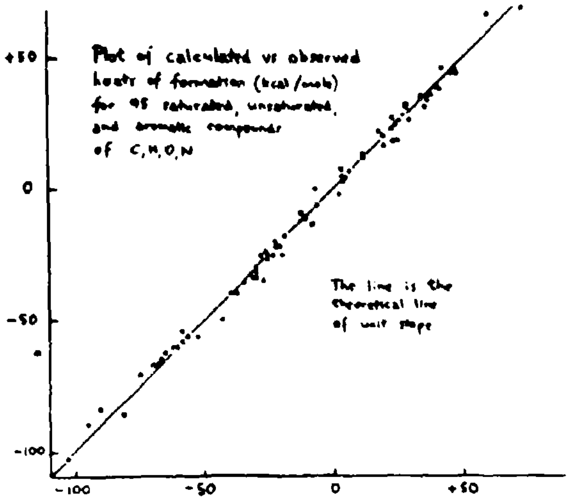


Fig. 2.

"Figure 3 illustrates another line on which we are working, the interpretation of nmr spectra. It seems that ^{19}F chemical shifts of conjugated fluorides are determined solely by the π electron distribution; by applying the Karplus-Das-Prosser-Goodman treatment of chemical shifts to our π calculations, we have been able to interpret nearly all the available data for fluoro derivatives of aromatic hydrocarbons and nitrogen heterocycles (including a number of new measurements of our own) in a very satisfactory manner. The only exceptions are sterically hindered fluorides, and compounds containing an excess of heteroatoms; our π treatment does not allow for steric effects, while in compounds of the latter type, σ contributions must be important. Although ^{19}F nmr is not of general importance, these results are significant in that previous theoretical treatments of chemical shifts have given very unsatisfactory results. We hope to extend our approach to more exciting nuclei, in particular ^{13}C, using our valence shell approach.

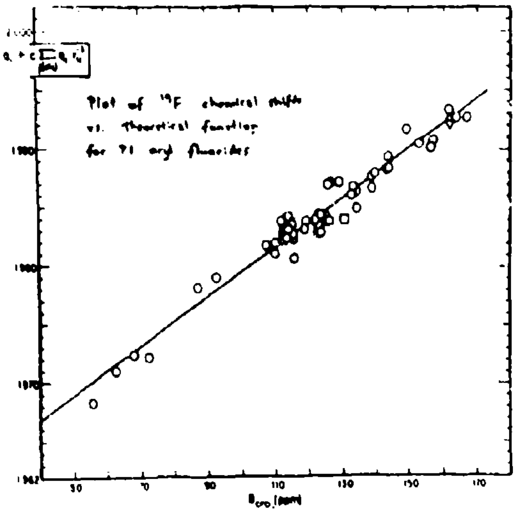


Fig.3.

"We therefore feel justified in hoping that we will before long have a solution to our problem; if so, theoretical chemistry would of course be revolutionized.

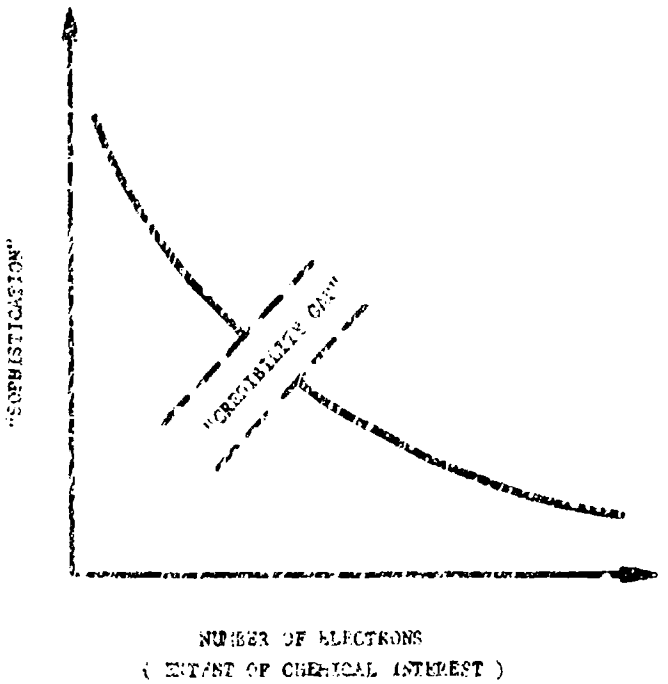
"One would be able to predict not only the geometries and heats of formation of molecules, but also the reactions they would undergo. Since moreover there seems no reason to believe that our approach cannot be generalized to cover other elements, the prospects seem very exciting."

BRIDGING THE CREDIBILITY GAP

Some reference has been made in the preceding to the main two approaches to quantum chemistry. These can be designated as *ab initio methods*, on the one hand, and *semi-empirical* methods on the other. By *ab initio* we mean "from scratch." Molecular properties are calculable -- at least in principal, but using a lot of computer time--without inclusion of adjustable parameters or even a hint of experimental information. The *ab initio* approach is necessarily restricted to relatively simple molecules. On the other hand, using a very limited amount of experimental information and a parametric approach, larger, more chemically interesting molecular systems may be considered. This is the *semi-empirical* method which in practice takes many forms. The mathematical *formalism is* rendered tractable because it is constrained to give the right answer for one molecular property and then used to calculate others.

The proponents of the two approaches have tended to cluster into two separate groups with less than optimum communication and interaction with one another. The situation has in fact been described graphically by Prof. J. A. Pople (J. Chem. Phys., 43, 5229 (1965)).

A sketch based on his ideas is given below.



The ordinate of the 'Pople Diagram" has been designated as a measure of "sophistication": the abscissa is the number of electrons in the system under study (or we might say the extent of chemical interest). The plot itself outlines the frontier of theoretical research over a broad front. It is regretted that, under this system, lack of sophistication is equated with greatest chemical interest. Fairer, but less colorful, terms may have to be found.

The namesof individual researches could be added at appropriate positions along the frontier. The important message, however, is the rather lamentable clustering of investigators into two points of view. The separation between these has been labeled the "credibility gap." Unfortunately, if left untended it seems to spontaneously grow larger.

There is a noteworthy theoretician under AFOSR support who keeps "a foot in each camp." His credentials are significant *ab initio* and *semi-empirical* researches. He is Prof. Leland C. Allen, Princeton University, who has made concerted efforts to bridge and, ultimately, reduce the gap between two points of view. Some of his more specific objectives, a bit of his philosophy, and some recent progress will be reviewed.

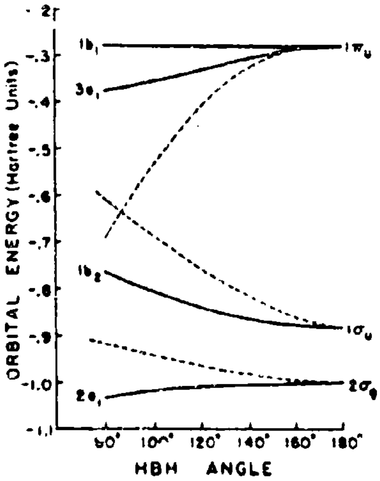
The basis for much of the significant impact of quantum theory on organic chemistry (i.e., large molecular systems) has been the three dimensional Huckel theory, which considers σ as well as π electrons. There have been, of course, modifications and extensions of this basic framework. It is at least basic in a historical sense and is workable only because of special assumptions. The most notable one is treatment of electrons as effectively independent. This obviously unrealistic assumption is the basis for much criticism of the Hückel Theory.

Prof. Allen prepared recently a review entitled "Why the Three Dimensional Hückel Theory Works and Where It Breaks Down." It was presented at Yale University recently at the Sigma Electron Symposium sponsored by Profs. K. Wiberg and O. Sinanoglu. Publication will follow in the conference proceedings.

Prof. Allen noted that strictly *ab initio* methods for constructing polyatomic electronic wave functions are still too time-consuming and size-limited to conquer problems in organic chemistry. He deemed this regrettable since, in his words, "greater overall unity can be brought to a chemical area when the theory has its direct origin in the basic laws of physics." However, since one cannot succeed in the problems of interest with direct use of *ab initio* theory, one has to be content with an indirect use. He sought, therefore, to identify the *ab initio* "underpinning" for the largely *ad hoc* three dimensional Hückel model. Specifically, the goal was to identify areas where the theory can be expected to succeed.

The inductive approach was to calculate a molecular property (for a large number of systems) by two means. The Hückel molecular orbital model was matched against a particular *ab initio* model. The latter was a linear combination of atomic orbitals molecular orbital (LCAO MO) approximation to the Hartree-Fock equations carried out via the Roothan scheme. By this choice, the input atomic orbital basis set, the output one-electron energies, and the definition of a one-electron molecular orbital could be made identical for both levels of theory.

The particular molecular property calculated was the "Walsh diagram," which displays graphically the functional dependence of molecular orbital energies on bond angle. These diagrams were first derived empirically from spectral data on ionization potentials and excitation energies. They have been useful in the past in elucidating and systemtizing many aspects of spectroscopy and inorganic chemistry. An example is given in the following figure.



Walsh's diagram for AH_2 species (dotted lines) and one-electron energies versus angle for BH_2^- (solid lines).

When valid, the Hückel Theory can generate a reasonably good Walsh diagram. By comparison to the more powerful *ab initio* method, when the Hückel Theory failed, the precise reasons could be identified. Very extensive *ab initio* calculations of Walsh diagrams have been made in Prof. Allen's laboratory. The molecules and ions considered contained three to eight atoms.

Further consideration will not be made of the details of the analysis. Instead, we must content ourselves with the main conclusions. The results by the Hückel method were found meaningful only when the charge distribution in the molecule was relatively uniform. The three dimensional Hückel Theory can give a good account of atomic orbital hybridization, molecular shape in ground and some excited states, and the ordering of molecular energy levels. The quality of the results is significantly better when a Hartree-Fock atomic orbital basis set is employed instead of the more usual single exponential set. In all cases the ability of the Hückel theory to represent adequately the true molecular charge distribution decreases as the electronegativity difference between adjacent atoms increases.

Prof. Allen has indeed made a significant contribution to relating the mathematical and physical bases of the *ab initio* approaches to the *semi-empirical* ones which are enjoying increasing success with large molecular systems. In so doing he has assisted the closing of the "credibility gap."

COMMUNICATIONS IN QUANTUM CHEMISTRY

(Section Prepared by LtCol R. T. Walford)

The field of quantum chemistry is closely related to quantum physics or quantum mechanics. By using quantum theory to ascribe wave-like properties to electrons chemists have gained new insights into the nature of matter. Some believe, hopefully, that quantum theory will eventually provide the unifying principle for the understanding of the whole of chemistry. This is the ultimate objective for research in this vital area of chemistry. AFOSR has a carefully selected group of investigators in this difficult, complex, way-out field of research. Their names will be found in the list of current research efforts. However, it is not our purpose in this article to further describe their important work but to discuss the communications problem in quantum chemistry and one effort at its solution.

In a recent article[1] Dr. Per-Olov Löwdin discussed the often-heard fallacy that quantum mechanics, with the help of sufficiently large electronic computers, should be able to completely replace experiments in physics and chemistry. In reality quantum mechanics is essentially the tool for handling the experimentally determined information about a given system. The theory should then produce the fundamental principles for understanding the system, once the system has been described by the proper experimental information. This is shown schematically by Figure 1., taken from Dr. Löwdin's article.

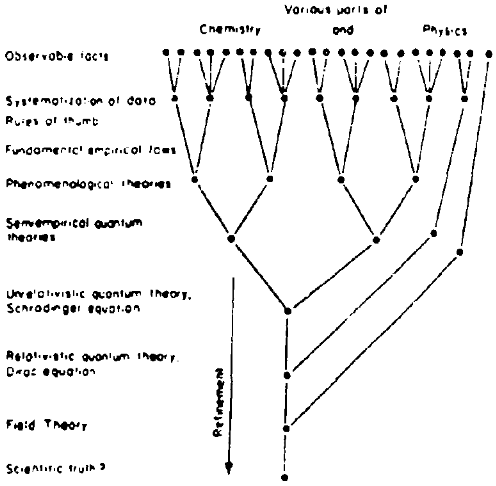


Figure 1. Schematic diagram of the hierarchy of theories concerning the structure of matter, showing the increase of correlated areas of observable facts with the refinement and deepening of the basic principles.

Unfortunately, quantum chemistry is more a conceptual framework than a nice set of mathematical laws. In advancing this area a horrendous effort must be spent on numerical analysis and numerical computation. The importance of electronic computers to the development of quantum chemistry cannot be over emphasized. Problems related to the electronic structure of atoms, molecules, and crystals lead to computations of a formidable order of magnitude. It is only after thorough numerical analysis and reduction that the present problems can even be treated by today's computers. Dr. Robert Mulliken, formerly an AFOSR investigator, addressed this problem in his recent acceptance speech[2] for the 1966 Nobel prize in chemistry.

> "I would like to emphasize strongly my belief that the era of computing chemists, when hundred if not thousands of chemists will go to the computing machine instead of the laboratory for increasingly many facets of chemical information, is already at hand. There is only one obstacle, namely, that someone must pay for the computing time. However, it seems clear that the provision of adequate funds by government and other organizations for computing molecular structures has at least as high an order of justification as the provision of adequate funds for the cyclotrons, bevatrons, and linear accelerators used in studying nuclear structure and high-energy particles, or for rockets to explore the moon, planets, and interplanetary space. Chemistry, together with the physics of solid matter on the earth, deals with the foundations of the material world on which all our life is built."

The Directorate of Chemical Sciences, AFOSR, is presently engaged in a key effort to alleviate the communications problem for chemists by its sponsorship of the Quantum Chemistry Program Exchange (QCPE). This program and its historical development under Dr. Harrison Shull at Indiana University may be explained as follows:

The efforts of scientists to understand the chemical properties of atoms and molecules from first principles, that is, based on quantum mechanical calculations is as old as quantum mechanics itself. Both efforts date from late 1920's. The high point of understanding in the pre-computer era was reached somewhere in the early 1930's with the work on the hydrogen-ion molecule and the hydrogen molecules. This work represented the upper limit of scientists with regard to doing calculations. This situation prevailed up through the mid 1950's.

In the later 1950's the first computers of any significance became available and with the advent of these computers the possibilities for doing meaningful calculations were also greatly increased. However, concomitant with this increase in possibilities was a requisite increase in investment of effort and manpower in the task of communicating with these computers. The traditional approaches which had dominated the pre-1958 period were of little value in the computer era. Problems had to be specifically formulated for the computer. As part of this formulation new techniques of numerical analysis had to be simultaneously developed. It was now necessary to code the problem to some form which the computer understood, i.e., the computer program, and finally the program had to be made error free - debugged - and certified as operational. All of this required time and money.

As the desire to understand larger systems from ab initio calculations became prevalent, it was not an uncommon practice for research groups to spend a year or more in the preparation of computer programs. It was immediately recognized by many workers in the field that in many cases duplicate efforts were taking place. It was also obvious that many groups were developing calculations that would be of distinct interest to many other groups. The early workers in this field wanted to utilize their resources, which were manpower, money and computer time, in an optimal fashion.

Toward this goal Dr. Harrison Shull of the Indiana University Department of Chemistry agreed to establish, at Indiana University, what is today known as the Quantum Chemistry Program Exchange (QCPE). Dr. Shull recognized that what was needed was a means of communication between workers in the field as well as a central point to where they could turn in order to obtain dependable computer programs.

In operation then, the QCPE relieves the investigators of many tedious hours of laborious work by providing tested computer programs upon request for a small handling fee. It serves as a central repository for these programs which are solicited from the contributing members. The members receive a quarterly news letter[3] which contains abstracts of the available programs. At the beginning of this program in 1964, there were 135 participants and 30 programs in the exchange. Today the exchange lists about 800 participants and 110 programs.

The QCPE requires each participant to reply to an annual questionnaire. This guarantees a maximum of genuine interest in the exchange and provides valuable feed-back information. For example, the participants have shown a continuing increase in computer time on large systems. The savings on this computer time, even if only 1%, are more than sufficient to pay for the program. But more importantly, the general availability of these programs saves enormous time in duplicative efforts. It permits the individual investigators to concentrate more directly upon quantum chemistry itself and, therefore, to produce more significant research.

A recent voluntary check of the participants showed that the QCPE was cited as the source of computer programs in 49 journal articles, mostly in the 1965-1966 time period. Data of this type show the QCPE is making an impact and is helping to relieve the shortage of computer funds. It is also evident that in sponsoring the QCPE that the AFOSR is helping to significantly advance an important research area of chemistry.

References

1. "Nature of Quantum Chemistry," Per-Olov Löwdin, Intl. J. of Quantum Chemistry, 1, 7 (1967).

2. "Spectroscopy, Molecular Orbitals, and Chemical Bonding," R. S. Mulliken, Science, 157, 13 (7 July 1967).

3. Quantum Chemistry Exchange Program Newsletter, H. Shull, Chemistry Department, Indiana University.

CHEMICAL SYNTHESIS AND DYNAMICS

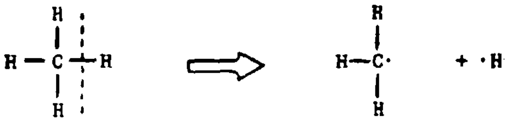
by Dr. Anthony J. Matuszko

Chemical synthesis and dynamics is concerned with the development of new and better synthetic methods and the study of reactivity and reaction mechanisms of organic, organometallic, and inorganic compounds. This includes detailed studies of the properties of, and methods of generating novel reactive intermediates for a variety of Air Force applications, particularly aerospace materials which are capable of withstanding exposure to extremes in temperature, pressure, and high energy radiation. Research in organometallic chemistry will yield understanding leading to compounds potentially useful as heat stable polymers, as catalysts in the synthesis of stereospecific polymers, as intermediates in the preparation of heretofore unattainable nonpolymeric materials, and as lubricants which retain their fluidity at wider ranges of temperature than presently available lubricants.

In this section of the Annual Review we present some of the highlights of our program in the area of chemical synthesis and dynamics with particular emphasis this year on reactive intermediates. The accounts of accomplishments which follow, concern chemical intermediates of increasing reactivity as we go from simple free radicals to carbenes to carbon vapors and atomic species.

A NEW TRAPPING TECHNIQUE FOR FREE RADICALS

When a chemical bond is broken, one result of the fragmentation might be the formation of reactive molecules with one or more unpaired electrons. Such a reactive species is called a "free radical." To illustrate, the homolytic cleavage of a carbon-hydrogen bond in methane would yield a methyl radical (as well as a hydrogen atom):

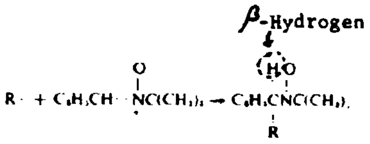


$$H-\overset{H}{\underset{H}{C}}-H \Longrightarrow H-\overset{H}{\underset{H}{C}}\cdot \quad + \cdot H$$

methyl
radical

Free radicals such as these may be the needed reactive intermediates in the synthesis of new materials, or they may be the breakdown products in the high energy radiative degradation of a structural material. In general free radicals are very short-lived species ($\sim 10^{-3}$ to 10^{-8} sec) and exist at low concentrations. Instrumentation which has evolved over the past eight to ten years and become an extremely useful tool for the study of chemical species with unpaired electrons is electron spin resonance (esr) spectroscopy. It can yield information not only of the presence and number of such unpaired electrons, but also of the distribution of the electrons in the molecule.

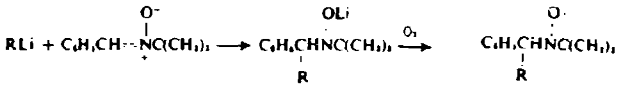
Relatively high concentrations (above 10^{-8}M) of free radicals are usually required for esr studies at room temperature with commonly available equipment. Numerous methods have been developed for studying short-lived free radicals by in situ irradiation or rapid mixing techniques. Biochemists have used a technique wherein the sample is frozen immediately after rapid mixing and studied at the experimenter's leisure. However, the esr signals are frequently broad and relatively featureless and cannot give much needed information for structural determination. A need has existed for readily applicable methods of detecting and identifying low concentrations of free radicals (below the esr detection threshold) in reacting systems. With grant support from the AFOSR Directorate of Chemical Sciences, Dr. Edward Janzen of the University of Georgia, has developed a trapping technique for this purpose. The approach is to have the generated radical react with a compound which can serve as an efficient radical trap. (For convenience we call these compounds spin traps.) Thus, a radical at low concentration and formed relatively slowly could be trapped to produce a new and more stable radical easily detectable by esr. (For convenience we call these new radicals spin adducts.) The nature of the resulting esr spectrum could then tell us the structure of the original radical. Of course, the spin adduct formed by this trapping technique must be reasonably stable and detectable by electron spin resonance. If the hyperfine spectrum of the resulting spin adduct has a characteristic feature which is sensitive to the detailed structure of the attached groups, the information can be used to identify the original radical. One such spin trap which Dr. Janzen and his research group have come up with is phenyl t-butyl nitrone (PBN) which has been used for identification of short-lived free radicals by the formation of stable nitroxides.



$$R\cdot + C_6H_5CH{-}\overset{\overset{O}{|}}{\underset{+}{N}}C(CH_3)_3 \rightarrow C_6H_5\overset{H}{\underset{\underset{R}{|}}{C}}\overset{\overset{O}{|}}{N}C(CH_3)_3$$

Whereas the original radical would have been difficult to detect, the esr spectrum of the nitroxide radical provides information not only about the existence of free radicals in the system but also the structure of the radicals. (The structural information is obtained from the magnitude of the hyperfine splitting of the β-hydrogen as observed in the esr spectrum)

In order to be an effective spin trap system, the reactions which give phenyl radicals should give the same spin adducts with the same characteristic features in the esr curve. In addition to phenyl radicals, the approach has been used successfully to define the structure of the radicals trapped in the case of benzyl, methyl, trifluoromethyl, ethyl, n-butyl, acetoxy and benzoyloxy radicals. The structure of a few spin adducts was verified by synthesis of the appropriate secondary amine followed by oxidation to the nitroxide. Further verification was obtained by addition of organolithium compounds to PBN followed by air oxidation to the nitroxide.



$$RLi + C_6H_5CH{-}\overset{\overset{O^-}{|}}{\underset{+}{N}}C(CH_3)_3 \longrightarrow C_6H_5\underset{\underset{R}{|}}{C}H\overset{OLi}{N}C(CH_3)_3 \xrightarrow{O_2} C_6H_5\underset{\underset{R}{|}}{C}H\overset{O\cdot}{N}C(CH_3)_3$$

The accompanying table summarizes the source of a number of radicals and the type of radical trapped. A recent communication in the Journal of the American Chemical Society [1] further describes methods used for generating the various free radicals and gives the calculated coupling constants of the nitroxide radicals formed. This paper together with Dr. Janzen's presentation on the subject at the National Meeting of the American Chemical Society in September 1968 has resulted in his being contacted by other researchers from various parts of the world. He has letters from two research groups (one from Strasbourg, France) which essentially ask what this new trapping technique can do to answer the question: "Are there free radical intermediates in the reaction I am studying?"

Table I
Free Radicals Studied
by the Trapping Technique

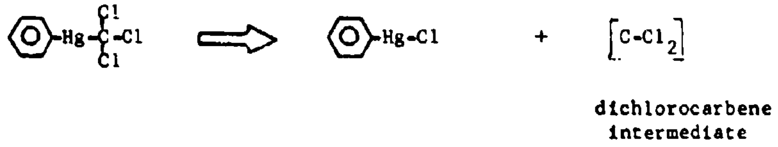
Radical source	Radical trapped
Phenylazotriphenylmethane	$C_6H_5\cdot$
Dibenzylmercury	$C_6H_5CH_2\cdot$
Trifluoromethyl iodide	$CF_3\cdot$
Dimethylmercury	$CH_3\cdot$
Diethylmercury	$C_2H_5\cdot$
Di-*n*-butyllead diacetate	$C_4H_9\cdot$
Lead tetraacetate	$CH_3COO\cdot$
Benzoyl peroxide	$C_6H_5COO\cdot$

This new method of detecting short-lived free radicals in low concentrations will be useful to the Air Force not only in the synthesis of new materials through free radical intermediates, but also as a sensitive technique for detecting degradation of polymeric materials upon exposure to high energy radiation of the upper atmosphere. Other general applications are spin trapping in biochemical systems, polymerizations, and air pollution studies.

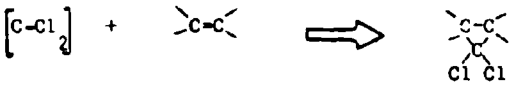
References:
1. "Detection and Identification of Short-Lived Free Radicals by an Electron Spin Resonance Trapping Technique," Edward G. Janzen and Barry J. Blackburn, J. Am. Chem., Soc., 90, 5909 (1968).

REACTIVE CARBENE INTERMEDIATES

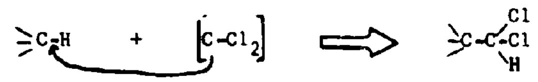
Chemists concerned with the synthesis of new materials have made use of a variety of highly reactive chemical species. These reactive species are often generated in situ and usually contain an element in an unstable low valency state. They occur as intermediates with short lifetimes, requiring low activation energies for reaction. Divalent carbon intermediates, commonly referred to as methylene derivatives or carbenes, are highly reactive substances of this type. With support from the AFOSR Directorate of Chemical Sciences, Dr. Dietmar Seyferth at the Massachusetts Institute of Technology has been investigating new ways of generating various carbenes in solution by way of elimination reactions from organometallic precursors. Typical of reactions studied by Dr. Seyferth and his research group is the following "extrusion" of a dihalocarbene from an organomercury compound.



The carbene may then react across a double bond to form a gem-dichlorocyclopropane, (the gem-dichlor-refers to the attachment of both chlorines to the same carbon atom),

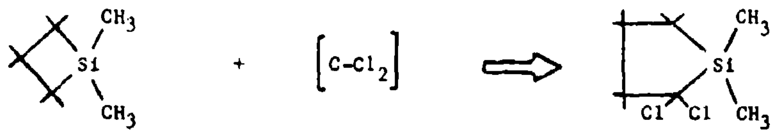


or it may take part in one of many "insertion" reactions.



Such reagent systems are of great value since they allow the generation and transfer to a substrate of a substituted carbene under very mild conditions in the virtual absence of complicating side reactions. This has allowed a study in detail of the chemistry of carbenes and has allowed the M.I.T. scientists to carry out carbene reactions which had never been observed before because alternate carbene generating systems were incompatible with product formation or existence. Organomercury systems have been developed which transfer CCl_2, CClF, CBr_2, CClBr, CHCl, CHBr and CH_2 to various organic and inorganic substrates. Since the reactions are carried out in situ without isolation of intermediates the actual formation of carbenes is not always a certainty. However, kinetic studies have established that CCl_2 was an intermediate in the reaction of C_6H_5-Hg-CCl_2Br with olefins in benzene solution[1].

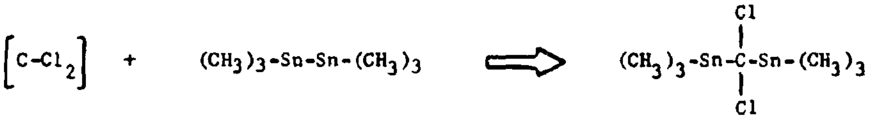
Recently, the M.I.T. research team reported a new reaction which was noteworthy for two reasons: it represented the first reported CCl_2 insertion into a silicon-carbon bond as well as the first insertion of CCl_2 (with ring expansion) into a strained cyclic system.[2]



4-membered carbon silicon ring

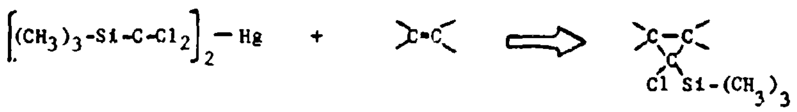
5-membered carbon-silicon ring

The study of compounds containing covalent metal-to-metal bonds has received much attention in the past few years. The discovery of the first case of dihalocarbene insertion into a metal-to-metal bond to give a stable $-M-CX_2-M-$ system has opened up a broad new field of research in the organometallic aspects of carbene chemistry.[3]



$$[C\text{-}Cl_2] + (CH_3)_3\text{-}Sn\text{-}Sn\text{-}(CH_3)_3 \Longrightarrow (CH_3)_3\text{-}Sn\text{-}\overset{Cl}{\underset{Cl}{C}}\text{-}Sn\text{-}(CH_3)_3$$

Recently, Seyferth and Hanson reported the preparation and reactions of the first functional carbene reagent, an organomercury compound which transfers $(CH_3)_3SiCCl$ to olefins and Si-H compounds.[4]



This compound may now be added to the arsenal of useful reagents in synthetic organosilicon chemistry.

These are only a few of the many new developments in the chemistry of reactive carbene intermediates coming out of Dr. Seyferth's laboratory. The C_6H_5-Hg-CX_3 reagents whose chemistry was developed with AFOSR support have been finding increasing use in organic synthesis, particularly in the preparation of cyclopropanes. One of these reagents, $C_6H_5HgCCl_3$ has found its way into the Eastman Catalog of chemical reagents commercially available for laboratory use. Dr. Seyferth has noted industrial interest in these mercury reagents which may be useful for adding dihalocarbenes to carbon-carbon double bonds in polymers from 1, 3-dienes.

References:

1. "Halomethyl-Metal Compounds. XIV. The Mechanism of the Phenyl(bromodichloromethyl) mercury-Olefin Reaction," Dietmar Seyferth, Jeffrey Pui Mui and James M. Burlitch, J. Am. Chem. Soc., 89, 4953 (1967).
2. "Insertion of CCl_2 into the Silicon-Carbon Bond of Silacyclobutanes," Dietmar Seyferth, Robert Damrauer and Stephen S. Washburne, J. Am. Chem. Soc., 89, 1538 (1967).

3. "The Reaction of Phenyl(trihalomethyl) mercurials with Hexamethylditin The First Case of Dihalocarbene Insertion into a Metal-Metal Bond to Give a Stable MCX_2M System," Dietmar Seyferth and Frank M. Armbrecht, J. Am. Chem. Soc., <u>89</u>, 2790 (1967); A full paper has been accepted for publication in J. Am. Chem. Soc. and will appear in early 1969.

4. "Bis (trimethylsilyldichloromethyl)mercury, a New and Useful Reagent in Synthetic Organosilicon Chemistry," Dietmar Seyferth and Earle Marie Hanson, J. Am. Chem. Soc., <u>90</u>, 2438 (1968).

LOW TEMPERATURE REACTIONS OF HIGH TEMPERATURE SPECIES

At Pennsylvania State University, Dr. Philip Skell has been studying labile species of carbon and other chemical elements. His early work resulted in new methods of generating monatomic carbon, C_1, and triatomic carbon, C_3. The chemical reactivity of these labile species with various organic molecules was highlighted in our 1965 Annual Review.[1] Since that time, Skell and his coworkers have obtained diatomic carbon, C_2, and have done detailed studies of the electronic and chemical properties of the various forms of reactive carbon. The method first used in the study involved vaporization of carbon across a graphite electrode arc under high vacuum and reaction of the carbon vapor with organic molecules at liquid nitrogen temperatures. Another method used for generating the labile species involves vaporization by resistive heating from a hot surface into a high vacuum. The Penn State researchers have now identified two singlet and one triplet states of C_1 and of C_3, and a singlet and a triplet state of C_2. The approximate percentages of C_1, C_2 and C_3 formed are shown in Table I.

TABLE I

COMPOSITION OF CARBON VAPOR FROM VACUUM ARCING AND RESISTIVE HEATING

Carbon Species	Vacuum Arc Vaporization	Resistive Heating Vaporization
C_1	68%	54%
C_2	24	11
C_3	7	33
Other	1	2

Skell's most reliable method of determining the composition of carbon vapor is by trapping with chlorine and identification of the organic perchlorides formed. In further work on carbon, a study is planned for the determination of carbon vapor composition as a function of arc parameters (i.e., effect of changes in voltage and current) and the type of carbon used. This information will be useful in the problems encountered in rocket re-entry into the atmosphere, and also in the use of labile carbon species as reactive intermediates in the synthesis of new materials.

The objective of the Penn State work on "Atomic Chemistry" has been the formation and study of the chemical reactivity of atomic species of a number of elements in addition to carbon. During the past year, a reaction of thermally vaporized silicon was reported in a short communication from this laboratory.[2] In an apparatus similar to that developed for carbon vaporizations, a properly doped silicon sample was heated resistively to 1400°C in vacuo to form a vapor of silicon atoms. The silicon atoms reacted with trimethylsilane which was trapped on the liquid nitrogen cooled walls and formed 1, 1, 1, 3, 3, 3-hexamethyltrisilane.

$$(CH_3)_3SiH + Si \longrightarrow (CH_3)_3SiSiH$$
$$(CH_3)_3SiSiH + (CH_3)_3SiH \longrightarrow (CH_3)_3SiSiH_2Si(CH_3)_3$$

However, silicon, as well as other poorly conducting materials, are exceedingly difficult to vaporize to the atomic state by resistive heating or vacuum arcing. A third method of generating highly active atomic species has only recently been used by Skell and coworkers with spectacular success in the vaporization of silicon. It involves a magnetically focused high voltage electron beam (Varian 2-KW Electron Gun). The earlier experiments on vaporization of silicon have now been repeated using the electron gun, confirming the major reaction of atomic silicon with trimethylsilane. Further work is now being done to understand the details of the interactions with atomic silicon.

Other atomic species which are being investigated at the present time are boron, magnesium, germanium and nickel. The co-condensation at -196°C of atomic magnesium with alkyl halides resulted in very little formation of Grignard reagent, indicating that Grignard formation is a property of the bulk metal rather than the atomic species. The major reaction of alkyl halide with atomic magnesium is radical formation. Hence, atomic magnesium should be useful in studying radical reactions at very low temperatures. Early experiments indicate that the electron gun vaporizations should yield atomic boron and atomic nickel, both of which were difficult to obtain by arcing or resistive heating.

Through the formation of atomic species of metal and metalloid elements such as carbon, silicon, germanium, magnesium, nickel, boron, etc., Dr. Skell and others actively working in the field, are making available an exciting new series of reactive intermediates. These intermediates will lead to the synthesis of a variety of new organometallic and organometalloid materials, some of which could be useful as semiconductors, thermally stable polymers, or lubricants.

References:

1. "Eleventh Annual Chemistry Program Review," AFOSR 65-1559, 13-15, 1965
2. "Atomic Silicon, Reaction with Trimethylsilane," P. S. Skell and P. W. Owen, J. Am. Chem. Soc., 89, 3922 (1967).

CHEMISTRY PROGRAM STATISTICS
for FY68 (Ending 30 June 1968)

	Number	Amount, Thousands
New Projects	23	$ 933
Renewals	53	2,396
Continuing Projects	55	
Completed Projects	31	
TOTAL	162	
Active Projects, 30 June 1968	131	
Monies Committed During FY68 (for 106 Project Years)		3,329
Cost per Project-Year		$ 31.4

PROPOSAL DATA, FY68

New Proposals Received	215
Renewal Proposals Received	50
TOTAL	265
New Proposals Declined, Withdrawn or Transferred	201
New Proposals Funded*	14
Percent Funded	6.5%
Renewal Proposals Funded**	49
Overall Percent Declined	76%
Overall Percent Funded	24%

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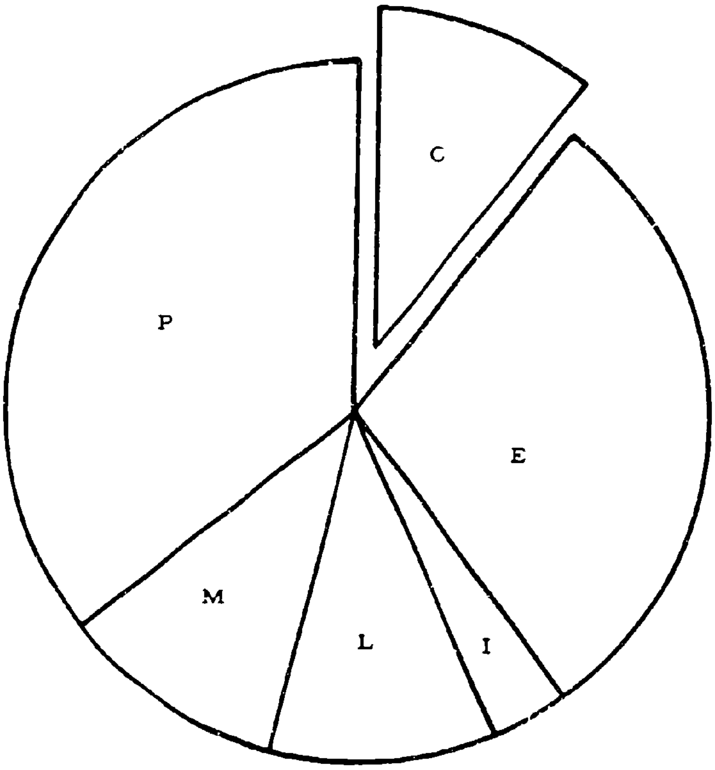
* 3 with FY68 funds; balance with FY69 funds.

** One renewal proposal withdrawn.

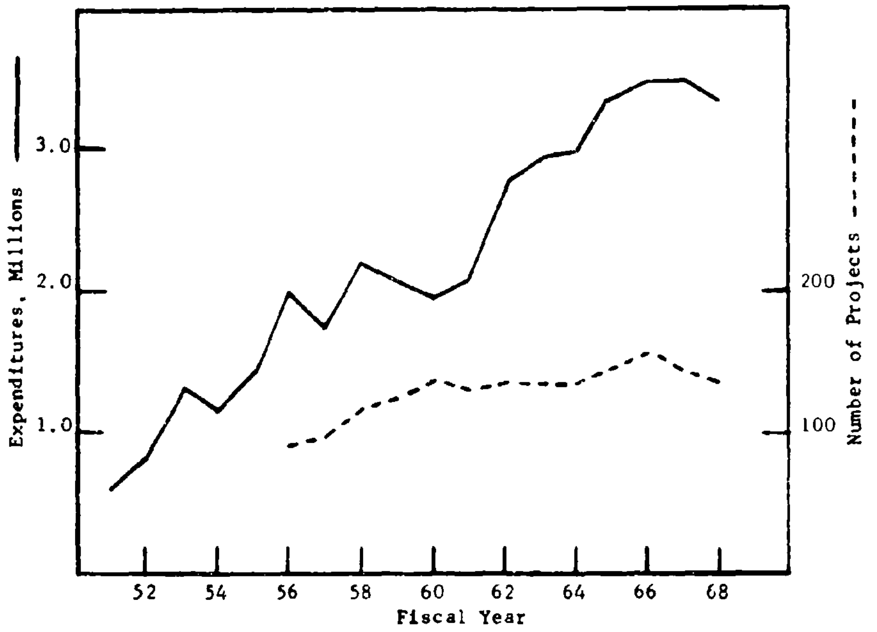
AFOSR BUDGET, FY68

Directorate	Symbol	Amount, Thousands	Percent
Chemical Sciences	C	$ 3,329	10.1
Engineering Sciences	E	9,807	29.6
Information Sciences	I	1,239	3.7
Life Sciences	L	3,448	10.4
Mathematical Sciences	M	3,275	9.9
Physical Sciences	P	12,048	36.3
		$ 33,146	100.0



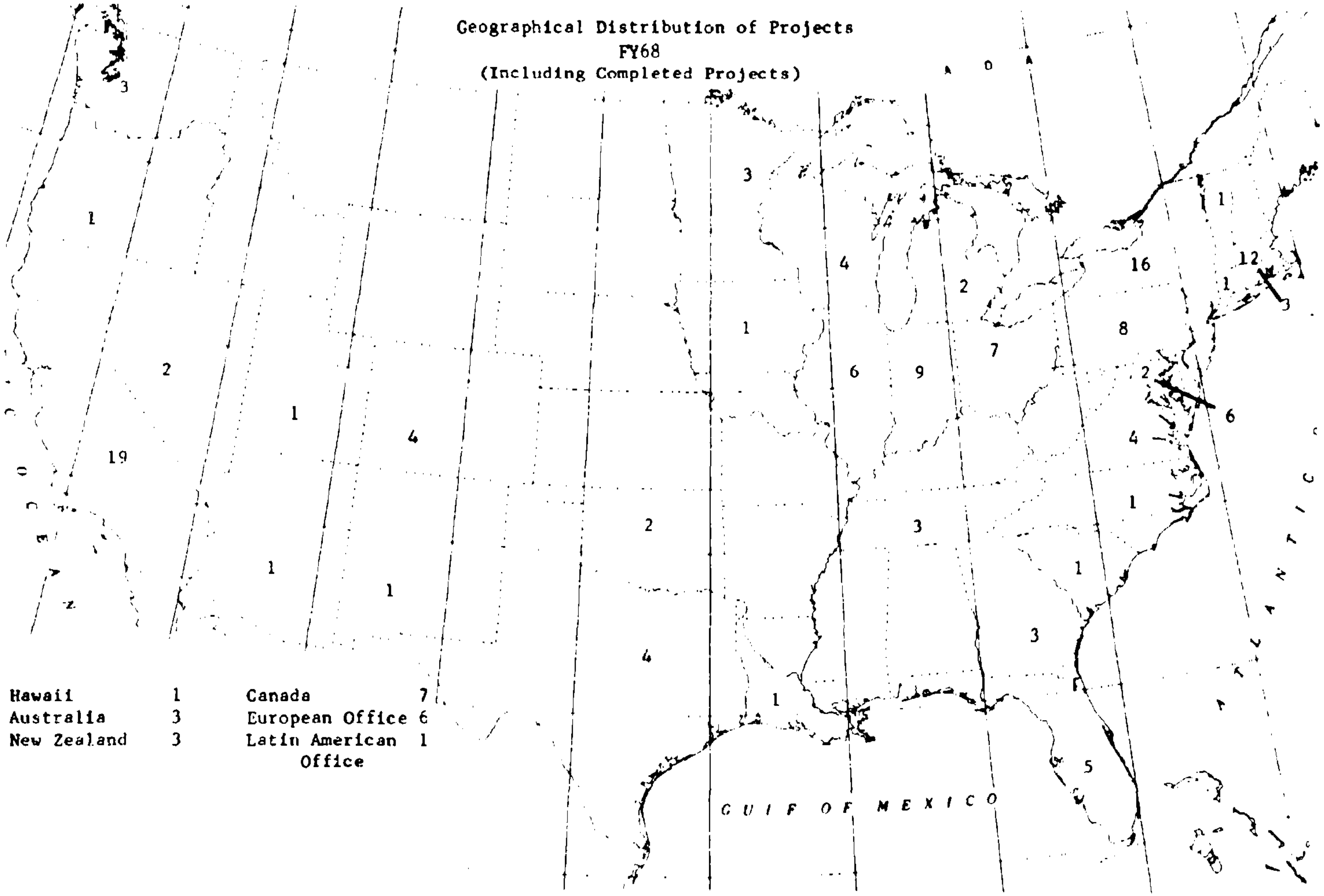
CHEMISTRY BUDGET

FY	Expenditures (Thousands)
51	$ 596
52	835
53	1,310
54	1,150
55	1,451
56	1,976
57	1,732
58	2,205
59	2,066
60	$1,964
61	2,086
62	2,700
63	2,922
64	2,959
65	3,356
66	3,475
67	3,480
68	3,329
69 (est.)	3,401



Plots are given of the year by year expenditures of the Directorate of Chemical Sciences (full line) and the number of projects supported (dashed line). A comparison of the two plots reveals the rising cost of basic research in chemistry.

Geographical Distribution of Projects
FY68
(Including Completed Projects)



Hawaii	1	Canada	7
Australia	3	European Office	6
New Zealand	3	Latin American Office	1

PROFESSIONAL ACTIVITIES BY MEMBERS OF THE DIRECTORATE OF CHEMICAL SCIENCES (DCS)

Attendance at Professional Meetings and Conferences	45
Visits to U. S. Government Installations	30
Papers Presented at Professional Meetings and Conferences (AGH)	1
Papers Published in Scientific Journals (DLB)	1
Professional Courses Completed	3
Professional Courses Taught (ETW)	3
Laboratory Visits to DCS Projects	125
Potential Investigators Briefed on DCS Program	200

PUBLICATIONS RECEIVED DURING FY 1968 ON PROJECTS EXPIRING PRIOR YEARS

Bonham, R.A.
Indiana University
Bloomington, Indiana
AF-AFOSR-602-64

"Effect of Bond Formation on Electron Scattering Cross Sections for Molecules," D. A. Kohl and R. A. Bonham, J. Chem. Phys., 47, 1634 (1967).

Cram, D.J.
University of California
Los Angeles, California
AF-AFOSR-124-65

"1, 3-Asymmetric Induction in a Transamination Reaction," Donald J. Cram, J. Am. Chem. Soc., 89, 5288 (1967).

Eggers, D. F.
University of Washington
Seattle, Washington
AF49(638)-797

"Vibrational Spectrum of Cyclopropene," D. F. Eggers, E. L. Wagner, J. W. Schultz, L. M. Jackman, K. B. Wiberg, and R. L. Erskine, J. Chem. Phys., 47, 946 (1967).

Freeman, P. K.
University of Idaho
Moscow, Idaho
AF-AFOSR-34-65

"The Reactions of Exo- and Endo-5-Chloromethylnorbornene with Sodium," Peter K. Freeman, V. N. Mallikarjuna Rao, Daniel E. George, and Gary L. Fenwick, J. Org. Chem., 32, 3958 (1967).

Griffin, C. E.
University of Pittsburgh
Pittsburgh, Pa.
AF-AFOSR-470-64

"Phosphonic Acids and Esters. XIX. Syntheses of Subsituted Phenyl- and Arylphosphonates by the Photoinitiated Arylation of Trialkyl Phosphites," R. Obrycki and C. E. Griffin, J. Org. Chem., 33, 632 (1968).

"Long-Range ^{31}O-^{1}H Spin-Spin Couplings in Benzyl and Tolyl Phosphorus Compounds," C. E. Griffin and M. Gordon, J. Am. Chem. Soc., 89, 4427 (1967).

Guyon, J. C.
University of Missouri
Columbia, Missouri
AF-AFOSR-205-63

"Spectrophotometric Determination of Zirconium," John C. Guyon, Anal. Chim. Acta., 37, 401 (1967).

"Spectrophotometric Determination of Bismuth," John C. Guyon and Linda J. Cline, Anal. Chem., 37, 1778 (1965).

Janz, G. J.
Rensselaer Polytechnic Institute
Troy, New York
AF-AFOSR-181-63

"Molten Salts Handbook," George J. Janz, Academic Press Inc., New York (1967).

Kice, J.L.
Oregon State University
Corvallis, Oregon
AF-AFOSR-106-65

"Mechanisms of Substitution Reactions at Sulfinyl Sulfur. V. Halide and Acetate Ion Catalysis of the Solvolysis of Arylsulfinyl Sulfones in Acetic Acid-Water," John L. Kice and Giancarlo Guaraldi, J. Org. Chem., 33, 793 (1968).

"Mechanisms of Substitution Reactions at Sulfinyl Sulfur. IV. the Hydrolysis of Sulfinyl Sulfones (Sulfinic Anhydrides) in Aqueous Dioxane," John L. Kice and Giancarlo Guaraldi, J. Am. Chem. Soc., 89, 4113 (1967).

"Mechanisms of Reactions of Thiolsulfinates (Sulfenic Anhydrides) I. The Thiolsulfinate-Sulfinic Acid Reaction," John L. Kice, Clifford G. Venier, and Leslie Heasley, J. Am. Chem. Soc., 89, 3557 (1967).

"The Effect of Ring Size on the Rate of Pyrolysis of Cycloalkyl Phenyl Sulfoxides," John L. Kice and J. Douglas Campbell, J. Org. Chem., 32, 1631 (1967).

Kwiatek, J.
U.S. Industrial Chemicals Co.
Cincinnati, Ohio
AF49(638)-1214

"Reactions Catalyzed by Pentacyanocobaltate(II)," Jack Kwiatek, Catalysis Rev., 1, 37 (1967).

Libby, W. F.
University of California
Los Angeles, California
AF-AFOSR-245-65

"Space Chemistry," W. F. Libby, Buletinul Institutului Politechnic Din Iasi, 13, 171 (1967).

"Chemical Ionization Mass Spectrometry. VII. Reactions of Benzene Ions with Benzene," F. H. Field, Peter Hamlet and W. F. Libby, J. Am. Chem. Soc., 89, 6035 (1967).

"High-Pressure Metallic Polymorph of Cadmium Arsenide," H. Katzman, Terence Donohue and W. F. Libby, Phys. Rev. Letters, 20, 442 (1968).

Lillien, I.
University of Miami
Coral Gables, Florida
AF-AFOSR-123-63

"Nonplanar Cyclobutane. Temperature Dependence of Infrared Spectra of Cis- and Trans-Methyl 3-Isopropylcyclobutanecarboxylate," I. Lillien, J. Org. Chem., 32, 4152 (1967).

"Nonplanar Cyclobutane. Steric Control in Deamination of cis- and trans-3-Isopropylcyclobutylamine," I. Lillien and R. A. Doughty, Tetrahedron Letters, 40, 3953 (1967).

"Nonplanar Cyclobutane-II The Methyl 3-Isopropylcyclobutane-carboxylate System," I. Lillien and R. A. Doughty, Tetrahedron Letters, 23, 3321 (1967).

Mayo, F. R.
Stanford Research Institute
Menlo Park, California
AF49(638)-1102

"Liquid Phase Oxidations of Cyclic Alkenes. II," Dale E. Van Sickel, Frank R. Mayo and Richard M. Arluck, J. Org. Chem., 32, 3680 (1967).

Moriconi, E. J.
Fordham University
New York, New York
AF-AFOSR-488-64

"The Reaction of Chlorosulfonyl Isocyanate with Bridged Bi- and Tricyclic Olefins," Emil J. Moriconi and Wheeler C. Crawford, J. Org. Chem., 33, 370 (1968).

Overend, J.
University of Minnesota
Minneapolis, Minnesota
AF-AFOSR-570-64

"On the Problem of Multiple Solutions in the Calculation of Force Constants by Least-Squares," C. D. Needham and J. Overend, Spectrochimica Acta, 22, 1383 (1966).

"Least-squares Adjustment of Anharmonic Potential Constants: Application to $^{12}CO_2$ and $^{13}CO_2$," M. A. Pariseau, I. Suzuki and John Overend J. Chem. Phys., 42, 2335 (1965).

Parravano, G.
University of Michigan
Ann Arbor, Michigan
AF49(638)-606

"The Low Temperature Oxidation of Ammonia Over a Supported Ruthenium Catalyst," T. J. Schriber and G. Parravano, Chem. Eng. Sci., 22, 1067 (1967).

"Polymerization of Styrene with Titanium Chloride Triethyl Aluminum Vanadium Chloride Catalyst," F. D. Otto and G. Parravano, J. Polymer Sci., 2, 5131 (1964).

"Polymerization of Vinylcyclohexane with Titanium Chloride-Triethyl Aluminum Catalysts," W. H. McCarty and G. Parravano, J. Polymer Sci., 3, 4029 (1965).

Peacock, R. D.
University of Birmingham
Birmingham, England
AF-AFOSR-63-96

"Dialkylaminotellurium (VI) Fluorides," G. W. Fraser, R. D. Peacock, and P. M. Watkins, Chem. Comm., 1248 (1967).

Schmidt, H. H.
University of California
Riverside, California
AF49(638)-284

"Heat Capacity in the Critical Region of Xenon," Ha[illegible]d H. Schmidt, Jack Opdycke, and Charles F. Gay, Phys. Rev. Letters, [illegible], 887 (1967).

Shine, H. J.
Texas Technological College
Lubbock, Texas
AF-AFOSR-23-63

"The Formation of Cations and Cation Radicals from Aromatic Sulfides and Sulfoxides," H. J. Shine, in "Organosulfur Chemistry," Ed. by M. J. Janssen, John Wiley, New York (1967).

Sillen, L. G.
Royal Institute of Technology
Stockholm, Sweden
AF61(052)-162; AF-EOAR-65-22; AF-EOAR-63-8

"The Crystal Structure of the Potassium Aluminate $K_2\left[Al_2O(OH)_6\right]$," Goerge Johansson, Acta Chem. Scand., 20, 505 (1966).

"A Calorimetric and Potentiometric Study of the System Cl^- -Hg^{2+} and Br^- -Hg^{2+} at 25° C in 3M$NaClO_4$ Medium," Robert Arnek, Arkiv Kemi, 24, 531 (1965).

"Studies Concerning Hydrolysis of Metallic Ions 55. Vanadium (III) in 3 Molar KCl Medium," Felipe Brito, Anales Real Soc. Espan. Fis. Quim., Ser B-Quimica, 62, 193 (1967).

"Studies Concerning the Equilibria of Polyanions," Felipe Brito, Anales Real Soc. Espan. Fis. Quim., Ser B-Quim, 62, 123 (1966).

"Studies Concerning the Equilibria of Polyanions XIII Polymerization of Tellurates in One Molar NaCl Solution at 25°C," Felipe Brito, Anales Real Soc. Espan. Fis. Quim., Ser B-Quimica, 62, 197 (1967).

"The Ion Activity Function--An Approach to the Study of Electrolyte Behaviour in Concentrated Solutions," L. Leifer and E. Hogfeldt, in "Electrochemistry" (Proc. 1st Australian Conference, Sydney, 13-15 Feb., Hobart, 18-20 Feb, 1963) 107, New York Pergamon Press (1964).

"On the Nature of Charge-Carriers in Liquid Se Containing Cl," Margareta Lundkvist and Lars Gunnar Sillen, Acta Chem. Scand. 20, 1723 (1966).

"Study on the Hydrolysis of Metal Ions. Part 56. Solvent Extraction Study of the Hydrolysis of Zinc (II) in 3M NaClO at Low Concentration," Sekine Tatsuya, Acta Chem. Scand. 19, 1526 (1965).

"The Crystal Structure of $Zr_2(OH)_2(SO_4)_3(H_2O)_4$," D. B. McWhat, Goerge Lundgen and Lars Gunnar Sillen, Inorg. Chem. 5, 284 (1966).

"On a Photometric Method for Concentration Determinations," Tom Wallin, Arkiv Kemi, 26, 13 (1966).

Trueblood, K.N.
University of California
Los Angeles, California
AF-AFOSR-240-63

"The Crystal Structure of the Hexahydrated Calcium Salt of Hexacyanisobutylene," D. A. Bekoe, P. K. Gantzel, and K. N. Trueblood, Acta Cryst., 22, 657 (1967).

"The Crystal and Molecular Structure of 1-Methylamino-7-Methylimino-1, 3, 5-Cycloheptatriene," Paul Goldstein and Kenneth N. Trueblood, Acta Cryst., 23, 148 (1967).

DIRECTORATE OF CHEMICAL SCIENCES

AFOSR ARLINGTON, VA.

RESEARCH EFFORTS

As of 1 July 1968

(Alphabetical by Principal Investigator)

Physical Adsorption of Vapors W4 (870) 60/1097-66	Arthur W. Adamson Department of Chemistry University of Southern Calif. Los Angeles, California
Chemical Electronic Structure Theory B4 (969) 39/1625	Leland C. Allen Department of Chemistry Princeton University Princeton, New Jersey
Mechanism of Nitrogen Fixation by Ultrasonic Radiation in Water E4 (1269) 60/67-24	Michael Anbar Department of Chemistry Weizmann Institute of Science Rehovoth, Israel
Kinetic Spectroscopy of Chemically Active Systems E4 (170) 60/1703	Edward J. Bair Department of Chemistry Indiana University Bloomington, Indiana
Multicharge Aromatic Ions M4 (1068) 62/738-67	Merle A. Battiste Department of Chemistry University of Florida Gainesville, Florida
Study of The Light Emitted by Atomic Flames B5 (968) 60/687-64	Kyle D. Bayes Department of Chemistry University of California Los Angeles, California
Microwave Spectroscopy of Boron Compounds R4 (769) 60/849-67	Robert A. Beaudet Department of Chemistry University of Southern Calif. Los Angeles, California
Electrolytic Reduction of Organic Compounds W4 (569) 62/822-67	Robert A. Benkeser Department of Chemistry Purdue University Lafayette, Indiana
Chemistry of Strained Olefins M4 (969) 62/68-1358	Jerome A. Berson Department of Chemistry University of Wisconsin Madison, Wisconsin

Some Thermochemical Studies by Mass Spectrometry R4 (869) 10/68-1356	D. R. Bidinosti Department of Chemistry University of Western Ontario London, Ontario, Canada
Theoretical Studies on the Structure of Inorganic and Organometallic Compounds M, H4 (1070) 39/67-1184A	J. E. Bloor Department of Chemistry University of Virginia Charlottesville, Virginia
The Solvolytic Reactivity of Pi-Complexed Compounds M4 (869) 62/991-67	Robert S. Bly, Jr. Department of Chemistry University of South Carolina Columbia, South Carolina
Theoretical and Experimental Analysis of Electron Scattering from Atoms and Molecules B4 (1169) 37/1681	Russell A. Bonham Department of Chemistry Indiana University Bloomington, Indiana
Nucleophilic Displacements by Organo-Phosphorus Compounds R4 (569) 62/1170-67	Irving J. Borowitz Department of Chemistry Yeshiva University New York, New York
Studies of Liquid Crystals as Related to Electro-Optical and Other Devices E2 (569) 9737/67-C-0103	Glenn H. Brown Department of Chemistry Kent State University Kent, Ohio
Detector Research Using Liquid Crystals E3 (871) 7921/69-C-0021	
Second International Liquid Crystal Conference W2 (869) 60/1345	
Photolytic and Pyrolytic Free Radicals R4 (270) 10/1085-66	A. S. Buchanan Department of Chemistry University of Melbourne Parkville, N. 2, Melbourne Australia
Studies in Ring Expansion M6 (1069) 62/67-13	George L. Buchanan Department of Chemistry University of Glasgow Glasgow, Scotland
Sixth International Symposium on the Reactivity of Solids B, H 1.5 (1068) 60/67-C-0078	A. M. Bueche Department of Chemistry General Electric Company Schenectady, New York

Kinetics of Atomic Association Reactions Using Flash Photolysis over a Wide Temperature Range R5 (1069) 38/69-1695	George Burns Department of Chemistry University of Toronto Toronto, Canada
Heterogeneous Catalysis in Liquid Systems E6 (968) 60/97-63	Robert L. Burwell, Jr. Department of Chemistry Northwestern University Evanston, Illinois
Synthesis of Triple Strand Polymers M4 (369) 62/817-67	George B. Butler Department of Chemistry University of Florida Gainesville, Florida
Density of Cryogenic Liquid Mixtures W4 (969) 37/1020-66B	Frank B. Canfield Department of Chemistry University of Oklahoma Norman, Oklahoma
Investigations of Energy Transformation in Luminescent Materials R2 (969) 38/68-1342A	Glenn A. Crosby Department of Chemistry Washington State University Pullman, Washington
Interaction of Molecules with Solid Surfaces B4 (969) 60/68-1388	A. D. Crowell Department of Chemistry University of Vermont Burlington, Vermont
The Gordon Research Conference on High Temperature Chemistry B1 (469) 60/68-1522	D. Cubicciotti Gordon Research Conferences University of Rhode Island Kingston, Rhode Island
The Single Electrode Potential and the Electrochemistry of the Hydrated Electron W2 ([illegible]) 60/68-1344	Robert deLevie Department of Chemistry Georgetown University Washington, D. C.
Organometallic Electrochemistry E2 (1070) 36/69-1694	Raymond E. Dessy Department of Chemistry Virginia Polytechnic Institute Blacksburg, Virginia
Organic Chemical Physics M4 (1169) 39/67-1050A	Michael J.S. Dewar Department of Chemistry University of Texas Austin, Texas

X-Ray Adsorption-Edge Fine-Structure Spectrometry of Glass and Glass-Crystal Materials R, H3 (1268) 10/1670	Charles G. Dodd (G.L. Gien) General Research Division Owens-Illinois Technical Center Toledo, Ohio
Reactions and Structures of Metal-Olefin Complexes and Related Substances W4 (1268) 10/763-67	John R. Doyle and Norman C. Baenziger Department of Chemistry State University of Iowa Iowa City, Iowa
Excited States of Uranium and Heavy Metals E4 (169) 60/865-67	Thomas Dunn Department of Chemistry University of Michigan Ann Arbor, Michigan
Reactions of Metallic Ions E4,25 (1270) 38/1225-67	Joseph E. Earley Department of Chemistry Georgetown University Washington, DC
Isotope Study of the Decomposition of Inorganic Peroxides B4 (1069) 10/68-1439	John O. Edwards Department of Chemistry Brown University Providence, Rhode Island
Chemical Dynamics on Crystal Surfaces R2 (170)	Gert Ehrlich Physical Chemistry Research and Development Center General Electric Schenectady, New York
Quantitative Conformational Analysis M4 (1068) 62/772-67	Ernest L. Eliel Department of Chemistry University of Notre Dame Notre Dame, Indiana
Laser-Temperature Jump Studies of Fast Reactions R5 (1268) 10/68-1383	Edward M. Eyring Department of Chemistry University of Utah Salt Lake City, Utah
Relaxation Method Rate Studies R1 (1269) 36/new	
Research on Inorganic Chemical Nomenclature W3 (269) 10/890-65	W. Conrad Fernelius National Academy of Sciences Washington, DC

High Resolution Raman Spectroscopy E4 (170) 36/1092-67	William H. Fletcher Department of Chemistry University of Tennessee Knoxville, Tennessee
The AFOSR Center for Macromolecular Research at Stanford University M6.75 (1268) 60/1341	Paul J. Flory Department of Chemistry Stanford University Stanford, California
Inorganic Diradicals: Carbenoids B1 (1268) 10/68-C-0005	W. B. Fox Inorganic Research Allied Chemical Corporation Morristown, New Jersey
Molecular Structure of Carbanions and Kinetics of their Exchange Processes in Solution W4.5 (968) 62/68-1441	Gideon Fraenkel Department of Chemistry Ohio State University Columbus, Ohio
Inorganic N.M.R. Spectroscopy R4 (370) 10/68-1567	R. J. Gillespie Department of Chemistry McMaster University Hamilton, Ontario, Canada
Stereochemical Aspects of Ionization Processes M4 (769) 62/847-67	Harlan L. Goering Department of Chemistry University of Wisconsin Madison, Wisconsin
Photochemically Generated Valence Tautomers B4 (469) 62/837-67	Theodore D. Goldfarb and Robert S. Boikess Department of Chemistry State University of New York Stony Brook, L.I., New York
X-ray Crystallographic Methods R4 (170) 62/68-1509	J. Zanos Gougoutas Department of Chemistry Harvard University Cambridge, Mass
Chemistry of Decaborane R4 (1270) 40/910	Norman N. Greenwood Department of Chemistry King's College University of Newcastle Newcastle-upon-Tyne, England
Phosphorus Coordination Compounds R4 (1068) 10/782-67	Samuel O. Grim Department of Chemistry University of Maryland College Park, Maryland

Inorganic Applications of Nuclear Quadrupole Resonance Spectroscopy R4 (169) 10/859-67	Terry E. Haas Department of Chemistry Tufts University Medford, Massachusetts
Inorganic Chemistry E2 (171) 39/69-1721	Jack Halpern Gordon Research Conferences University of Rhode Island Kingston, Rhode Island
Transfer of Excitation in Solution B5 (1069) 38/1479	George S. Hammond Department of Chemistry California Institute of Technology Pasadena, California
Kinetic Spectroscopy in the Infrared R4 (769) 36/66-0976C	Robert M. Hexter Clifford W. Hand Carnegie-Mellon University Pittsburgh, Pennsylvania
Bibliographic File of Abstracts on Photographic Science W,H1,5(769) 10/1112-66	Thomas Hill Rochester Institute of Technology 69 Plymouth Avenue South Rochester, New York
Spectroscopic Studies of Chemical Reactions in the Solid State E4 (869) 36/67-0907A	I. C. Hisatsune Department of Chemistry Pennsylvania State University University Park, Pennsylvania
Chemical Characterization of Molecules Adsorbed on a Foreign Solid B4 (1068) 60/734-67	Melvin C. Hobson, Jr. Department of Chemistry Virginia Institute of Scientific Research Richmond, Virginia
Inorganic Structure and Spectra R6,17 (869) 37/1492	William D. Horrocks, Jr. Department of Chemistry Princeton University Princeton, New Jersey
Reaction of Organometallic Intermediates M2 (1269) 62/68-1518	Herbert O. House Department of Chemistry Massachusetts Institute of Tech. Cambridge, Massachusetts
Properties of Solid, Non-Stoichiometric Lanthanide Oxide Phases E4 (269) 60/853-67	Bruce G. Hyde Department of Physical Chemistry University of Western Australia Nedlands, W.A., Australia

Far Infrared Studies of the Hydrogen Bond F4.5 (1069) 36/69-1621	Robert Jakobsen Organic Chemistry Division Battelle Memorial Institute Columbus, Ohio
ESR Thermal Decomposition Studies of Nitroaromatic Compounds and Inorganic Salts M4 (270) 62/68-1554	Edward G. Janzen Department of Chemistry University of Georgia Athens, Georgia
The Mechanisms of Substitution Reactions of Niobium Compounds B3 (970) 40/68-1355	Ronald C. Johnson Department of Chemistry Emory University Atlanta, Georgia
Coordination, Ligand Reactivity, and Catalysis W4.5 (1268) 60/630-66	Mark M. Jones Department of Chemistry Vanderbilt University Nashville, Tennessee
The Solution Chemistry of Polyhedral Boron Hydride Ions R5.5 (969) 37/69-1665	Alexander Kaczmarczyk Department of Chemistry Tufts University Medford, Massachusetts
Calorimetric Studies of Polymers B2 (1069) 37/68-1434	Frank E. Karasz Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts
Effects of High Pressure on Materials: Crystal Chemistry Studies B1-66 (869) 37/68-C-0047	J. S. Kasper Physical Chemistry Laboratory Research and Development Center General Electric Schenectady, New York
Factors Affecting the Utilization of Research Investigations in Chemistry B1.5 (1169) 10/68-C-0080	John A. King Science Communication, Inc. McLean, Virginia
Coordination Compounds of the Transition Metals E2 (1269) 40/68-1435	R. Bruce King Department of Chemistry University of Georgia Athens, Georgia
Photo-Induced Redox Reactions B7 (969) 10/68-1347	Jay K. Kochi Department of Chemistry Case Western Reserve University Cleveland, Ohio

Acid-Base Equilibria and Titrations and Electrochemical Equilibria in Acetonitrile W3 (969) 10/1223-67	I. M. Kolthoff Department of Chemistry University of Minnesota Minneapolis, Minnesota
Upper Atmosphere Ion-Molecule Reactions E5 (868) 60/1301	Walter S. Koski Department of Chemistry Johns Hopkins University Baltimore, Maryland
Electrochemistry of Solids W4 (969) 37/68-1405	Ferdinand A. Kroger Department of Chemistry University of Southern California Los Angeles, California
Mass Spectrometric, Thermochemical and Related Studies on Series of Inorganic Compounds R3 (969) 10/67-C-0005	Michael F. Lappert Department of Chemistry University of Sussex Falmer, Brighton Sussex, England
The AFOSR Program in Space Chemistry at UCLA W3 (1269) 38/67-1255A	Willard F. Libby Department of Chemistry University of California Los Angeles, California
Study of N_2 A-Triplet-Sigma State Generated by 1849 Å Mercury Photosensitization B4 (569) 60/765-65	Norman N. Lichtin and Morton Z. Hoffman Department of Chemistry Boston University Boston, Massachusetts
Charge and Energy Transfer in Organic Systems E4,17 (570) 60/68-1561	Lawrence E. Lyons Department of Chemistry University of Queensland St. Lucia, Brisbane Australia
High Pressure (3-5 Kb.) Inorganic and Organometallic Syntheses R4,5 (869) 10/1519	Alan G. MacDiarmid Department of Chemistry University of Pennsylvania Philadelphia, Pennsylvania
Structural Relaxation in Molten Glasses R2 (869) 37/68-1376A	Pedro B. Macedo Department of Chemistry Catholic University of America Washington, DC

Viscous Flow and Compressibility of Molten Borates at High Pressure R4 (968) 10/1460	John D. Mackenzie Department of Chemistry Rensselaer Polytechnic Institute Troy, New York
Viscosity and Electrical Conductivity of Glasses at Constant Volume R1 (969) 37/69-C-0041	
Defect States and Structure of Oxide Glasses R4 (869) 37/67-0974A	John H. Mackey, Jr. Carnegie-Mellon University Pittsburgh, Pennsylvania
Plasma Pinch Flash Photolysis B4 (869) 60/980-67	Gilbert J. Mains Department of Chemistry University of Detroit Detroit, Michigan
Investigation of Photochemistry Related to Polymerization R2 (1269) 36/68-C-0043	J. David Margerum Photochemistry Section Hughes Research Laboratories Malibu, California
Study of Kinetic Methods of Chemical Analysis E3 (1069) 36/1212-67	Dale W. Margerum Harry L. Pardue Department of Chemistry Purdue University Lafayette, Indiana
The Solvent Extraction Behavior of Inorganic Complexes E4 (969) 10/1387-68	Ray L. McDonald Department of Chemistry University of Hawaii Honolulu, Hawaii
The Interaction of Molecular Beams with Atomically Clean Metal Single Crystals which are Chemically Reactive B2 (969) 38/68-1409	Robert P. Merrill Department of Chemistry University of California Berkeley, California
Studies in Stereochemistry M3 (769) 62/1188-67A	Kurt Mislow Department of Chemistry Princeton University Princeton, New Jersey
Adsorption of Organic Molecules at Electrodes W2 (1269) 60/68-1451	David M. Mohilner Department of Chemistry Colorado State University Fort Collins, Colorado

Chemistry of Organolithium Compounds and Acetylenes M4 (968) 62/720-65	James Mulvaney Department of Chemistry University of Arizona Tucson, Arizona
Fundamental Studies of Electrochemical Processes E2 (970) 36/69-1625	Royce W. Murray and Charles N. Reilley Department of Chemistry University of North Carolina Chapel Hill, North Carolina
Structure of Molten Salts and Glasses E4 (170) 10/1086-66	Norman H. Nachtrieb Department of Chemistry University of Chicago Chicago, Illinois
Reactions of Molecules in Excited States with Paramagnetic Gases W4 (1268) 60/778-67	W. Albert Noyes, Jr. Department of Chemistry University of Texas Austin, Texas
The Detailed Photochemical Primary Process, the Role of Vibrational Relaxation E2 (1270) 38/69-1682	
Molecular Interactions and Crystal Structures at Low Temperatures W4 (170) 60/68-1549	Stanley Nyburg Department of Chemistry University of Toronto Toronto, Canada
An Investigation of the Mechanism of the Reaction Between Boron Trifluoride and Nitrogen (III, IV, V) E4 (570) 10/68-1556	P. R. Ogle, Jr. Department of Chemistry Otterbein College Westerville, Ohio
Electrochemistry of Transition Metal Ions in Acetonitrile W4 (1168) 10/777-67	John W. Olver Department of Chemistry University of Massachusetts Amherst, Massachusetts
Vibrational Anharmonicity and Rotation-Vibration Interaction in Polyatomic Molecules E3 (969) 39/67-0570A	John Overend Department of Chemistry University of Minnesota Minneapolis, Minnesota
Chemistry of Radiation Protecting Agents B4 (270) 60/68-1417	John Packer Department of Chemistry University of Auckland Auckland, New Zealand

Photochemical Generation of Divalent Carbon Derivatives M4 (269) 62/1213-67	Albert Padwa Department of Chemistry State University of New York Buffalo, New York
Vapor Phase Calorimetry W4 (369) 62/810-67	Joseph D. Park and John R. Lacher Department of Chemistry University of Colorado Boulder, Colorado
Kinetics of Ion-Complex Formation in Mixtures of Fused Salts Studied by Ultrasonic Absorption R4 (970) 38/67-1185A	Sergio Petrucci Department of Chemistry Brooklyn Polytechnic Institute Brooklyn, New York
Gas Phase Reaction of Atoms, Radicals and Simple Molecules B4 (271) 38/67-1265A	Leon F. Phillips Department of Chemistry University of Canterbury Christchurch, New Zealand
Ultrarapid-scan Infrared Spectroscopy E4 (170) 60/68-1536	George C. Pimentel Department of Chemistry University of California Berkeley, California
Chemical Reactions in Frozen Solutions M4 (270) 62/66-1102A	Richard E. Pincock Department of Chemistry University of British Columbia Vancouver, Canada
AFOSR Program for Research on Liquid Structure B2 (869) 37/68-1382A	C. J. Pings Department of Chemical Engineering California Institute of Technology Pasadena, California
Heteropoly Compounds of Group VB Elements E4 (270) 10/1066-66	Michael T. Pope Department of Chemistry Georgetown University Washington, DC
Primary Photoprocesses in Organic Materials B1 (1069) 38/68-C-0010	G. Porter Department of Chemistry Royal Institute of Great Britain London W.1., England
Intermolecular Energy Transfer B4 (969) 38/1633	B. S. Rabinovitch Department of Chemistry University of Washington Seattle, Washington

Theoretical and Experimental Studies in Chemical Physics B4 (1068) 60/781-67	Stuart A. Rice Department of Chemistry University of Chicago Chicago, Illinois
Experimental and Theoretical Studies of Matter and Radiation and Their Interaction B1 (1069) 39/69-1663	
High-Resolution Spectroscopy of Small Molecules in the Gaseous State E4 (170) 40/1644	G. Wilse Robinson Department of Chemistry California Institute of Technology Pasadena, California
Photochemical Studies in Atomic Chemistry B2 (1269) 60/68-1493	John W. Root Department of Chemistry University of California Davis, California
Basic Studies of Liquid Crystals as Related to Electro-Optical and Other Devices E2 (569) 9737/67-C-0102	H. C. Scala Chemical Technology Westinghouse Research Labs Pittsburgh, Pennsylvania
Lifetime Spectrometry B3.17 (769) 38/68-1615	Edward W. Schlag Department of Chemistry Northwestern University Evanston, Illinois
Differential Electrical Double Layer Capacities on Liquid and Solid Electrodes W4 (1269) 60/68-1452	Gerhard M. Schmid Department of Chemistry University of Florida Gainesville, Florida
Hot Atom Chemistry of Oxygen and Nitrogen B4 (1069) 38/68-1437A	Friedrich Schmidt-Bleek Department of Chemistry Purdue University Lafayette, Indiana
Organometallics as Reagents for the Generation of Reactive Intermediates M2 (1069) 40/68-1350A	Dietmar Seyferth Department of Chemistry Massachusetts Institute of Tech. Cambridge, Massachusetts
Inelastic Collisions between Molecular Systems B2 (869) 60/68-1354	Kyung Kyu Shin Department of Chemistry University of Nevada Reno, Nevada

Ion-Radicals of Organic Sulfur, Selenium, Tellurium and Phosphorus Compounds M4 (969) 40/69-1635	Henry J. Shine Department of Chemistry Texas Technological College Lubbock, Texas
Quantum Chemistry Program Exchange W6 (870) 39/67-0767A	Harrison Shull Department of Chemistry Indiana University Bloomington, Indiana
Electronic Computer Calculations on Simple Diatomic and Polyatomic Molecules E3,67 (869) 39/67-1242C	Harrison Shull and Stanley A. Hagstrom Department of Chemistry Indiana University Bloomington, Indiana
Atomic Chemistry M4 (1169) 40/69-1702	P. S. Skell Department of Chemistry Pennsylvania State University University Park, Pennsylvania
Applications of Preferential Solvation Studies to Inorganic Reaction Mechanisms M2 (969) 10/68-1384	Thomas R. Stengle Department of Chemistry University of Massachusetts Amherst, Massachusetts
Fifth International Congress of Photobiology R1 (369) 62/68-1546	Russell B. Stevens National Academy of Sciences Washington, DC
Organometallic Chemistry E4 (969) 40/69-C-0011	F. G. A. Stone Department of Chemistry University of Bristol Bristol, England
Quantum Organic Chemistry M4 (969) 39/68-1364	Andrew Streitwieser, Jr. Department of Chemistry University of California Berkeley, California
Polynuclear Hydroxo Complexes R4 (968) 10/691-67	R. Stuart Tobias Department of Chemistry University of Minnesota Minneapolis, Minnesota
Metallocene Chemistry and the Chemistry of Oxy Radicals W1 (869) 40/69-1639	T. G. Traylor Department of Chemistry University of California La Jolla, California

Sigma Pi Rearrangement M4 (269) 62/824-67	Minoru Tsutsui Department of Chemistry New York University New York, New York
Chemistry of Strained Ring Compounds M4 (1269) 40/68-1381A	Nicholas J. Turro Department of Chemistry Columbia University New York, New York
Kinetic Energy of Ionic Products from Electron and Ion-Molecule Reactions W4 (969) 60/1380-68	Eugene R. Weiner Department of Chemistry University of Denver Denver, Colorado
Electron Paramagnetic Resonance of Matrix-Isolated Molecules R1.5 (1169) 60/68-1588	William Weltner, Jr. Department of Chemistry University of Florida Gainesville, Florida
Transition Metal Ammine Complexes at High Pressures and Temperatures E6 (870) 36/69-1620	Wesley W. Wendlandt Department of Chemistry University of Houston Houston, Texas
Novel Organometallic Compounds M4 (270) 40/68-1521A	Robert C. West Department of Chemistry University of Wisconsin Madison, Wisconsin
Development of a Molecular Beam Accelerator B4.5 (869) 10/67-0886A	Lennard Wharton Department of Chemistry University of Chicago Chicago, Illinois
Electronic Structures of Molecules by Variational Methods and Correlation Corrections B4 (1069) 39/68-1438A	Donald R. Whitman and Douglas Carlson Department of Chemistry Case Western Reserve University Cleveland, Ohio
Laser Photolysis and Spectroscopy in the Nanosecond Time Range B1 (969) 38/69-C-0029	Maurice W. Windsor Chemical Sciences TRW Systems Redondo Beach, California
Flame Spectrometry and Gas Chromatographic Detectors R6 (1069) 36/69-1685	James D. Winefordner Department of Chemistry University of Florida Gainesville, Florida

SRC INSTITUTION LISTING

July 1968

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Harrison Shull
Harrison Shull &
Stanley A. Hagstrom

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Kent State U.
Glenn H. Brown (3)

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Samuel O. Grim

Mass. Inst. of Tech.
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Dietmar Seyferth

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Edward W. Schlag

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Va. Polytechnic Inst.
Raymond E. Dessy

Washington, U.

B. S. Rabinovitch

Washington State U.
Glenn A. Crosby

Weizmann Inst. of Science
Michael Anbar

Western Australia, U.
Bruce G. Hyde

Western Ontario, U.
D. R. Bidinosti

Westinghouse Rsch. Labs
H. C. Scala

Wisconsin, University
Jerome A. Berson
Harlan L. Goering
Robert C. West

Yeshiva University
Irving J. Borowitz

DIRECTORATE OF CHEMICAL SCIENCES

AFOSR ARLINGTON, VA.

RESEARCH PROJECTS COMPLETED IN FY 1968

(Alphabetic by Principal Investigator)

Nucleophilic Displacements on Trivalent Phosphorus R5 (967) 62/132-67	K. Darrell Berlin Department of Chemistry Oklahoma State University Stillwater, Oklahoma
Fundamental Investigations of Luminescent Materials R4 (967) 10/269-67	G. A. Crosby Department of Chemistry University of New Mexico Albuquerque, New Mexico
Structural Chemistry and Bonding in Inorganic Compounds E4 (1167) 10/518-66	Lawrence F. Dahl Department of Chemistry University of Wisconsin Madison, Wisconsin
Kinetics of Ion Formation in Shock Waves R4 (468) 60/504-66	John E. Dove Department of Chemistry University of Toronto Toronto, Canada
Atomic and Molecular Kinetics on Solid Surfaces R4 (168) 60/1362	Gert Ehrlich Structures and Reactions Branch General Electric Company Schenectady, New York
The AFOSR Center for Macromolecular Research at Stanford University M6.75 (1068) 60/1341	Paul J. Flory Department of Chemistry Stanford University Stanford, California
Electron Spin Resonance of Free Radicals E4 (767) 10/285-67	George K. Fraenkel Department of Chemistry Columbia University New York, New York
Pressure Dependence of Electrolytic Conductance R5 (668) 60/1148-66	Raymond M. Fuoss Department of Chemistry Yale University New Haven, Connecticut

Surface Stabilized Radicals R4 (168) 60/642-66	Hyman Gesser Department of Chemistry University of Manitoba Winnipeg, Canada
Liquid Crystal Reactions by Ellipsometry E. 33 (867) 67-C-0091	E. L. Grove Department of Chemistry IIT Research Institute Chicago, Illinois
NMR Studies of Intra- and Intermolecular Interactions W4 (867) 10/216-65	Melvin W. Hanna Department of Chemistry University of Colorado Boulder, Colorado
The Chemistry of Carbanions M4, 5 (668) 62/573-66	H. O. House Department of Chemistry Massachusetts Institute of Technology Cambridge, Mass
Crystal Chemistry of New High Pressure Phases R, H4 (1267) 10/1361	J. S. Kasper Metallurgy and Ceramics Lab General Electric Company Schenectady, New York
Transition Metal Complexes Containing Nitrogen, Phosphorus, or Sulfur E5 (1267) 10/1211-67	R. Bruce King Department of Chemistry University of Georgia Athens, Georgia
Sixth Rare Earth Research Conference M1 (1067) 10/1-67	Wallace C. Koehler Solid State Division Atomic Energy Commission (ONRL) Oak Ridge, Tennessee
Kinetics of Transition-Metal Ions of d^8 Electronic Configuration B3 (668) 10/66-994A	David J. MacDonald Department of Chemistry University of Nevada Reno, Nevada
The Acid-Base Characteristics of Phototropism M4 (967) 62/1264	J. David Margerum Photochemistry Section Hughes Research Labs. Malibu, California
Oxidation of Arsenic (III) and Antimony (III) E4 (967) 10/210-65	John G. Mason Department of Chemistry Virginia Polytechnic Institute Blacksburg, Virginia

Electrochemical Studies of Kinetics Adsorption, and Excited Electronic States E4 (368) 60/584-66	Royce W. Murray and Charles N. Reilley Department of Chemistry University of North Carolina Chapel Hill, North Carolina
Characterization of Macromolecular Structure M2 (568) 60/1179-66	Martin A. Paul National Research Council National Academy of Sciences Washington, DC
A Study of the Support of Fundamental Research in the Chemistry of the AFOSR B1 (268) 62/1302-67	Martin A. Paul Lockhart B. Rogers National Research Council National Academy of Sciences Washington, DC
AFOSR Program for Research on Liquid Structures B4 (967) 10/1273	C. J. Pings Department of Chemical Engineering California Institute of Technology Pasadena, California
Displacement (Reactions by Free Radicals) on S-S and O-O Bonds M4 (867) 62/540-66	William Pryor Department of Chemistry Louisiana State University Baton Rouge, Louisiana
Acidity Dependence of Reaction Rates and Equilibria in Strong Aqueous Acids M4 (1267) 62/590-66	William M. Schubert Department of Chemistry University of Washington Seattle, Washington
Organometallic Synthesis of Reactive Intermediates M4 (1067) 62/502-66	Dietmar Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, Mass
Electronic Computer Calculations on Simple Diatomic and Polyatomic Molecules E1 (1267) 60/1242-67	Harrison Shull Stanley A. Hagstrom Department of Chemistry Indiana University Bloomington, Indiana

Photochemistry of Azo Compounds and Studies in Unimolecular Reactions B4 (1267) 60/583-66	Colin Steel Department of Chemistry Brandeis University Waltham, Mass
Rates of Exchange of Solvent Molecules with Paramagnetic Ions M4.5 (867) 60/212-65	T. R. Stengle C. H. Langford Department of Chemistry University of Massachusetts Amherst, Mass
Structure and Reactivity of Solutions of Metals in Non-Metallic Solvents W6 (1267) 10/64-80	M.C.R. Symons Department of Chemistry University of Leicester Leicester, England
Reaction Rate Studies of Gaseous Unimolecular Isomerizations E5 (867) 60/119-65	Frederick D. Tabbutt Department of Chemistry Reed College Portland, Oregon
Solvent Isotope Effects for CH_3OH vs. CD_3OH M4.5 (1067) 62/431-65	Edward R. Thornton Department of Chemistry University of Pennsylvania Philadelphia, Pennsylvania
Carbonium Ion Radicals and Oxy Radicals M4.5 (368) 62/514-66	Teddy G. Traylor Department of Chemistry University of California San Diego, LaJolla, Calif.
Concentration Fluctuations in the Vicinity of the Critical Point B2 (1267) 60/1253-67	Benjamin Widom Department of Chemistry Cornell University Ithaca, New York
Unimolecular Decomposition of Cyclobutane Derivatives at High Pressure W4 (568) 60/575-66	David J. Wilson Department of Chemistry University of Rochester Rochester, New York
Gordon Research Conference on Inorganic Chemistry E2 (369) 10/1103-67	Seymour Yolles and Grant W. Urry Gordon Research Conferences University of Rhode Island Kingston, Rhode Island

COMPLETED PROJECT SUMMARY

1. TITLE: Nucleophilic Displacements on Phosphorus Esters

2. PRINCIPAL INVESTIGATOR: Dr. K. D. Berlin
Department of Chemistry
Oklahoma State University
Stillwater, Oklahoma

3. INCLUSIVE DATES: 1 October 1962 - 31 August 1967

4. GRANT NOS: AF-AFOSR-132-63; AF-AFOSR-132-65; AF-AFOSR-132-67

5. COSTS AND FY SOURCE: $21,708 FY63; $24,283 FY65; $6000 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. Mandava Nagabhushanam
Dr. R. U. Pagilagan

7. JUNIOR RESEARCH PERSONNEL: T. Howard Austin
Herbert E. Peterson

8. PUBLICATIONS:

"Nucleophilic Displacement Reactions on Organophosphorus Esters by Grignard Reagents. I." K. D. Berlin, T. H. Austin, and K. L. Stone, J. Am. Chem. Soc., 86, 1787 (1964).

"Nucleophilic Displacement Reactions on Organophosphorus Esters and Halides by Grignard and Lithium Reagents," chapter in Topics in Phosphorus Chemistry, M. Grayson and E. Griffith, Eds., Interscience Publishers, New York; K. D. Berlin, T. H. Austin, M. E. Peterson and M. Nagabhushanam, Vol. I., 17 (1964).

"Unsymmetrical Tertiary Phosphine Oxides from Diphenyl Phenylphosphinate. A Convenient Synthesis," K. D. Berlin and M. Nagabhushanam, Chem. Ind. (London), 974 (1964).

"A Convenient Synthesis of Esters of Diphenylphosphinic Acid. III," K. D. Berlin, T. H. Austin, and M. Nagabhushanam, J. Org. Chem., 30, 1267 (1965).

"The Pyrolysis of Alkyl Diphenylphosphinates," K. D. Berlin and T. H. Austin, J. Org. Chem., 30, 2745 (1965).

"Gas Chromatographic Analyses of Organophosphorus Compounds Using a Hydrogen Flame Ionization Detector. The use of Chromosorb G as a Solid Support," K. D. Berlin, T. H. Austin, M. Nagabhushanam, M. Peterson, J. Calvert, L. A. Wilson and D. Hopper, J. Gas Chromatorgraphy. 3, 256 (1965).

"Structural Effects on the Complexing Ability of Alkyl Diphenylphosphinates With Magnesium Iodide," K. D. Berlin and R. U. Pagilagan, Chem. Commun., 19, 687 (1966).

"Nucleophilic Displacement Reactions on Organophosphorus Esters by Grignard Reagents. II. Evidence for Competitive Displacements on Carbon and Phosphorus in the Reaction of Grignard Reagents with Simple Phosphates." K. D. Berlin and M. E. Peterson, J. Org. Chem., 32, 125 (1967).

"Nucleophilic Displacement Reactions on Organophosphorus Esters by Grignard Reagents. III. The Reactions of Alkyl Diphenylphosphinates With Alkyl Grignards." K. D. Berlin and R. U. Pagilagan, J. Org. Chem., 32, 129 (1967).

"Studies on the Mechanism of Thermal Decomposition of Alkyl Diphenylphosphinates," K. D. Berlin, M. E. Peterson, W. Pivonka, and T. H. Austin, manuscript in preparation.

"Nucleophilic Displacements on Phosphorus Esters," Final Technical Report, AFOSR 67-2247.

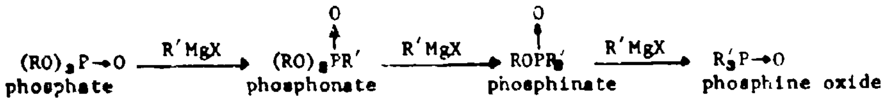
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This study was undertaken in an effort to determine the chemistry of reactions involving attack of Grignard reagents on phosphorus esters. Phosphites, phosphonites, phosphinites, phosphates, phosphonates, and phosphinates were examined, and the following sequence of steps for the reactions was established.

Trivalent Phosphorus Esters

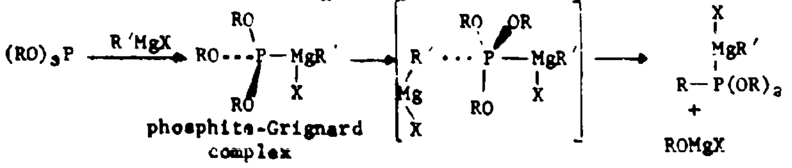
$$\underset{\text{phosphite}}{(RO)_3P:} \xrightarrow{R'MgX} \underset{\text{phosphonite}}{(RO)_2PR'} \xrightarrow{R'MgX} \underset{\text{phosphinite}}{ROPR'_2} \xrightarrow{R'MgX} \underset{\text{phosphine}}{R'_3P}$$

Tetrasubstituted Phosphorus Esters



$$\underset{\text{phosphate}}{(RO)_3P\rightarrow O} \xrightarrow{R'MgX} \underset{\text{phosphonate}}{(RO)_2\overset{\overset{O}{\uparrow}}{P}R'} \xrightarrow{R'MgX} \underset{\text{phosphinate}}{RO\overset{\overset{O}{\uparrow}}{P}R'_2} \xrightarrow{R'MgX} \underset{\text{phosphine oxide}}{R'_3P\rightarrow O}$$

Evidence based on an isolated solid complex and careful analysis of the reaction mixture by gas chromatography suggests the displacement of OR from phosphorus is stepwise. An S_n2 mechanism in the displacement appears likely.



The stability of the complexes of the esters is believed to be in the following decreasing order: $(CH_3O)_3P > (CH_3O)_2PR' > CH_3OPR'$. A special column for gas chromatographic analysis was developed which consisted of silanized Chromosorb G as support with 5% Silicone 30 as the substrate coating. Complex mixtures containing as many as ten different phosphorus compounds could be separated by a single injection on the column.

It was found that coordination of Grignard reagent with a phosphate, phosphonate or phosphinate was required before tetrasubstiuted phosphorus esters would undergo extensive nucleophilic displacement. An investigation of the kinetics of reaction of several phosphonates with methyl Grignard reagent (CH_3MgI) gave results which indicated the process did not follow a simple first, second or third kinetic order.

During the course of synthesizing the phosphinates, it was discovered that the esters with at least one β-porton in the alcoholic portion underwent thermal decomposition below 250°. Virtually free of side reactions, the pyrolysis proceeds smoothly to diphenyl phosphinic acid and an alkene in near quantitative yield with fifteen esters. This novel elimination does not appear plagued with skeletal rearrangements in the alkenes produced since diphenylphosphinic acid (the only acidic product) is markedly insoluble in most organic liquids. Consequently, the process has promise of being a useful method of producing a alkenes without creating complex mixtures.

Dr. W. L. Ruigh
(Reviewed by LtCol L. D. Whipple)

COMPLETED PROJECT SUMMARY

1. TITLE: Fundamental Investigations of Luminescent Materials

2. PRINCIPAL INVESTIGATOR: Dr. G. A. Crosby
Department of Chemistry
University of New Mexico
Albuquerque, New Mexico

3. INCLUSIVE DATES: 1 January 1963 - 14 September 1967

4. GRANT NOS: AF-AFOSR-269-63; AF-AFOSR-269-63A; AF-AFOSR-269-65; AF-AFOSR-269-67

5. COSTS AND FY SOURCE: $57,380.66 FY63; $20,000 (RADC): $83,922 (including $20,000 from RADC) FY65; $19,518 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. S. J. Ladner
Dr. C. M. O'Donnell
Dr. W. G. Perkins

7. JUNIOR RESEARCH PERSONNEL: Dean H. W. Carstens
H. James Clifford
Jane L. Crosby
James N. Demas
Raymond W. Harrigan
David M. Klassen
Richard B. Lehmann
Brian J. Pankuch
Jea Y. Rhee
Sonia L. Sabath
Thomas R. Thomas

8. PUBLICATIONS:

"Luminescence from Transition-Metal Complexes: Tris(2,2'-bipyridine)- and Tris(1,10-phenanthroline)Ruthenium(II)", G. A. Crosby, W. G. Perkins, and D. M. Klassen, J. Chem. Phys., 43,1498 (1965).

"Luminescent Organic Complexes of the Rare Earths", G. A. Crosby, Molecular Crystals, 1, 37(1966).

"Intramolecular Energy Transfer in Osmium(II) Complexes", G. A. Crosby, D. M. Klassen, and S. L. Sabath, Molecular Crystals, 1, 453 (1966).

"Optical Excitation of Transition-Metal Ions Via Intramolecular Energy Transfer", G. A. Crosby, J. Chem. Phys. (Paris) 64 160 (1967).

"Reassignment of the Luminescence From Ruthenium(II) Complexes", D. M. Klassen and G. A. Crosby, Chem. Phys. Letters, 1, 127 (1967).

"Ligand-Field Transitions in Tertiary Phosphine and Arsine Complexes", D. M. Klassen and G. A. Crosby, J. Mol. Spectry. (in press).

"Spectroscopic Studiesof Ruthenium(II) Complexes", D. M. Klassen and G. A. Crosby, J. Chem. Phys. (in press).

"On the Multiplicity of the Emitting State of Ruthenium(II) Complexes", J. N. Demas and G. A. Crosby, J. Mol. Spectry. (in press).

"Luminescent Organic Complexes of the Transition Metals", a review, D. H. W. Carstens and G. A. Crosby (to be submitted to Molecular Crystals).

"Quantum Yields of Photoluminescent Compounds", a review, J. N. Demas and G. A. Crosby (in preparation).

"Fundamental Investigations of Luminescent Materials", Final Technical Report, AFOSR, 68-0213.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main purpose of the research was to study the fundamental processes occurring in luminescent materials after the primary act of energy absorption. A second objective was to search for new luminescent substances of possible technological importance guided by the criteria established by our concomitant fundamental studies on energy transfer.

Numerous complexes of ruthenium(II), cobalt(III), osmium(II), iridium(III), rhodium(II , and platinum(IV) having π-conjugated ligands were studied spectroscopically. Many of the materials were discovered to be highly-efficient, photochemically-stable, luminescent substances. Some of them exhibit properties which suggest potential value as active materials for electro-optical and laser devices.

Considerable progress was made toward the elucidation of the systematics of energy migration in transition-metal complexes. The role of charge-transfer $(d\text{-}\pi^*)$ states relative to $d\text{-}d^*$ and $\pi\text{-}\pi^*$ states in controlling the optical behavior of the molecules was defined. General experimental criteria were formulated which can be used to aid significantly in the task of making state assignments for new luminescent complexes of transition metals.

For some substances we succeeded in completely changing the nature of the emissions observed by making minor modifications in the structure of the molecules which led to excited-state level inversion.

Triplet states in rhodium complexes which are inaccessible by absorption measurements have been located experimentally via emission spectroscopy.

A novel photochemical reaction was discovered involving the ruthenium(II) ion which has an interesting electronic interpretation and points toward the existence of other photochemical reactions of the same general type.

Dr. W. L. Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Structural Chemistry and Bonding in Inorganic Compounds

2. PRINCIPAL INVESTIGATOR: Dr. Lawrence F. Dahl
Department of Chemistry
University of Wisconsin
Madison, Wisconsin

3. INCLUSIVE DATES: 1 October 1963 - 30 September 1967

4. GRANT NUMBER: AF-AFOSR-518-64; AF-AFOSR-518-66

5. COSTS AND FY SOURCE: $48,420 FY63; $58,020 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. C. H. Wei
Dr. P. Woodward

7. JUNIOR RESEARCH PERSONNEL:
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D. L. Stevenson
J. F. Blount
S. F. Watkins
W. R. Costello
G. R. Wilkes
M. A. Neuman
R. W. Perry
J. A. Coleman
V. R. Magnuson
J. A. Molin-Case
R. P. White
R. M. Sweet

8. PUBLICATIONS:

"The Molecular Structure of a Tricyclic Complex, $SFe(CO)_3\ {}_2$," C. H. Wei and L. F. Dahl, Inorg. Chem., 4, 1(1965).

"Crystal Structure of a 1:1 Mixture of Two Iron Carbonyl Sulfur Complexes, $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$," C. H. Wei and L. F. Dahl, Inorg. Chem., 4, 493 (1965).

"The Structure of Hexamethylbenzene Chromium Tricarbonyl with Comments on the Dibenzene Chromium Structure," M. F. Bailey and L. F. Dahl, Inorg. Chem. 4, 1298 (1965).

"Structure of Thiophene Chromium Tricarbonyl, $C_4H_4SCr(CO)_3$," M. F. Bailey and L. F. Dahl, Inorg. Chem., 4, 1306 (1965).

"Three-Dimensional Crystal Structure of Benzene Chromium Tricarbonyl with Further Comments on the Dibenzene Chromium Structure," M. F. Bailey and L. F. Dahl, Inorg. Chem., 4, 1314 (1965).

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"Structure and Bonding of the (Substituted Thiophene)-Metal Complex, $2,5\text{-}(CH_3)_2C_4H_2SCr(CO)_3$," R. W. Perry and L. F. Dahl, in preparation.

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"Structural Chemistry and Bonding in Inorganic Compounds," Final Report, AFOSR

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Symmetematic structural investigations not only have led to the characterization of new general types of organometallic complexes but also have provided new structural and bonding principles. These investigations have included studies on a wide variety of unusual organo(transition metal) sulfur complexes. It has been shown that a sulfur atom can function as a doubly-bridging two-electron donating group, a triply-bridging four-electron donating group, a quadruply bridging four-electron donating group, and a quadruply-bridging six-electron donating group in organometallic complexes. This work has also uncovered the fact that disulfide groups can be coordinated to one, two, or four transition metals. In addition, several new kinds of metal atom cluster systems have been uncovered, and the importance of metal-metal interactions on the molecular geometries of polynuclear metal carbonyl and cyclopentadienyl complexes has been assessed for several complexes. A brief summary of this work is given below.

The molecular structure of $(C_5H_5MoO)_2\ S_2$ (Stevenson and Dahl) revealed the first known example of an organometallic complex which contains doubly bridging sulfur atoms linking two transition metals. A direct molybdenum-molydenum electron-pair bond of considerable strength is necessary to account for the sharply acute bridging angles in diamagnetic complexes.

A structural study of a new cluster system, $Co_3(CO)_9S$, prepared by the reaction of dicobalt octacarbonyl with phenol mercaptan, has shown it to contain a sulfur atom symmetrically bridging three metal atoms. The molecular configuration of C_{3v} symmetry consists of an apical sulfur atom coordinated by three cobalt-sulfur bonds to a $Co_3(CO)_9$ fragment of three equilaterally arranged cobalt tricarbonyl groups linked to one another by Co-Co bonds. Comparison was made of the prominent structural features of $Co_3(CO)_9S$ with those of $Co_3(CO)_9CCH_3$ and other related molecular complexes.

An X-ray analysis of $[Co_3(CO)_7S]_2S_2$ established the first example of a disulfide bridging group symmetrically linked to four transition metals. The molecular geometry of C_{2v} symmetry has two $Co_3(CO)_7$ moieties connected to each other by a disulfide bridge. Comparison of its structural features with those of its closely-related chemical precursor, $Co_3(CO)_9S$, indicated that the significant difference of 0.1 Å in Co-Co bond lengths in the latter molecule must be primarily a consequence of the unpaired electron in $Co_3(CO)_9S$. This prediction was verified, and subsequent work on related cluster systems has shown that valence electrons can drastically influence molecular geometries.

A chemical and physical characterization of the complex $[CH_3SFe_2(CO)_6]_2S$ revealed the first known case of an organometallic complex containing a tetrahedral-like sulfur atom bridging four metal atoms. The molecular geometry of C_2 symmetry is comprised of two identical $[CH_3SFe_2(CO)_6]$ fragments bridged by a metal-coordinated tetrahedral-like sulfur atom which donates six of its valence electrons to the four iron atoms. The properties and structural features of this compound were compared to those of $[C_2H_5SFe(CO)_3]_2$ and other related systems.

Structural investigations of the Treichel-Werber compounds $(C_5H_5)_2NbS_2X$ (X = Cl, I) and $(C_5H_5)_2NbOCl$ have yielded molecular parameters for the first known examples of an S_2 group bonded to only one transition metal atom. The structure of $(C_5H_5)_2NbS_2Cl$ shows the two bonded sulfur atoms to be equidistant from the niobium metal and oriented such that the niobium, chlorine, and both sulfur atoms are coplanar. The S_2 group, the chlorine atom, and the two cyclopentadienyl rings are disposed in a distorted tetrahedral arrangement about the central niobium atom. The remarkable feature of this chlorine complex is the unusually short S-S distance of only 1.76 Å which is 0.13 Å less than that of 1.89 Å in free S_2 which exists only at high temperatures. In contrast the O-O distances in all the structurally-characterized metal-O_2 compounds invariably are greater than that of 1.21 Å in free O_2. These opposite changes in O-O and S-S distances on metal complexation were rationalized from molecular orbital energy diagrams. Subsequently, the structural analysis of $(C_5H_5)_2NbS_2I$ verified the hypothesis based on these MO correlation diagrams that the iodide derivative possesses a different electronic ground state configuration from that of the chloride complex.

A new cyclopentadienyl metal cluster $C_5H_5FeS_4$, prepared by the reaction of $[C_5H_5Fe(CO)_2]_2$ with cyclohexene sulfide, was characterized by a structural study as a tetrameric system. This structural analysis showed that the observed configuration of D_{2d} tetragonal symmetry can be rationalized as a stereochemical consequence of each iron atom attaining a closed-shell configuration by formation of only one metal-metal bond.

A structural investigation of $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ revealed a new basic polyhedral unit for a triangular metal cluster. Comparison of the structural and bonding features was made with the $[Re_3Cl_{12}]^{3-}$ triangular cluster. A preparation and structural characterization of the complex $Co_5(CO)_{10}(SC_2H_5)_5$ and the structural analysis of $SCo_6(CO)_{11}(SC_2H_5)_4$ showed these systems to be closely related to the trimeric cobalt carbonyl complex. The application of a metal-atom cluster molecular orbital model showed that in contrast to the metal cluster halide and oxide systems that these metal carbonyl clusters contain electrons in antibonding metal symmetry orbitals.

Deuton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Kinetics of Ion Formation During Chemical Reaction in Shock Waves

2. PRINCIPAL INVESTIGATOR: Dr. J. E. Dove
Department of Chemistry
University of Toronto
Toronto 5, Ontario
Canada

3. INCLUSIVE DATES: 15 October 1963 - 14 April 1968

4. GRANT NOS: AF-AFOSR-504-64; AF-AFOSR-504-66

5. COSTS AND FY SOURCE: $17,528 FY64; $25,170 FY66

6. SENIOR RESEARCH PERSONNEL: Dr. R. Burke
Dr. R. A. Kane

7. JUNIOR RESEARCH PERSONNEL: R. A. Creswell
M. A. Di Valentin

8. PUBLICATIONS:

"Mass Spectrometric Observation of Ions Formed During Shock Wave Heating of Gaseous Krypton and Xenon," R. Creswell, M. A. Di Valentin and J. E. Dove, Phys. Fluids 9, 2285 (1966).

"Shock Tube Studies of Thermal Ionization of NO Using Mass Spectrometric Detection," R. Creswell, M. A. Di Valentin and J. E. Dove, Phys. Fluids (to be published).

"Mass Spectrometric Studies of Chemical Reactions in Shock Waves. III. Ionization in the C_2H_2-O_2 and C_2H_2-H_2-O_2 Systems," R. Burke, J. E. Dove and R. A. Kane (in preparation).

"Kinetics of Ion Formation During Chemical Reaction in Shock Waves," Final Technical Report, AFOSR

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to study the mechanism and rates of processes which form ions in high temperature gases. Two types of interaction were the object of particular attention, (i) direct formation of ions as a result of chemical reaction, and (ii) energy transfer processes leading to electronic excitation, with subsequent formation of positive ions and free electrons or negative ions.

The apparatus which was built for this work included a quadrupole mass spectrometer, and a stainless steel shock tube with its associated instrumentation. The gas to be studied was heated to a chosen temperature in the range 1700 to 8000°K in the shock tube. The formation of ions was followed by sampling the heated gas directly from the reflected shock region into the ion focusing system of the mass spectrometer. The mass spectrometer had previously been set at a chosen mass number so that the time-dependence of the concentration of a particular ion could be followed.

Using this apparatus, a detailed kinetic study has been made of the formation of positive ions during hydrocarbon oxidation. These ions evidently result from a direct chemical reaction process. Most of the experiments were made on C_2H_2-O_2-Ar and C_2H_2-H_2-O_2-Ar mixtures of various reactant ratios at 1700 to 2700°K. The principal ions, which were found in all mixtures, were mass 19 (H_3O^+), 29 (HCO^+), and 39 ($C_3H_3^+$). The kinetic behaviour of each of these ions was studied, measurements being made of the induction period for ion formation, the time constant of the exponential growth period of formation, and the decay rate. H_3O^+ and HCO^+ showed very similar kinetic behaviour, but there were significant differences between their behaviour and that of $C_3H_3^+$. Small amounts of mass 51 ($C_4H_3^+$) and 63 ($C_5H_3^+$) were also found.

A study has been made of the initial ionization processes in gaseous krypton and xenon at 3600 to 7800°K. Earlier workers had found that there was an initial burst of ionization, which was followed by a much slower growth to the equilibrium degree of ionization. In the present work, it was shown that the initial burst is due to impurity ionization. A number of different impurity ions were identified and their behaviour studied.

Thermal ionization of gaseous NO, highly dilute in krypton, has been studied at 3500 to 6100°K. Analysis of the results strongly suggests that ionization occurs through a direct excitation of the NO molecule, rather than by the chemi-ionization process which has been postulated to account for the ionization of high temperature air.

Dr. W. L. Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Atomic and Molecular Kinetics on Solid Surfaces

2. PRINCIPAL INVESTIGATOR: Dr. Gert Ehrlich
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3. INCLUSIVE DATES: 1 February 1964 - 31 January 1968

4. CONTRACT NO: AF49(638)-1362

5. COSTS AND FY SOURCE: $40,120 FY64; $41,185 FY65; $42,724 FY66;
$42,772 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. T. A. Delchor
Dr. H. Heyne

7. JUNIOR RESEARCH PERSONNEL: F. G. Hudda
C. F. Kirk

8. PUBLICATIONS:

"Chemisorption on Solids," G. Ehrlich, in *Third International Congress on Catalysis*, W. M. H. Sachtler, G. C. A. Schuit, and P. Zwieterling, eds., North-Holland Publishing Co., Amsterdam, 113-145 (1965).

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" Atomic Processes at Solid Surfaces," G. Ehrlich, Ann. Rev. Phys. Chem., 17, 295 (1966).

"Chemisorption on Single-Crystal Planes," G. Ehrlich, Faraday Soc. Disc., 41, 7 (1966).

"Binding and Field Desorption of Individual Tungsten Atoms," G. Ehrlich and C. F. Kirk, J. Chem. Phys., 48 (1968).

"Atomistics of Metal Surfaces" G. Ehrlich, *Proceedings of the International Symposium on Surface Phenomena of Metals*, to be published.

"Atomic and Molecular Kinetics on Solid Surfaces," Final Technical Report, AFOSR-68-0456.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to study and elucidate the atomic phenomena basic to the process of adsorpti on. Two areas of work were emhasized: (1) The mechanism of activated adsorption and (2) The behavior of individual absorbed atoms. In the first area molecular beam techniques were planned to specify the atomic mechanism. In the second area it was hoped to obtain a view of the surface and the properties of adsorbed entities on an atomic scale through the use of the field ion microscope.

Contact potential measurements on single-crystal planes have established that specific chemical interactions occur at the gas-solid interface depending upon the orientation of the surface. This specificity has been achieved in massive specimens, prepared by standard techniques, pointing to possible utilization of such effects in practical problems.

The first studies of surface self-diffusion on different crystal planes have been carried out for tungsten adatoms. With the exception of the (211) plane, the diffusion coefficient, deduced from observations on individual atoms with the field ion microscope, is normal. Unexpected differences in the barriers to migration, as well as unusual effects at lattice steps, are observed on crystal planes of different orientations.

The first measurements to ascertain the binding energy of metal atoms on different faces of the parent crystal have been made. Determinations on the (110), (211), (310), (111), (321), and (411) reveal that binding of tungsten adatoms does not obey the rules of pairwise additivity. Contrary to expectation, the rougher surfaces interact less strongly than smooth planes like (211), leading to the view that electron redistribution at protruding surface sites lowers the binding energy.

A new mechanism for surface self-diffusion is proposed involving the coordinated motion of lattice atoms in the activated complex. This should be of importance on all planes with surface atoms of low coordination.

The first observations of physical adsorption on atomically smooth f.c.c. metals reveal a strong structural specificity; this is in agreement with the predictions of pair-interactions obeying a Lennard-Jones potential.

Dr. W. L. Ruigh
(Reviewed by LtCol [illegible] D. Whipple)

COMPLETED PROJECT SUMMARY

1. TITLE: AFOSR Center for Macromolecular Research at Stanford University

2. PRINCIPAL INVESTIGATOR: Dr. Paul J. Flory
Department of Chemistry
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3. INCLUSIVE DATES: 1 September 1962 - 30 June 1968

4. GRANT/CONTRACT NOS: AF-AFOSR-62-131; AF49(638)-1341

5. COSTS AND FY SOURCE: $167,020 FY62; $178,705 FY64; $84,842 FY66;
$88,394 FY67; $54,018 FY68

6. SENIOR RESEARCH PERSONNEL:

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Dr. A. Abe
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R. G. Ireson
J. L. Ellenson
Robert Holwerda
W. P. Gorth

8. PUBLICATIONS:

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"Thermodynamic Properties of Binary Mixtures of n-Alkanes," R. A. Orwoll and P. J. Flory, J. Am. Chem. Soc., 89, 6822 (1967).

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"The Thermodynamics of Polymer Solutions. IV. Polyisobutylene and n-Pentane," B. E. Eichinger and P. J. Flory, Trans. Faraday Soc., 64, 2066 (1968).

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"Strain Birefringence of Polymer Chains," P. J. Flory, R. L. Jernigan and A. E. Tonelli, J. Chem. Phys., 48, 3822 (1968).

"The Kerr Effect in Polymer Chains," P. J. Flory and R. L. Jernigan, J. Chem. Phys., 48, 3823 (1968).

"Analysis of the Random Configuration of the Polycarbonate of Diphenylol-2,2'-Propane," A. D. Williams and P. J. Flory, J. Poly. Sci., A-2, in press (1968).

"Configurational Distribution for Finite Chain Molecules," R. L. Jernigan and P. J. Flory, J. Poly. Sci., C, in press (1968).

"Research on Macromolecules," Final Technical Report, AFOSR-68-

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A program of research on macromolecules was initiated at Stanford University under the sponsorship of the United State Air Force in September of 1961. This Project Summary covers the period of AFOSR Grant 62-131 from September 1961 to January 1964 and of AFOSR Contract AF49(638)-1341 from February 1964 to June 1968.

Organic structural materials, including both those of natural origin and man-made synthetics as well, invariably are composed of macromolecular structures. The essence of this form of chemical constitution is the polymeric chain comprising a sequence of hundreds, thousands, or more, of atoms or groups linked covalently in linear sequence. In view of the prominence of the macromolecular theme at the level of chemical architecture amongst the essential materials of living organisms on the one hand and the synthetic polymers which find innumerable practical applications on the other, the study of this broad class of substances is scarcely in need of justification. Dr. Flory's investigations have been directed toward comprehension and formulation of basis of principles applicable to macromolecules generally. He and his co-workers were not concerned directly with particular areas or applications. Much is to be gained from this broad approach, for it offers the opportunity for the stimulation to be derived from cross-fertilization between different areas, and in particular from the co-related investigation of the chemically simpler synthetic polymers on the one hand and of the enormously more complex biopolymers on the other.

The research pursued by Dr. Flory and his research group include the following areas:

1. Theory of Network Elasticity.
2. The Crystalline State in Polymers.
3. Mechanochemical Transformations in Polymers.
4. Thermodynamics of Solutions.
5. Configurational Statistics of Polymer Chains and Treatment of Their Configuration-Dependent Properties.
6. Configurations of Polypeptide Chains and of Biopolymers.

The last three topics represent those fields in which the greatest progress has been made in this AFOSR-sponsored program. In brief, new methods have been developed (items 5 and 6) for treating the complexities posed by the immense variety of spatial configurations of a long macromolecular chain. These methods are mathematically exact. They are generally applicable to any chain of specified structure. This achievement opens the way for rational treatment of various properties of macromolecules in terms of chemical constitution, and Dr. Flory is confident that much progress will be forthcoming in this direction. A book has been written covering these and related developments.

Treatment of liquid solutions (item 4) for many years had made little progress beyond the early precepts of Raoult, Hildebrand, and van Laar. To be sure, theories have been generated by the hundreds, but in an artificial framework of idealized spherical particles and semi-arbitrary force fields that all but denied application to real systems. Dr. Flory's approach has been less ambitious, in a sense, for he and his co-workers rely on empirical information to characterize the pure liquid components, thereby avoiding the unsolved complexities of the real liquid state. On the other hand, his approach is applicable to mixtures of molecules of any size and shape, and hence offers the advantage of general applicability to actual solutions. It has been particularly successful in affording an understanding of the characteristics of polymer solutions which previous theories failed to explain.

Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Electron Spin Resonance of Free Radicals

2. PRINCIPAL INVESTIGATOR: Dr. George K. Fraenkel
Department of Chemistry
Columbia University
P. O. Box 866
New York 27, New York

3. INCLUSIVE DATES: 1 May 1963 - 31 July 1967

4. GRANT NOS: AF-AFOSR 285-63; AF-AFOSR 285-65; AF-AFOSR 285-67

5. COSTS AND FY SOURCE: $119,892 FY63; $129,962 FY65; $15,000 FY67

6. SENIOR RESEARCH PERSONNEL:
Dr. N. A. Ashford
Dr. B. L. Barton
Dr. J. R. Bolton
Dr. M. R. Das
Dr. R. E. Dehl
Dr. R. J. Faber
Dr. J. Gendell
Dr. O. W. Howarth
Dr. R. G. Lawler
Dr. R. E. Moss
Dr. M. K. M. Ng
Dr. J. M . Riveros
Dr. B. G. Segal
Dr. B. Venkataraman
Dr. W. G. Williams

7. JUNIOR RESEARCH PERSONNEL:
I. Bernal
W. J. Campion
E. Finkel
J. H. Freed
R. E. Hamby, Jr.
M. Kaplan
J. Marovskis
W. R. Miller
F. Millett
J. A. Nurmi
A. Reymond
S. Shih
L. C. Siew
N. Smith
N. Steinberger
I. Zlochower

8. PUBLICATIONS:

"Electron Spin Resonance Spectra of Cyclic Ketyls and Ortho Semiquinones," R. Dehl and G. K. Fraenkel, J. Chem. Phys. 39, 1793 (1963).

"Electron Spin Resonance Studies of Aromatic Polynitro Compounds," I. Bernal and G. K. Fraenkel, J. Chem. Phys., 40, 723 (1964).

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"Theory of Line Widths in Electron Spin Resonance Spectra: Motion of Methyl Groups," J. H. Freed and G. K. Fraenkel, J. Am. Chem. Soc. 86, 3477 (1964).

"Alternating Linewidths and Related Phenomena in the Electron Spin Resonance Spectra of Nitro-Substituted Benzene Anions," J. H. Freed and G. K. Fraenkel, J. Chem. Phys. 41, 699 (1964).

"Line Shapes in Electron Spin Resonance Spectra," J. Gendell, J. H. Freed, and G. K. Fraenkel, J. Chem. Phys. 41, 949 (1964).

"Electron Spin Resonance Spectra of Methyl-Substituted Dihydropyrazine Cations and Related Radicals," B. L. Barton and G. K. Fraenkel, J. Chem. Phys. 41, 1455 (1964).

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"Temperature Dependence of the Hyperfine Splitting of the Methyl Radical," I. A. Zlochower, W. R. Miller, and G. K. Fraenkel, J. Chem. Phys. 42, 3339 (1965).

"Electron Spin Resonance Studies of Deuterium Isotope Effects. A Novel Resonance-Integral Perturbation," M. Karplus, R. G. Lawler, and G. K. Fraenkel, J. Am. Chem. Soc. 87, 5260 (1965).

"Measurement of g Values in the Electron Spin Resonance Spectra of Free Radicals," B. G. Segal, M. Kaplan, and G. K. Fraenkel, J. Chem. Phys. 43, 4191 (1965).

"Electron Spin Resonance Study of Mono- and Dimeric Cations of Aromatic Hydrocarbons," O. W. Howarth and G. K. Fraenkel, J. Am. Chem. Soc. 88, 4514 (1966).

"Deuterium Isotope Effects in the Electron Spin Resonance Spectra of Naphthalene Negative Ions," R. G. Lawler, J. R. Bolton, M. Karplus and G. K. Fraenkel, J. Chem. Phys. 47, 2149 (1967).

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"Proton Hyperfine Splittings in the Electron Spin Resonance Spectra of Hydrocarbon Ions: A Comparison of the Colpa-Bolton and Giacometti-Nordio-Pavan Relations," R. E. Moss and G. K. Fraenkel, J. Chem. Phys. (submitted for publication).

"Electron Spin Resonance Spectra of Methyl-Substituted Naphthalene Anion Radicals," R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel, (to be submitted)

"Electron Spin Resonance Studies of Mono- and Dimeric Cations of Aromatic Hydrocarbons. II," O. W. Howarth and G. K. Fraenkel, (to be submitted).

"Temperature Variation of Electron Spin Resonance Spectra of Benzene and Cyclooctatetraene Anion Radicals," R. G. Lawler, M. K. Das, L. C. Siew, and G. K. Fraenkel, (to be submitted).

"Electron Spin Resonance Spectra of Radicals Formed From Dicyanohydroquinone," W. R. Miller, I. Bernal, R. Dehl and G. K. Fraenkel, (to be submitted).

"Electron Spin Resonance of Free Radicals," Final Technical Report, AFOSR 68-0060.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research was concerned with the application of electron spin resonance spectroscopy to the determination of molecular wavefunctions of organic free radicals from measurements of the isotropic hyperfine interaction with protons, carbon-13, and other magnetic nuclei. Both theoretical and experimental investigations were involved. Radicals were prepared both by chemical means and by electrolytic generation. The results obtained by electrolytic generation were correlated with direct and alternating current polarographic investigations to elucidate the nature of a variety of oxidation and reduction reactions. Relaxation, line width, and saturation studies were undertaken. The design and development of versatile high sensitivity ESR spectrometers were pursued.

Other work included an investigation of the pairing theorem through the study of positive and negative hydrocarbon ion radicals; an investigation of orbitally degenerate radicals and the effects of deuterium substitution; studies of compounds exhibiting intramolecular hydrogen bonding; and the use of linewidth variations to determine approximate spin-density distributions.

Dr. Fraenkel was a pioneer in electron spin resonance research. He was the first to report the ESR spectra on a multitude of organic free radicals (see publications). He developed the theory of linewidths in the ESR spectra of free radicals which predicts that composite lines arising from a set of degenerate nuclear spin states should not be Lorentzian in shape, and that the shapes of different lines in the same spectrum should be different. He has also developed a number of classical, dynamical models for describing the effects of internal rotational motions and solvent-complex formation on the ESR hyperfine linewidths of free radicals in solution.

Measurements have been made by this group of the g values in the electron spin resonance spectra of 20 aromatic free radicals with an accuracy which has not previously been attained.

High resolution ESR spectra were obtained of the anion radicals of naphthalene and of ten different deuterium substituted naphthalenes. Deuterium substitution at one position was found to alter the hyperfine splittings of the protons at other positions

D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Pressure Dependence of Electrolytic Conductance

2. PRINCIPAL INVESTIGATOR: Dr. Raymond M. Fuoss
Sterling Chemistry Laboratory
Yale University
New Haven, Connecticut

3. INCLUSIVE DATES: 1 January 1963 - 30 June 1968

4. GRANT NOS: AF-AFOSR-244-63; AF-AFOSR-244-65

5. COSTS AND FY SOURCE: $33,133 FY63; $36,088 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. Claude Treiner
Dr. James F. Skinner
Dr. Edward L. Cussler

7. JUNIOR RESEARCH PERSONNEL: Thomas M. Hammond
Carl G. Seefried

8. PUBLICATIONS:

"Dipole Association," C. Treiner, J. F. Skinner and R. M. Fuoss, J. Phys. Chem., 68, 3406 (1964).

"Effects of Pressure on Conductance. I. Tetra-iso-amylammonium Picrate in Diethyl Ether and in Benzene," J. F. Skinner and R. M. Fuoss, J. Phys. Chem., 69, 1437 (1965).

"Effects of Pressure on Conductance. II. Walden Products and Association Constants in Methanol," J. F. Skinner and R. M. Fuoss, J. Phys. Chem., 70, 1426 (1966).

"Effects of Pressure on Conductance. III. Tetra-iso-amylammonium Picrate in Anisole," J. F. Skinner, E. L. Cussler and R. M. Fuoss, J. Phys. Chem., 71, 4455 (1967).

"Effects of Pressure on Conductance. IV. Ionic Association and Walden Products in Ethanol," E. L. Cussler and R. M. Fuoss, J. Phys. Chem., 71, 4459 (1967).

"A Remote Control Viscometer," E. L. Cussler and R. M. Fuoss, Rev. Sci. Inst. 39, 524 (1968).

"Pressure Dependence of Dielectric Constant and Density," J. F. Skinner, E. L. Cussler, and R. M. Fuoss, J. Phys. Chem., 72, 1057 (1968).

"Pressure Dependence of Electrolytic Conductance," Final Technical Report, AFOSR 68-1617.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of this research program was to investigate the dependence on pressure of the electrical properties of non-aqueous solutions of electrolytes.

The effects of pressure on the conductances of a variety of 1-1 electrolytes in diethyl ether, benzene, anisole, methanol and ethanol have been measured and the results used to test current theories of ionic interaction. The dielectric constant can be increased without changing the chemical nature of the solvent; for example, diethyl ether with a dielectric constant of 6.19 at 5000 atms. The increase of nearly 50% can be expected to produce a marked increase in ionic association because the dielectric constant appears in the exponent of a factor in the association equilibrium constant.

Pressure can affect conductances through two other properties of the solvent in addition to the dielectric constant. Viscosity increases very rapidly with increasing pressure; for example, the viscosity of diethyl ether at 5000 atms is nearly ten times what it is at 1 atm. Density increases as pressure increases and, therefore, the concentration of ions per unit volume increases. This effect is small compared to the effects of viscosity and dielectric constant, although not negligible. It amounts to 30% for solutions in diethyl ether at 5000 atms.

The experimental work involved the determination of conductance of solutions as a function of concentration and pressure, and the measurement of the dielectric constant, viscosity, and density of the various solvents used as a function of pressure. Apparatus and methods for determining these physical properties were developed during the research.

Dr. W. L. Ruigh
(Reviewed by LtCol L.D. Whipple)

COMPLETED PROJECT SUMMARY

1. TITLE: Surface Stabilized Free Radicals

2. PRINCIPAL INVESTIGATOR: Dr. H. D. Gesser
Department of Chemistry
University of Manitoba
Winnipeg, Manitoba

3. INCLUSIVE DATES: 1 April 1964 - 31 January 1968

4. GRANT NO: AF-AFOSR-642-64 and AF-AFOSR-642-66

5. COSTS AND FY SOURCE: $19,733 FY64; $20,600 Y64

6. SENIOR RESEARCH PERSONNEL: Dr. A. Cohen
Dr. M. Zammit
Dr. M. Shimizu

7. JUNIOR RESEARCH PERSONNEL: L. Bader
B. Garbutt
R. Long

8. PUBLICATIONS:

"Electron Paramagnetic Resonance of Methyl Radicals on Porous Glass Surface." M. Fujimoto, H. D. Gesser, B. Garbutt and A. Cohen, Science <u>154</u>,381 (1966).

"Paramagnetic Resonance Spectra of Methyl Radicals in Porous Glass Surfaces." M. Fujimoto, H. D. Gesser, B. Garbutt and M. Shimizu. Science <u>156</u>,1105 (1967).

"Temperature Dependences of the Hyperfine Interaction Line Widths, and Line Asymmetries in Methyl Radicals Stabilized on Porous Glass Surfaces." G. B. Garbutt, H. D. Gesser, and M. Fujimoto. J. Chem. Phys. in press (1968).

"IR- study on the Adsorption-Desorption and degassing Process of Trimethyl Borate-Porous Vycor System." M. Shimizu and H. D. Gesser. In preparation.

"IR- study of Methanol Adsorbed on Porous Vycor Glass." M. Shimizu and H. D. Gesser. In preparation.

"ESR- study on Photolysed Methanol." M. Shimizu, M. Fujimoto, and H. D. Gesser. In preparation.

"The Impregnation of TiO_2 on Porous Vycor Glass." M. Shimizu and H. D. Gesser. In preparation.

"Surface Stabilized Free Radicals, Final Technical Report, AFOSR-68-1313

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The object of this program was to produce free radicals on the surface of porous glass and to study the factors which influence their stabilization on the surface and their decay rates. Methyl radicals, formed by the photolysis of CH_3I at 77°K were stabilized on the porous glass indefinitely at this temperature and decayed with first order kinetics at higher temperatures with an activation energy of about 2 kcal/mole. The decay showed a cascade effect indicating the presence of a multi site surface. High resolution ESR spectra gave a further splitting of the hyperfine lines which were interpreted in terms of H-CH_3 interaction. This was subsequently shown to be probably due to water on the surface and the degassing condition since a deuterated surface almost eliminated the effect.

Line width measurement for CH_3 has led to a tumbling frequency which is of the order of 10^8 sec^{-1} and an activation energy for tumbling of about 300 cal/mole for CH_3 on the surface.

The photolysis of CH_3OH (and its deuterated isomers) on porous glass was also examined and interpreted in terms of the I.R. absorption studies. Comparable studies were also made with a TiO_2 impregnated surface.

The stabilization of hydrogen atoms was also examined and was similar in behaviour to CH_3 except that the decay was 2nd order and the H atom showed definite decay at 77°K.

Dr. William L. Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Liquid Crystal Reactions by Ellipsometry

2. PRINCIPAL INVESTIGATOR: Dr. E. L. Grove
Department of Analytical Chemistry
Illinois Institute of Technology
Chicago, Illinois

3. INCLUSIVE DATES: 1 May 1967 - 31 August 1967

4. CONTRACT NO: F44620-67-C-0091 (ARPA Contract)

5. COSTS AND FY SOURCE: $9,923 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. Isaac Daniel
Dr. Harold S. Weber
Dr. Marvin Camras

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS: None

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This study was a brief exploratory program to evaluate the effectof the four areas in the scope on the optical properties of selected, commercially available liquid crystal compounds. Minute changes in the optical properties of these compounds can be readily detected by elliptically polarized light. Therefore, ellipsometry was selected as a tool to follow any changes. The four areas chosen for the exploratory study were: (1) detection of oriented magnetic fields in recording tapes; (2) measurement of orientation induced in liquid substrate; (3) measurement of the Kerr effect constant in suitable liquid crystals; and (4) effect of DMMP (dimethyl methyl phosphonate) vapor on liquid crystals. In this study in which four areas were briefly surveyed, thin coatings of barium stearate showed changes in ellipticity, probably due to the strain in the sample. Since only one substance was studied, other materials or combinations of materials should be studied to see if such patterns can be more sharply defined or if other materials are more sensitive to the changes produced by a strain.

The opacity of the compounds studied made it impossible to obtain data with the Kerr cell. Thus this study would be limited only to those compounds that may be transparent to the visible light. More compounds should be surveyed.

A previous study showed liquid crystals to be very sensitive to compounds soluble in a given liquid crystal. Preliminary experiments with the simulant DMMP showed little sensitivity since the material showed very limited solubility. Additional work along this line should include a study of solubility or possible reactions of the particular agent with the liquid crystal compound.

The exploratory study with magnetic tapes indicated the magnetic tapes produced insufficient magnetic fields to have any measurable orientation effect on cholesterol ester mixtures, p-azoxyanisole, or p-n-butoxybenzoic acid.

Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: NMR Studies of Intra- and Intermolecular Interations

2. PRINCIPAL INVESTIGATOR: Dr. Melvin W. Hanna
Department of Chemistry
University of Colorado
Boulder, Colorado

3. INCLUSIVE DATES: 1 January 1963 - 31 August 1967

4. GRANT NO: AF-AFOSR 216-63; AF-AFOSR 216-65

5. COSTS AND FY SOURCE: $39,730 FY63; $44,755 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. James Sinclair
Dr. Antonia Sandoval

7. JUNIOR RESEARCH PERSONNEL: Alan Ashbaugh
Peter J. Berkeley
Dwight Williams
Philip Trotter
James Mengenhauser
John Lehman

8. PUBLICATIONS:

"Nuclear Magnetic Resonance Studies of Hydrogen Bonding. II. Calculation of the Shift upon Complex Formation," Peter J. Berkeley, Jr. and Melvin W. Hanna, J. Am. Chem. Soc. 86, 2900 (1964).

"NMR Study of π-Molecular Complexes of 7,7,8,8-Tetracyanoquinodimethane and Aromatic Donors," M. W. Hanna and A.L. Ashbaugh, J. Phys. Chem. 68, 811 (1964).

"Relative Stabilities of Weak Hydrogen Bonds to Nitrogen," Peter J. Berkeley, Jr. and Melvin W. Hanna, J. Chem. Phys. 41, 2530 (1964).

"Nuclear Magnetic Resonance Study of Molecular Complexes of Dimethylformamide with Aromatic Donors," Antonia A. Sandoval and Melvin W. Hanna, J. Phys. Chem. 70, 1203 (1966).

"Molecular Complex Equilibria: Solution Ideality, Solvent Interactions, and Concentration Scale Dependence," Philip J. Trotter and Melvin W. Hanna, J. Am. Chem. Soc. 88, 3724 (1966).

"Spectra of Weak Chemical Complexes. Internal Compression Effects." P. J. Trotter, J. Am. Chem. Soc. 88, 5721 (1966).

"Internal Compression Effects II. Frequency and Intensity Changes in Charge-Transfer and Hydrogen-Bonded Complex Spectra," P. J. Trotter. Submitted to J. Am. Chem. Soc.

"Bonding in Donor-Acceptor Compplexes I. Electrostatic Contributions to the Ground State Properties of Benzene-Halogen Complexes," M. W. Hanna, Submitted to J. Am. Chem. Soc.

"NMR Studies of Intrs- and Intermolecular Interactions," Final Technical Report, AFOSR 67-2180.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main goal of this research was to study, in solution, the relative strengths of hydrogen bonds, the structure of charge transfer complexes and the properties of metal olefin complexes. Nuclear magnetic resonance spectroscopy (NMR) was the principal experimental tool that was used. This research has shown that these interactions are quite similar in nature and that experimental properties characteristic of them are the results of a complex interplay of several factors. One of these contributions is usually called the electrostatic contribution, and it was our finding that this interaction played an important role in both hydrogen bonds and charge transfer complexes. The hydrogen bond shift observed in NMR spectra can be completely rationalized in terms of an electric field effect and, if this explanation is accepted, the hydrogen bond shift can be used in conjunction with calculated electric fields to give an estimate of hydrogen bond distances. In charge transfer complexes there was no evidence from the NMR spectrum that charge transfer played an important role in the ground state. The NMR shifts of acceptor protons could be explained in terms of magnetic anisotropy and electric field effects of the donor. This result led to an exploration of the importance of electrostatic interactions in stabilizing the ground states of charge transfer complexes and the conclusion was that these interactions are much more important than had previously been realized.

As by products of this main line of research we have also studied the errors inherent in the Benesi-Hildebrand procedure for determining complex properties, the structure of the benzene caffeine complex, the factors important in aromatic dimethylformamide complexes, internal compression effects on the characteristics of the charge-transfer band in going from the vapor to the liquid phases and the electrostatic contributions to changes in the infrared spectrum of donor-acceptor complexes.

LtCol E. T. Walford
(Reviewed by Dr. D.L.Ball)

COMPLETED PROJECT SUMMARY

1. TITLE: The Chemistry of Carbanions

2. PRINCIPAL INVESTIGATOR: Dr. Herbert O. House
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts

3. INCLUSIVE DATES: 1 January 1964 - 30 June 1968

4. GRANT NOS: AF-AFOSR-573-64; AF-AFOSR-573-66

5. COSTS AND FY SOURCES: $50,000 FY64; $58,800 FY66

6. SENIOR RESEARCH PERSONNEL: Dr. William G. Kenyon
Dr. James E. Oliver
Dr. Jean-Jacques Riehl

7. JUNIOR RESEARCH PERSONNEL: Roger A. Latham
Frederick J. Sauter
Ben A. Tefertiller
Hugh D. Olmstead
Thomas M. Bare
William F. Fischer

8. PUBLICATIONS:

"The Standardization of Solutions of Methyllithium and Methylmagnesium Derivatives," Herbert O. House and William L. Repess, J. Organometal. Chem., 4, 95 (1965).

"The Chemistry of Carbanions. VIII. The Intramolecular Alkylation of Ketyl Radical Anions," Herbert O. House, Jean-Jacques Reihl, and Colin G. Pitt, J. Org. Chem., 30, 650 (1965).

"The Chemistry of Carbanions. X. The Selective Alkylation of Unsymmetrical Ketones," Herbert O. House and Barry M. Trost, J. Org. Chem., 30, 2502 (1965).

"By-products of the Robinson Annelation Reaction with Cyclohexanone, Cyclopentanone, and Cyclopentane-1,2-dione," Herbert O. House, Barry M. Trost, and (in part) Ralph W. Magin, Robert G. Carlson, Richard W. Franck, and Gary H. Rasmusson, J. Org. Chem., 30, 2513 (1965).

"Perhydroindan Derivatives. VI. Derivatives of 1, 1a, 2, 3, 4a-Hexahydrofluorene-2,9-dione," Herbert O. House and Roland Darms, J. Org. Chem, 30, 2528 (1965).

"The Chemistry of Carbanions. XI. Michael Reactions with 2-Methylcyclopentanone and 2-Methylcyclohexanone," Herbert O. House, Wendell L. Roelofs, and Barry M. Trost, J. Org. Chem., 31, 646 (1966).

"The Chemistry of Carbanions. XII.The Role of Copper in the Conjugate Addition of Organometallic Reagents," Herbert O. House, William L. Repess, and George M. Whitesides, J. Org. Chem, 31, 3128 (1966).

"The Solvolysis of Derivatives of 3-Azabicyclo [3.3.1] nonane," Herbert O. House and Walter M. Bryant, III, J. Org. Chem., 31, 3582 (1966).

"The Chemistry of Carbanions. XIV. Factors Influencing the Rate of Addition of Dimethylmagnesium to Benzophenone." Herbert O. House and James E. Oliver, submitted for publication.

"The Chemistry of Carbanions. XV. The Stereochemistry of Alkylation of 4-t-Butylcyclohexanone," Herbert O. House, Ben A. Tefertiller, and Hugh D. Olmstead, submitted for publication.

"The Chemistry of Carbanions. XVI. The Stereochemistry of Alkylation of the 1-Acetyl and 1-Cyano Derivatives of 4-(t-Butyl)-cyclohexane." Herbert O. House and Thomas M. Bare, submitted for publication.

"The Chemistry of Carbanions. XVII. The Addition of Methyl Organometallic Reagents to Cyclohexenone Derivatives." Herbert O. House and William F. Fischer, Jr., submitted for publication.

"The Chemistry of Carbanions," Final Technical Report, AFOSR-68- 2591

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this investigation has been to study the preparation, properties, and reactions of compounds which are either real or potential carbanions, in an effort to improve the utility of these compounds as synthetic intermediates in organic chemistry. The results of these studies may be most conveniently summarized in two separate categories: (1) enolate anions and related substances, and (2) organometallic compounds of magnesium lithium, and copper.

Dr. House's investigation of enolate anions has served to provide methods for the analysis of mixtures of isomeric enolate anions, for the preparation of specific structural and stereoisomers of enolate anions, and for measuring the rates and extent of equilibration of enolate anions in the aprotic media where these intermediates are commonly used synthetically. He and his research group are continuing to utilize these specifically generated enolate anions to achieve selectivity in various standard synthetic operations including alkylation, acylation, Michael reactions, and aldol condensations. In addition to examining these methods to permit structural specificity in synthetic operations, they have and are continuing to examine methods by which the stereochemistry of new carbon-carbon bond formation can be controlled.

The investigations of organometallic derivatives have been directed toward gaining an understanding of additions of thse reagents to carbonyl groups and the C-C double bonds of conjugated systems. As before, the ultimate objective is the development of reagents which will be selective in both a structural and a stereochemical sense for accomplishing a certain synthetic objective. One illustration of this goal is the development of organocopper (I) reagents, rendered more stable and soluble by certain ligands, which are extremely selective in their addition only to the C-C double bond of unsaturated ketones. Investigations of organomagnesium compounds have provided evidence about the structure and interchange of alkyl groups in these substances. A number of specific ligands have been found which, at a 1:1 mole ratio, can modify substantially the reactivity of organomagnesium reagents. It is hoped that use of such ligands will allow a number of organomagnesium reactions to be run under conditions where the stereochemistry of the magnesium reagent and the product may be controlled.

Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Crystal Chemistry of New High-Pressure Phases

2. PRINCIPAL INVESTIGATOR: Dr. John S. Kasper
Inorganic and Structures Branch
Physical Chemistry Laboratory
General Electric Research and
Development Center
Schenectady, New York

3. INCLUSIVE DATES: 1 January 1964 - 31 December 1967

4. CONTRACT NO: AF49(638)-1361

5. COSTS AND FY SOURCES: $31,982 FY64; $32,225 FY65
$32,645 FY66; $33,460 FY67

6. SENIOR RESEARCH PERSONNEL:

Dr. Michael J. Moore

7. JUNIOR RESEARCH PERSONNEL:

8. PUBLICATIONS:

"Hexagonal Diamond -- A New Form of Carbon," F. P. Bundy and J. S. Kasper, J. Chem. Phys., 46, 3437 (1967).

"Spectroscopic Evidence for the Formation of I_3^- in Silver Iodide at High Pressures," M. J. Moore and D. W. Skelly, J. Chem. Phys., 46, 3676 (1967).

"The Crystal Structure of AgI at 3 Kilobars," M. J. Moore and J. S. Kasper, J. Chem. Phys., 48, 2446 (1968).

"Crystal Chemistry of New High-Pressure Phases," Final Technical Report, AFOSR-68-0342.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main objective of the program has been to learn the nature of high-pressure phases and thereby contribute toward a better understanding of crystal chemistry and structural principles underlying the solid state. Another motivation has been to provide guidelines for the synthesis of new materials with new properties. For the most part, attention has been focused on substances which ordinarily have open, tetrahedral crystal structures, since a valid expectation for this class of materials is that pressure should produce denser structures with higher atomic coordinations. These materials at atmospheric pressure are either semiconductors or insulators and usually transform to metals with much higher conductivity.

Specific accomplishments include the following. Lattice parameters were determined for high pressure phases of CdS, CdTe, HgSe, and HgTe. The cadmium compounds were of the rock salt structure, the mercury compounds of the cinnabar type. The high pressure phase formed with Ge, Si, and GaSb has been reported by others to be of the β-Sn type. Efforts of this investigation were unable to resolve the structure; it is regarded as more complex than reported. Transformations under pressure to complex, recoverable phases were observed with In_2Te_3 and Ga_2Te_3. Phase relations and compressibilities were investigated for several compounds of the chalcopyrites type. The structure of AgI stable in the pressure range 3-4 kb was elucidated; it is tetragonal or pseudo-tetragonal.

Above 4 kb AgI possesses the rock-salt structure; spectroscopic evidenced revealed the occurrence of I_3^- in amounts dependent on the pressure. Two high pressure phases of Ag_2HgI_4 (one rock salt, one tetragonal) were determined. A cubic phase, forming at 16 kb, was observed for CuI. Surprisingly, the new phase does not exhibit higher coordination but rather has a statistical distribution of Cu ions over two kinds of tetrahedral sites. With AuI, application of pressure (about 4 kb) results in decomposition into the component elements. The crystal structure of a new form of carbon (hexagonal diamond) was determined.

Dr. W. L. Ruigh
(Reviewed by Dr. D.L.Ball)

COMPLETED PROJECT SUMMARY

1. TITLE: Transition Metal Complexes Containing Nitrogen, Phosphorus, or Sulfur

2. PRINCIPAL INVESTIGATOR: R. Bruce King
Department of Chemistry
University of Georgia
Athens, Georgia
(Fomerly at Mellon Inst., Pittsburgh, Pa.)

3. INCLUSIVE DATES: 1 January 1964 - 31 December 1967

4. GRANT NOS: AF-AFOSR 580-64; AF-AFOSR 580-66; AF-AFOSR 1211-67

5. COSTS AND FY SOURCES: $50,119 FY64; $54,711 FY66

6. SENIOR RESEARCH PERSONNEL: at University of Georgia

K. H. Pannell
C. A. Eggers
J. P. Hargaden
L. W. Houk

7. JUNIOR RESEARCH PERSONNEL:

at University of Georgia	at Mellon Inst.
T. F. Korenowski	M. B. Bisnette
	A. Fronzaglia
	T. F. Korenowski

8. PUBLICATIONS:

"New Types of Organosulfur Derivatives of Metal Carbonyls," R. B. King and M. B. Bisnette, J. Am. Chem. Soc., 86, 1267 (1964).

"Cyclopentadienylcobalt Carbonyl Diiodide," R. B. King, Z Naturforsch, 19b, 1160 (1964).

"An Arylazo Derivative of Molybdenum," R. B. King and M. B. Bisnette, J. Am. Chem. Soc., 86, 5694 (1964).

"Organosulfur Derivatives of The Metal Carbonyls. VI. Monomeric $CH_3SFe(CO)_2C_5H_5$ and Related Compounds," R. B. King and M. B. Bisnette, Inorg. Chem. 4, 482 (1965).

"Organosulfur Derivatives of the Metal Carbonyls. VII. Reactions between Chloroalkyl Sulfides and Metal Carbonyl Anion," R. B. King and M. B. Bisnette, Inorg. Chem., 4, 486 (1965).

"Reactions of Alkali-Metal Derivatives of Metal Carbonyls. VIII. Some Reactions of Anions Prepared from Indenylmolybdenum Tricarbonyl Dimer and Azulene-Dimolybdenum Hexacarbonyl," R. B. King and M. B. Bisnette, Inorg. Chem. 4, 475 (1965).

"Methoxycarbonyl Derivatives of the Cyclopentadienylmetal Carbonyls," R. B. King, M. B. Bisnette, and A. Fronzaglia, J. Organometal. Chem., 4, 256 (1965)

"Octamethyloxamidinium Salts of Metal Carbonyl Anions," R. B. King, Inorg. Chem. 4, 1519 (1965).

"Organosulfur Derivatives of the Metal Carbonyls. VIII. New Aspects of the Chemistry of Methylthio Derivatives of Iron Carbonyl, R. B. King and M. B. Bisnette, Inorg. Chem., 4, 1663 (1965).

"Organometallic Chemistry of the Transition Metals. XI. Some New Cyclopentadienyl Derivatives of Cobalt and Rhodium," R. B. King, Inorg. Chem., 5, 82 (1966).

"Organometallic Chemistry of the Transition Metals. XII. Some Alkoxycarbonyl Derivatives of the Cyclopentadienylmetal Carbonyls," R. B. King, M. B. Bisnette, and A. Fronzaglia, J. Organometal. Chem., 5, 341 (1966).

"Organonitrogen Derivatives of Metal Carbonyls. I. Reactions between Metal Carbonyl Anions and Haloalkyl Amines," R. B. King and M. B. Bisnette, Inorg. Chem., 5, 293 (1966).

"Organonitrogen Derivatives of Metal Carbonyls. II. Arylazo Derivatives of Molybdenum," R. B. King and M. B. Bisnette, Inorg. Chem., 5 300 (1966).

"Organonitrogen Derivatives of Metal Carbonyls. III Reactions between Metal Carbonyl Anions and Chloromethyl Isocyanate," R. B. King and M. B. Bisnette, Inorg. Chem., 5, 306 (1966).

"Organometallic Chemistry of the Transition Metals. XIII. A π-Benzyl Derivative of Molybdenum with a Temperature Dependent Proton N.M.R. Spectrum," R. B. King and A. Fronzaglia, J. Am. Chem. Soc., 88, 709 (1966).

"New Olefinic and Acetylenic Complexes of Tungsten," R. B. King and A. Fronzaglia, Chem. Comm., 547 (1965).

"Organometallic Chemistry of the Transition Metals. XV. New Olefinic and Acetylenic Derivatives of Tungsten," R. B. King and A. Fronzaglia, Inorg. Chem., 5, 1837 (1966).

"Reactions of Alkali-Metal Derivatives of Metal Carbonyls. VII. Reactions of the Sodium Cyclopentadienyltricarbonylmetallates of Molybdenum and Tungsten with Certain Organic Polyhalides," R. B. King and M. B. Bisnette, J. Organometal Chem. 7, 311 (1967).

"Organometallic Chemistry of the Transition Metals. XVI. Polynuclear Cyclopentadienylmetal Carbonyls of Iron and Cobalt," R. B. King, Inorg. Chem. 5, 2227 (1966).

"Organometallic Chemistry of the Transition Metals. XVII. Cyclopentadienylvanadium Diacetate," R. B. King, Inorg. Chem. 5,2231 (1966)

"Organometallic Chemistry of the Transition Metals. XVIII. Some New Cyclopentadienylmetal Nitrosyl Derivatives of Molybdenum and Manganese," R. B. King, Inorg. Chem., 6, 30 (1967)

"Organometallic Chemistry of the Transition Metals. XX. Some Reactions of Acetonitrile Derivatives of Molybdenum and Chromium Carbonyls with Olefinic and Acetylenic Compounds," R. B. King, J. Organometal. Chem., 8, 137 (1967).

"Organometallic Chemistry of the Transition Metals. XXI. Some π-Pentamethylcyclopentadienyl Derivatives of Various Transition Metals," R. B. King and M. B. Bisnette, J. Organometal. Chem., 8, 287 (1967).

"Reactions of Alkali-Metal Derivatives of Metal Carbonyls. VIII. Preparation, Protonation, and Alkylation of Sodium Cyanopentacarbonyl-metallates" R. B. King, Inorg. Chem., 6, 25 (1967).

"Organosulfur Derivatives of the Metal Carbonyls, IX. Some Transition-Metal Derivatives Containing both π-Cyclopentadienyl and Bis(trifluoromethyl) ethylene Dithiolate Ligands," R. B. King and M. B. Bisnette, Inorg. Chem., 6, 469 (1967).

"The Nature of the Product from the Reaction between Octacarbonyldicobalt and Bis (trifluoromethyl) dithientene," R. B. King and T. F. Korenowski, Chem. Comm. 771 (1966).

"Reactions of Rhenium Carbonyl Derivatives with Antimony Pentachloride, R. B. King, J. Inorg. Nucl. Chem., 29, 2119 (1967).

"Organometallic Chemistry of the Transition Metals. XXII. The Synthesis of Unusual Cyclopentadienylmolybdenum Nitrosyl Derivatives Using Thallium Cyclopentadienide," R. B. King, Inorg. Chem. 7, 90 (1968).

"Complexes of Trivalent Phosphorus Derivatives. III. Metal Carbonyl Complexes of 9-Phenyl-9-Phosphabicyclo [4,2,1]nonatriene," R. B. King and K. H. Pannell, Inorg. Chem. 7, 273 (1968).

"Some Transition Metal Derivatives Containing both π-Cyclopentadienyl and Cis-1,2-Ethylenedithiolate Ligands," R. B. King and C. A. Eggers, Inorg. Chem. 7, 340 (1968).

"Organosulfur Derivatives of the Metal Carbonyls. XI. Some Cis-1,2-Ethylenedithiolate Derivatives of Manganese Carbonyl and Related Compounds," R. B. King and C. A. Eggers, Inorg. Chem. 7, 1214 (1968).

"A Convenient Synthesis of Dimanganese Decacarbonyl from Inexpensive Starting Materials at Atmospheric Pressure," R. B. King, J. C. Strokes, and T. F. Korenowski, J. Organometal. Chem., 11, 641 (1968).

"Mass Spectra of Organometallic Compounds. I. Metal Carbonyl Complexes of Tris (dimethylamino) phosphine," R. B. King, J. Am. Chem. Soc., 90, 1412 (1968).

"Mass Spectra of Organometallic Compounds. III. Organosulfur Derivatives of Metal Carbonyls," R. B. King, J. Am. Chem. Soc., 90, 1429 (1968).

"Organonitrogen Derivatives of Metal Carbonyls. IV. The Reaction between σ-Methyl -π-Cyclopentadienyliron Dicarbonyl and Trifluoroacetonitrile," R. B. King and K. H. Pannell, J. Am. Chem. Soc., 90, 3984 (1968).

"Complexes of Trivalent Phosphorus Derivatives. IV. Metal Carbonyl Complexes of Cis-Bis(1,2-diphenylphosphino)ethylene," R. B. King and C. A. Eggers, Inorg. Chem.Acta, 2,33 (1968).

"Transition Metal Complexes containing Nitrogen, Phosphorus, or Sulfur," R. B. King, Final Report, AFOSR 68-0343 .

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The ultimate aim of this research was the elucidation of the nature of the chemical bonding in transition-metal derivatives also containing nitrogen, phosphorus, or sulfur ligands. The approach used in this research was the synthesis of a variety of unusual types of such compounds followed by an investigation of their chemical reactions and spectra. It was felt that this approach would provide new information not only of general interest, but also of potential practical value in suggesting new catalytic systems either for more efficient preparations of useful organic compounds or for inhibiting undesirable chemical processes.

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

(a) New Nitrogen Derivatives:

Compounds of the type $RN_2Mo(CO)_2C_5H_5$ (R = phenyl, p-tolyl, p-anisyl, or p-nitrophenyl) were prepared by treatment of $NaMo(CO)_3C_5H_5$ with the appropriate diazonium salts. These compounds were the first known arylazometal derivatives. Reaction of $C_5H_5Mo(CO)_2NO$ with iodine in dichloromethane solution gave $[C_5H_5Mo(NO)I_2]_2$; this was a useful intermediate for the preparation of novel coordination compounds of the type $C_5H_5Mo(NO)I_2L$ (L = triphenylphosphine, triphenylphosphite, or pyridine) and for the preparation of $(C_5H_5)_2Mo(NO)I$. This latter compound appears to contain a novel π-cyclopentadienyl ring with only three of the five carbon atoms bonded to the metal atom. Reaction of $Na[M(CO)_5CN]$ with aqueous hydrochloric acid gave the white volatile complexes $HNCM(CO)_5$, the first metal complexes of the hydrogen isocyanide ligand. The acetonitrile complex $(CH_3CN)_3W(CO)_3$ was shown to be a useful intermediate for the preparation of olefin-tungsten carbonyl derivative not readily accessible directly from tungsten hexacarbonyl and the olefin. Reaction of $CH_3Fe(CO)_2C_5H_5$ with trifluoroacetonitrile under pressure gave the black volatile complex $CF_3C(NH)Fe(CO)(NCCF_3)(C_5H_5)$; this is the first known metal complex of trifluoroacetonitrile. Reactions between metal carbonyl anions and the haloalkylamines 2-chloromethylpyridine and 2-chloroethyldimethylamine gave several new cyclic acyl derivatives such as the molybdenum compound $NC_5H_4CH_2COMo(CO)_2C_5H_5$.

(b) New Phosphorus Derivatives:

The unsaturated phosphines 9-phenyl-9-phosphabicyclo[4,2,1]octatriene ($C_8H_8PC_6H_5$) and cis-bis(1,2-diphenylphosphine)ethylene ($(C_6H_5)_2PCH = CHP(C_6H_5)_2$) were investigated as possible ligands. In almost all cases the phosphorus atoms were shown to coordinate to metal atoms in preference to the carbon-carbon double bonds.

(c) New Sulfur Derivatives:

Reactions of chloromethyl methyl sulfide ($ClCH_2SCH_3$) with certain metal carbonyl anions gave novel π-CH_3SCH_2 derivatives such as π-$CH_3SCH_2Mo(CO)_2C_5H_5$. Reactions of 2-chloroethyl methyl sulfide ($ClCH_2CH_2SCH_3$) with certain metal carbonyl anions gave novel cyclic acyl derivatives such as $CH_3SCH_2CH_2COMn(CO)_4$. Several syntheses for $C_5H_5Fe(CO)_2SCH_3$ were developed; this was the first metal carbonyl derivative with a non-briding CH_3S group. A greatly improved preparation of $[CH_3SFe(CO)_3]_2$ was developed; by slight modification of the preparation conditions the coordination polymer $[(CH_3S)_2Fe(CO)_2]_n$ could be obtained. A variety of unusual complexes were obtained from metal carbonyl derivatives and bis(trifluoromethyl) dithietene, $(CF_3)_2C_2S_2$, and from metal halide derivatives and sodium cis-ethylenedithiolate, $Na_2S_2C_2H_2$. Of particular interest among complexes of the latter type was the manganese complex

$H_2C_2S_2Mn_2(CO)_6$ which appears to contain a manganese-manganese multiple bond. This manganese complex reacts with Lewis bases to form yellow addition products $H_2C_2S_2Mn_2(CO)_6 \cdot L$ under mild conditions and dark red-brown substitution products $H_2C_2S_2Mn_2(CO)_4L_2$ under more vigorous conditions.

(d) New Chemistry of the Metal Carbonyl Anions:

Metal carbonyl anions are often useful intermediates for the preparation of transition-metal complexes including those containing nitrogen, phosphorus, or sulfur. Therefore, additional work was carried out to develop metal carbonyl anions as preparative reagents. Highlights of this work include the first study of metal carbonyl anions with indenyl and azulene ligands ($[C_9H_7Mo(CO)_3]^-$ and $[C_{10}H_8Mo(CO)_3]_2^{-2}$), the development of tetrakis (dimethylamino) ethylene as a reducing agent for the preparation of metal carbonyl anions, and new preparative applications of metal carbonyl anions. This study resulted in the discovery of the first π-benzyl derivative $C_6H_5CH_2Mo(CO)_2C_5H_5$ which exhibited a novel temperature-dependent proton n.m.r. spectrum.

(e) Miscellaneous Preparative Studies:

The complex $C_5H_5Co(CO)I_2$ was discovered and used to prepare a variety of novel coordination complexes of cobalt including $C_5H_5CoI_2NC_5H_5$, $[C_5H_5CoN_2C_{10}I]$, and $C_5H_5CoY_2P(C_6H_5)_3$ (Y = I or CH_3) Several π-pentamethylcyclopentadienyl complexes were prepared. The most interesting of these complexes was $[(CH_3)_5C_5Mo(CO)_2]_2$ apparently containing a molydenum-molybdenum triple bond. Pyrolysis of $[C_5H_5Fe(CO)_2]_2$ in boiling xylene was found to give the green very stable tetrametallic complex $[C_5H_5FeCO]_4$. The structure of this compound has a tetrahedral cluster of iron atoms with a carbonyl group in each face of the tetrahedron and a cyclopentadienyl ring bonded to each iron atom. A convenient synthesis of the extremely useful intermediate $Mn_2(CO)_{10}$ was developed which uses inexpensive starting materials and conventional laboratory glassware (rather than high-pressure autoclaves).

Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: The Sixth Rare Earth Research Conference

2. PRINCIPAL INVESTIGATOR: Dr. Wallace C. Koehler
Solid State Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee

3. INCLUSIVE DATES: 1 September 1966; 31 August 1967

4. GRANT NO: Project Order to AEC (ORNL) AFOSR-67-0226

5. COSTS AND FY SOURCE: $4,500 FY67

6. PUBLICATIONS:

"Abstracts of the Sixth Rare Earth Research Conference," Final Report, AFOSR-67-1214.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The Sixth Rare Earth Research Conference was held at Gatlinburg, Tennessee on May 3 - 5, 1967, under the joint sponsorship of the Air Force Office of Scientific Research and the Oak Ridge National Laboratory. The Conference Chairman was Wallace C. Koehler.

As in previous conferences of this series, scientists of diverse disciplines whose interests lie in the study of the properties of the rare earth metals, alloys, and compounds were brought together in an atmosphere and location conducive to the exchange of ideas and information. A special effort was made to recognize scientists working in the rare earth industry in that a separate session devoted exclusively to "Industrial Processes" was organized.

The response to the call for papers was overwhelming -- so much so that parallel sessions were required in order to conduct the business of the Conference in a three-day period. The Conference was attended by some 220 persons representing nine different countries. The formal program was divided into thirteen sessions. Following the keynote address, delivered by Howard E. Kremers of the American Potash and Chemical Corporation, on "Rare Earth Uses" there were sessions on Solid State (5), Chemistry (5), Metallurgy (1), and as mentioned above, Industrial Processes (1).

The principal areas of emphasis in current chemical research were described by three invited speakers, Professor J. S. Anderson of Oxford University, Dr. P. [illegible] Yocom of the RCA Laboratories, and Professor Therald Moeller of the University of Illinois. Current research in solid state studies were described by the following invited speakers: Prof K. H. Hellwege, Institut für Technische Physik, Darmstadt, Germany; Prof R. Pauthenet, University of Grenoble, France; Dr. D. B. McWhan, Bell Telephone Laboratories; Dr. H. Bjerrum-Møller, AEK Research Establishment, Risö, Denmark; Prof Kei Yosida, University of Tokyo, Japan; and Dr. A. J. Freeman, National Magnet Laboratory. Representing the general area of metallurgy was Prof Karl Gschneidner, Iowa State University.

Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Kinetics of Transition-Metal Ions of d^8 Electronic Configuration

2. PRINCIPAL INVESTIGATOR: Dr. David J. MacDonald
Department of Chemistry
University of Nevada
Reno, Nevada

3. INCLUSIVE DATES: 1 November 1965 - 30 June 1968

4. GRANT NO: AF-AFOSR 994-66

5. COSTS AND FY SOURCES: $13,634 FY66; $9,606 FY68

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: A. L. Rafferto
R. E. Smith
B. A. Sok
W. N. Marchant

8. PUBLICATIONS:

"Kinetics and Mechanism of Acid Hydrolysis of Ethylenebisbiguanidenickel (II) Ion," D. J. MacDonald, J. Inorg. Nucl. Chem., 29, 1271 (1967).

"Absorption Spectra of Square-Planar Complexes of Ethylenebisbiguanide with Nickel(II) and Palladium(II)," D. J. MacDonald, Inorg. Chem., 6, 2269 (1967).

"Hydrolysis of Ethylenebisbiguanidepalladium(II) Ion," J. Inorg. Nucl. Chem., in press.

"A Chemical Kinetic Study of Substitution Reactions in Coordination Compounds Involving Transition-Metal Ions Having d^8 Electronic Configuration," Final Technical Report, AFOSR-68-1620.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Detailed studies were completed of the kinetics and mechanisms of the acid hydrolyses of the Ni(II) and Pd(II) complexes with ethylenebisbiguanide. The stability constant for the Ni(II) complex with ethylenebisbiguanide was determined. Employing a computer program developed from evaluating the ionization constants of ethylenebisbiguanidinium ion, the two acid dissociation constants of squaric acid were redetermined.

The research has provided better understanding of the rather unique ligand, ethylenebisbiguanide. Square-planar complexes of transition metals had not, heretofore, been studied extensively.

Dr. D. L. Ball

COMPLETED PROJECT SUMMARY

1. TITLE: The Acid Base Characteristics of Phototropism

2. PRINCIPAL INVESTIGATOR: Dr. J. David Margerum
Chemical Physics Department
Hughes Research Laboratories
Malibu, California

3. INCLUSIVE DATES: 1 October 1963 - 30 September 1967

4. CONTRACT NO: AF49(638)-1264

5. COSTS AND FY SOURCES: \$22,538 FY64; \$46,713 FY65; \$23,004 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. Robert G. Brault
Dr. Concetto R. Giuliano
Dr. L. D. Hess

7. JUNIOR RESEARCH PERSONNEL: Mrs. Cunegunda T. Petrusis
Mr. Harley J. Moe

8. PUBLICATIONS:

"New Photochromic Compounds with *p*-Nitrobenzyl Structures," J. D. Margerum and R. G. Brault, J. Am. Chem. Soc., **88**, 4733 (1966).

"Transient Photodecarboxylation Intermediates," J. D. Margerum, J. Am. Chem. Soc., **87**, 3772 (1965).

"*Cis-Trans* Isomerization and Pulsed Laser Studies of Substituted Indigo Dyes," C. R. Giuliano, L. D. Hess, and J. D. Margerum, J. Am. Chem. Soc., **90**, 587 (1968).

"Acid-Base Characteristics of Photochromism," Final Technical Report, AFOSR 68-0345.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The mechanisms of several organic photochemical reactions have been studied in regard to their acid-base characteristics. Photochromic structures have been proposed and model compounds have been prepared for studies with flash photolysis and laser photolysis techniques. Twenty-three new compounds were synthesized, including several nitroanthrone structures from some unique Friedel-Crafts condensation reactions. A new group of photochromic compounds has been found and studied in detail with appropriate model compounds. They consist of structures in which intramolecular hydrogen transfer reactions can occur between nitrobenzyl groups and carboxylate groups to form *aci*-nitro structures in aqueous solutions. For example, 2-(4-nitrobenzyl) benzoate ion shows an efficient photochromic process whose back-reaction rate can be controlled over seven orders of magnitude by pH variations. A new type of efficient photodecarboxylation reaction was also found and studied for a group of nitrophenylacetate structures in which an irreversible acid-base reaction produces *aci*-nitro intermediates similar to those found in the photochromic reactions. For example, 4-nitrophenylacetate ions decarboxylate with a quantum yield of 0.6 to produce an intermediate lasting up to several minutes. *Aci*-anions from both photochromic and photodecarboxylation reactions were observed to be good chemical reducing agents, and these reactions are a convenient source of reactive intermediates. Photo-oxidation of 2-propanol was observed with 2-methyl-5-nitrobenzophenone, and transient intermediates were also noted. Photochromic trans-cis isomerizations, with acid catalyzed cis-trans back reactions, were found in N,N'-dimethylindigo dyes. Giant pulse ruby laser studies indicated the existence of a strongly absorbing species lasting only 10^{-7} to 10^{-9} sec, possibly the triplet state intermediate in the isomerization process. The photochromic reaction of platinum dithizonate was found to produce an isomerized state lasting several seconds, which has a strong near infrared absorption band as well as one in the visible region. Solutions of this chelate were found to work effectively as a passive Q-switch material for giant pulse operation of ruby lasers. Photochemical dye formation from colorless rhodamine B lactone solutions was found to arise from irreversible acid forming reactions, which occur readily as free radical processes in the presence of halocarbon solvents. Photochromic reactions were demonstrated to be an exceptionally sensitive optical method for the control and modulation of cw gas lasers with auxiliary light sources when the photochromic materials are used inside the laser cavity.

Dr. A. J. Matuszko
(Reviewed by Dr. D. L. Ball)

COMPLETED PROJECT SUMMARY

1. TITLE: The Oxidation of Arsenic(III) and Antimony(III)

2. PRINCIPAL INVESTIGATOR: John G. Mason
Department of Chemistry
Virginia Polytechnic Institute
Blacksburg, Va.

3. INCLUSIVE DATES: 1 February 1963 to 30 September 1967

4. GRANT NOS: AF-AFOSR-210-63; AF-AFOSR-210-65

5. COST AND FY SOURCES: $14,840 FY63; $15,912 FY65

6. SENIOR RESEARCH PERSONNEL:

7. JUNIOR RESEARCH PERSONNEL: A. D. Kowalak

8. PUBLICATION:

"The Kinetics of the Chromium (VI) - Arsenic(III) Reaction in Acetic Acid - Acetate Buffer Solutions," Inorg. Chem. 3, 1248 (1964)

"The Oxidation of Arsenic(III) and Antimony(III)," Final Technical Report

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Arsenic(IV) was proposed as an intermediate in certain oxidations of arsenic(III). It was proposed to make a kinetic study of the oxidations of arsenic(III) and antimony(III) by cerium(IV) and Cr(VI), to explore catalysis by metallic species and complexing agents, and investigate induced reactions in the Cr(VI)-Sb(III) and Cr(VI)-As(III) systems.

The oxidation of As(III) by Cr(VI) has been studied in detail for a variety of systems. In acetic acid-acetate buffers and aqueous acetic acid the rate law obtained is of the general form:

$$\frac{-d[\mathrm{Cr(VI)}]}{dt} = \frac{(ko + k_1[\mathrm{HOAc}])K[\mathrm{As(III)}][\mathrm{Cr(VI)}]}{1 + K[\mathrm{As(III)}]}$$

Numerical values of K and k_o are the same for both systems, but the coefficient for the acetic acid catalyzed system is different. The mechanism suggested by the rate law is

$$\mathrm{As(III)} + \mathrm{HCrO_4^-} \rightleftharpoons [\mathrm{As(III)} \cdot \mathrm{HCrO_4^-}]\ K$$
$$[\mathrm{As(III)} \cdot \mathrm{HCrO_4^-}] \xrightarrow{k} \text{products}$$

The decomposition of the mixed anhydride is acid-catalyzed.

In dilute perchloric acid solution the rate law found was

$$\frac{-d[\mathrm{Cr(VI)}]}{dt} = \frac{\{k_o + k_1[\mathrm{H^+}] + k_2[\mathrm{H^+}]^2\}K[\mathrm{As(III)}][\mathrm{Cr(VI)}]}{1 + K[\mathrm{As(III)}]}$$

The interpretation here is essentially the same since k_o and K have approximately the same values as before. The two-term hydrogen ion dependence is taken to be the protonation of the mixed anhydride.

In hydrogen phosphate ($HPO_4^{=}$) - dihydrogen phosphate ($H_2PO_4^-$) buffers a different mechanism is operative. The reaction appears to be simple first order in As(III) and first order in Cr(VI). The Cr(VI) complexes with the buffer components and analysis of the data shows the most significant activated complex to have the composition ($HCrO_4^- \cdot HPO_4^{=}$) or ($CrO_4^{=} \cdot H_2PO_4^-$). The most significant solution complex was found to be $HCrO_4^- + H_2PO_4^- \rightleftarrows HCrPO_7^{=} + H_2O$. No evidence for As(III)-Cr(VI) association was found in NH_4NO_3-KNO_3 media.

The primary reaction between As(III) and Cr(VI) was found to induce the oxidation of tartaric acid producing a catalytic rate enhancement. Detailed kinetic studies showed that the catalysis was pH dependent in acetic acid-acetate buffers in contrast to the primary reaction and that the most reasonable reactant was the monoanion of tartaric acid. Tartaric acid was found incorporated in the reduction product of Cr(VI). Essentially the same spectrum was produced by heating Cr(III) with tartaric acid as by reduction of Cr(VI) in tartrate medium. The kinetics thus far have been too complex for simple interpretation. Oxalate ion also exhibited a "catalytic" effect on the disappearance of Cr(VI), presumably by induced oxidation.

The reaction of Cr(VI) with antimony tartrate was much too rapid to measure. However, essentially the same observations with respect to both the stoichiometry and to the nature of the Cr(III) product were made.

Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE. Electrochemical Studies of Kinetics, Adsorption, and Excited Electronic States

2. PRINCIPAL INVESTIGATOR: Dr. R. W. Murray
Dr. C. N. Reilley
Department of Chemistry
University of North Carolina
Chapel Hill, N. C.

3. INCLUSIVE DATES: 1 January 1964 - 30 June 1968

4. GRANT NOS.: F-AFOSR-584-64; AF-AFOSR-584-66

5. COST AND FY SOURCE: $62,284 FY64; $81,276 FY66

6. SENIOR RESEARCH PERSONNEL:
Dr. D. E. Leyden
Dr. L. B. Anderson
Dr. Robert F. Broman
Dr. John W. Hayes
Dr. George W. O'Dom
Dr Bruce McDuffie
Dr. Donald J. Gross
Dr. Mutsuo Kodama

7. JUNIOR RESEARCH PERSONNEL:
P. T. Kissinger
Donald J. Gross
A. Yildiz
W. R. Heineman
R. L. McNeely
J. H. Holloway
D. M. Oglesby
L. K. Hiller
J. R. Cockrell
J. N. Burnett
D. L. Wright

8. PUBLICATIONS:

"Kinetic Control by Chemical Step at an Adsorption-Blocked Electrode Surface," R. W. Murray and Mutsuo Kodama, Anal. Chem., 37, 1638 (1965).

"Discriminating Effect of Adsorbed Asymmetric Film Electrode toward Electroactive Metal Complex Enantiomers," R. W. Murray and Mutsuo Kodama, Anal. Chem., 37, 1759 (1965).

"Chronopotentiometric Study of Phenylmercuric Ion Adsorption on a Mercury Electrode," R. W. Murray and R. F. Broman. Anal. Chem., 37, [illegible] ([illegible]).

"Inhibition of Electrode Reactions by Adsorbed Lead Iodide, Bromide, and Thiocyanate," R. W. Murray and Donald J. Gross, Anal. Chem., 38, [illegible] ([illegible]).

"Instrument for Functional Readout of Chronocoulometric Data. Application to [illegible] Adsorption from Iodide Medium," R. W. Murray and George W. O'Dom, Anal. Chem., 39, 51(1967).

"Chronocoulometric Measurement of Indium (III) Adsorption from Thiocyanate Media," R. W. Murray and George W. O'Dom, J. Electroanal. Chem., 16, [illegible]

"An Optically Transparent Thin Layer Electrochemical Cell." R. W. Murray, W. R. Heineman, and G. W. O'Dom. Anal. Chem., 39, 1666, (1967).

"Electrochemical Masking with an Adsorbed Metal Complex: Determination of Silver-Mercury Mixtures," R. W. Murray and R. L. McNeely, Anal. Chem., 39, 1661, (1967).

"Thin-Layer Electrochemistry: Use of Twin Working Electrodes for Study of Chemical Kinetics," Charles N. Reilley and L. B. Anderson. J. Electroanal. Chem., 10, 538 (1965).

"Heats and Entropies of Formation of Metal Chelates of Polyamine and Polyaminocarboxylate Ligands," Charles N. Reilley, D. L. Wright, and J. H. Holloway. Anal. Chem., 37, 884 (1965).

"An Operational Amplifier A. C. Polarograph with Admittance Recording," Charles N. Reilley and J. W. Hayes, Anal. Chem., 37, 1322 (1965).

"Polarographic Drop-Time Measurement Using an A. C. Technique," Charles N. Reilley, J. W. Hayes, and D. E. Leyden, Anal. Chem., 37, 1444 (1965).

"Thin-Layer Potential Scan Coulometry. Determination of Metal Ions and of Halide Ions Using a Mercury-Coated Platinum Electrode," Charles N. Reilley, D. M. Oglesby, L. B. Anderson, and B. McDuffie, Anal. Chem., 37, 1317 (1965).

"Twin-Electrode Thin-Layer Electrochemistry: Determination of Chemical Reaction Rates by Decay of Steady-State Current," Charles N. Reilley, Bruce McDuffie, and L. B. Anderson, Anal. Chem., 38, 883 (1966).

"Twin-Electrode Thin-Layer Electrochemistry: Kinetics of Second-Order Disproportionation of Uranium(V) by Decay of Steady-State Current." Charles N. Reilley and B. McDuffie. Anal. Chem., 38, 1881 (1966).

"Diagnostic Criteria for the Study of Chemical and Physical Processes by Twin-Electrode Thin-Layer Electrochemistry," Charles N. Reilley, L. B. Anderson, and B. McDuffie. J. Electroanal. Chem., 12, 477 (1966).

"Supporting Electrolyte Effects in Non-Aqueous Electrochemistry. Coordinative Relaxation Reactions of Reduced Metal Acetylacetonates in Acetonitryl," R. W. Murray and L. K. Hiller, Anal. Chem., 39,1221,(1967).

"Dilithium Complexes of Beta-diketonate in Acetonitryl," L. K. Hiller, J. R. Cockrell, R. W. Murray, J. Inorganic and Nuclear Chemistry (in press).

"Optically transparent Thin-layer Electrodes: Studies of Iron II - III Acetylacetonate Ligand Exchange Reactions in Acetonitryl," W. R. Heineman, J. N. Burnett, and R. W. Murray, Anal. Chem., 40, 1970,(1968).

"Optically Transprent Thin-layer Electrodes: Ninhydrin reduction in an Infrared Transparent Cell," W. R. Heineman, J. N. Burnett, R. W Murray, Anal. Chem., 40, 1974(1968).

"Evaluation of an Improved Thin Layer Electrode," A. Yildiz, P. T. Kissinger, and C. N. Reilley, Anal. Chem., 40, 1018 (1968).

"Electrochemistry Using Thin Layer Cells," C. N. Reilley, Rev. Pure and Applied Chem., 18, 137 (1968).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research is concerned with the study of the chemical nature of electrochemical processes (in particular the kinetic and mechanistic study of chemical reactions prior to or following electron transfer), the adsorption of electroactive species on the electrode, and the electrochemical behavior of molecules in their excited electronic states.

The initial work was carried out on the electrolysis between two closely spaced parallel electrode faces. Appropriate circuits using these working electrodes allow independent control of the current on potential at each of the two working electrodes. Chemical changes initiated at one electrode may be observed or modified at the other electrode with only a small time lag. This technique was used to determine diffusion coefficients and diffusion coefficients ratios.

A direct recording AC admittance instrument has been built, tested and modified. A paper on this instrument has been published in Analytical Chemistry, 37, 884 (1965).

Another instrument, which allows automatic measurement of the drop-time of a polarographic capillary was designed and constructed. The instrument is a simple extension of an operational amplifier AC polarograph and provides a means for observing alternating current-time curves while measuring the drop-time. This can be important in adsorption studies.

A study has been made of the AC polarography of trisethylenediaminecobalt /III/ ion and cobalt-EDTA ion.

Work on thin-layer electrochemical technique continued using the micrometer-type cell designed in this laboratory and the method of potential scan coulometry. This work has also been published in Analytical Chemistry. See publications 13 through 22.

Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Conference on Characterization of Macromolecular Structure

2. PRINCIPAL INVESTIGATOR: Dr. Martin Paul
Division of Chemistry and
Chemical Technology
National Academy of Sciences
2101 Constitution Avenue
Washington, D. C.

3. INCLUSIVE DATES: 16 May 1966 - 31 May 1968

4. GRANT NO: AF-AFOSR-1179-66

5. COST AND FY SOURCE: $13,000 FY66

6. PUBLICATIONS:

"Characterization of Macromolecular Structure," National Academy of Sciences, Washington, D. C. Publication 1573 (1968); Final Technical Report, AFOSR-68-2197

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A conference organizing committee consisting of Dr. Donald McIntyre (University of Akron), Chairman, Dr. Fred W. Billmeyer (Rensselaer Polytechnic Institute), Dr. William E. Gibbs (Air Force Materials Laboratory), and Dr. Allan R. Shultz (General Electric Company) was deputized by the NRC Committee on Macromolecular Chemistry to prepare a program for and issue invitations to a Conference on Characterization of Macromolecular Structure, which was held at Airlie House, Warrenton, Virginia, 5-7 April 1967. The objective of the conference was to review critically the various methods now in use for the determination of molecular weight, molecular-weight distribution, and other physical properties characterizing the molecular size and shape of macromolecular materials in liquid solution, including synthetic high polymers and also materials of natural origin. The measuring capabilities of modern instrumentation appear in some situations to have outrun the theoretical interpretation of the results, so that a conference bringing together experts in the instrumentation and theory utilized in research on macromolecular structure offered promise of improving understanding of the uses and limitations of the electronically based instrumentation now widely available.

The conference was attended by 77 invited scientists, of whom 30 presented papers. Eleven of the participants were from foreign nations, so that representation was international. Half-day sessions were devoted to each of the following major topics: molecular-weight determinations from colligative properties, molecular-weight and molecular-size determinations by scattering measurements and by ultracentrifugation, separations by solubility methods, separations by flow methods, characterization by transport methods, and characterization of branched and cross-linked macromolecules. The papers presented, many of which were distributed in pre-print form in advance of the conference, stimulated the most lively discussion.

Following the conference, most of the papers were collected from the authors, and published in the form of a book, "Characterization of Macromolecular Structure," NAS Publication 1573, issued in July 1968.

Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: A Study of the Support of Fundamental Research in the Chemistry Program of the Air Force Office of Scientific Research.

2. PRINCIPAL INVESTIGATORS: Dr. Martin Paul
Dr. Lockhart B. Rogers
National Research Council
Division of Chemistry and
Chemical Technology
National Academy of Sciences
Washington, D. C.

3. INCLUSIVE DATES: 1 March 1967 - 29 February 1968

4. GRANT NO: AF-AFOSR-1302-67

5. COST AND FY SOURCE: $3,000 FY67

6. SENIOR RESEARCH PERSONNEL: Jerome A. Berson
Jacob Bigeleisen
R. A. Bonham
N. Bruce Hannay
R. K. Iler

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Report on the Chemistry Program of the Air Force Office of Scientific Research" Final Technical Report, AFOSR 67-2806

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

With the approval of the Governing Board of the National Research Council, National Academy of Sciences, the authors of this report were selected as a representative committee of research chemists to advise on what specific areas of chemistry should receive primary emphasis in the AFOSR sponsored research program. The report of this committee was appended to the "13th Annual Chemistry Program Review" (AFOSR 67-2237). The conclusions of the committee are listed below.

(1) Because of the extremely wide range of applications of chemistry by the Air Force, it is virtually impossible to single out any aspect of chemistry that is not of potential value to the Air Force. However, a broad area in which the Air Force does have a primary long-range interest is the synthesis, characterization, and theoretical understanding of new materials and new chemical reactions. The Air Force must have materials that not only perform well under extreme conditions but also are capable of withstanding rapid changes from one extreme to another.

(2) Specification in further detail of research areas considered to be most deserving of support within the broad area of primary interestis undesirable, especially if the topics are selected mainly on the basis of their relevance to current developmental problems. Instead, reliance upon the scientific and technical judgment of the Chemistry Research Evaluation Panel and the staff of the Directorate of Chemical Sciences is recommended for the

selection of appropriate proposals, freely conceived and submitted.

(3) As general guidelines for selecting proposals, the Committee recommend that emphasis be placed on novelty of concept, with special attention to neglected areas or new, unexplored areas of chemistry, and that the AFOSR not concentrate a significant fraction of its funds in areas clearly falling within the province of another mission-oriented funding agency.

(4) The possibility of stretching available funds by sharing costs for major research instruments with institutions or with other funding agencies should be explored.

(5) The Directorate of Chemical Sciences, AFOSR is to be commended for having assembled and maintained a basic research program of high quality. The sharp down-trend in percentage support of high quality proposals received during the last two years is disturbing and may soon lead to a significant decrease in the number of such proposals received. With additional funding, the Directorate would be in a better position, both now and in the future, to provide the Air Force with an enlarged program of basic research more commensurate with its needs.

Denton W. Elliott
(Reviewed by Dr. Donald L. Ball)

COMPLETED PROJECT SUMMARY

1. TITLE: AFOSR Program on Liquid Structure

2. PRINCIPAL INVESTIGATOR: Dr. C. J. Pings
Division of Chemistry and
Chemical Engineering
California Institute of Technology
Pasadena, California

3. INCLUSIVE DATES: 1 October 1963 - 30 September 1967

4. CONTRACT NO: AF49(638)-1273

5. COSTS AND FY SOURCES: $163,586 FY64; $75,447 FY66
$72,335 FY67

6. SENIOR RESEARCH PERSONNEL:

Dr. Charles M. Knobler
Dr. Paul G. Mikolaj
Dr. Sergio E. Rodriguez
Dr. A. V. Anantaraman
Dr. George T. Chang
Dr. Anthony F. Collings
Dr. Brian L. Smith

7. JUNIOR RESEARCH PERSONNEL:

Wallace I. Honeywell
Paul G. Mikolaj
Roger W. Caputi
Albert P. Kendig
Colin P. Abbiss
E. B. Nebeker
Richard K. Teague
Arden B. Walters
Raymond C. Cej
Steven C. Smelser
Paul F. Morrison
Joseph F. Karnicky
James R. Boyd
John P. Walters
Vincent P. Gutschick
Paul K. Salzman
Alvin H. Larsen
Michael J. Lindenfeld
James J. Horwitz
Christopher J. Cunningham

8. PUBLICATIONS:

"Comment on Absorption and Dispersion of Sound in Critical Mixtures" A. P. Kendig, R. H. Bigelow, P. D. Edmonds, and C. J. Pings, J. Chem. Phys., 40, 1451 (1964).

"Apparatus for X-Ray Diffraction Studies of Confined Liquids," W. I. Honeywell, C. M. Knobler, B. L. Smith, and C. J. Pings, Rev. Sci. Instr., 35, 1216 (1964).

"Lorentz-Lorenz Functions for Simple Molecules in the Liquid and Gaseous States," C. M. Knobler, C. P. Abbiss, and C. J. Pings, J. Chem. Phys., 41, 2200 (1964).

"X-ray Absorption Factors for Partially Exposed Cylindrical Samples and Annular Sample Cells," A. P. Kendig and C. J. Pings, J. Appl. Phys., 36, 1692 (1965).

"Thermodynamics of Chemical Coupling," C. J. Pings and E. B. Nebeker, I and E C Fundamentals, 4, 376 (1965).

"The Saturated Liquid Density of Carbon-Tetrafluoride from 90-130°K," C. M. Knobler and C. J. Pings, J. Chem. Eng. Data, 10, 129 (1965).

"Flexible Diaphragm Pressure Transducer, W. I. Honeywell and C. J. Pings, Rev. Sci. Instr., 36, 754 (1965)

"Improved Approximations for Incoherent X-Ray Scattering," S. E. Rodriquez and C. J. Pings, Acta Cryst., 18, 979 (1965).

"X-Ray Diffraction Studies of Stable and Supercooled Liquid Gallium," S. E. Rodriquez and C. J. Pings, J. Chem. Phys., 42, 2435 (1965).

"Absorption of Sound in Critical Mixtures," C. J. Pings and A. V. Anantaraman, Phys. Rev. Letters, 14, 798 (1965).

"Refractive Index and Lorentz-Lorenz Function for Saturated Argon, Methane, and Carbon-Tetrafluoride," C. P. Abbiss, C. M. Knobler, R. K. Teague, and C. J. Pings, J. Chem. Phys., 42, 4145 (1965).

"The Continuous Absorption Spectrum of ICl," E. B. Nebeker and C. J. Pings, J. Phys. Chem., 69, 2483 (1965).

"An Experimental Test of the PY and CHNC Integral Equation," P. K. Mikolaj and C. J. Pings, Phys. Rev. Letters, 15, 849 (1966).

"Direct Determination of the Intermolecular Potential Function for Argon From X-Ray Scattering Data,"Phys. Rev. Letters, 16, 4 (1966).

"Absorption of Sound Near the Consolute Point of the Nitrobenzene-Isoctane System," A. V. Anantaraman, A. B. Walters, P. D. Edmonds, and C. J. Pings, J. Chem. Phys., 44, 2651 (1966).

"An Experimental Study of Chemical Coupling," E. B. Nebeker and C. J. Pings, Ind. Eng. Chem. Fundamentals, 5, 310 (1966).

"Structure of Liquids. III. An X-Ray Diffraction Study of Fluid Argon," P. G. Mikolaj and C. J. Pings, J. Chem. Phys., 46, 1401 (1967).

"Structure of Liquids. IV. Direct Correlation Functions for Liquid Argon," P. G. Mikolaj and C. J. Pings, J. Chem.Phys., 46, 1412 (1967).

"Structure of Liquids. VI. Some Characteristics of First-Order Density Expansions of Radial Distribution, Direct Correlation, and Scattering Intensity Functions," C. J. Pings, Molecular Physics, 12, 501 (1967).

"A Simplification and Symmetrization of the Fixman Relation for Viscosity of Critical Mixtures," C. J. Pings, J. Chem. Phys., 46, 2013 (1967).

"Lorentz-Lorenz Function for Solid Argon," C. J. Pings, Physics 33, 473 1967).

"Comments on Friction Constant Formalism," A. F. Collings, J. Chem. Phys., 47, 1265 (1967).

"Structure of Liquids. VII. Determination of Intermolecular Potential Functions and Correlation Functions in Fluid Argon by X-Ray Diffraction Techniques," C. J. Pings, Discussions of the Faraday Society, No. 43, p 89 (1967).

"Self-Diffusion in Simple Liquids. The Linear Trajectory Approximation," A. F. Collings and C. J. Pings, J. Phys. Chem., 71, 3710 (1967).

"Structure of Liquids. V. The Use of the Coordination Number in the Interpretation of Fluid Structure," P. G. Mikolaj and C. J. Pings, J. Phys. and Chem. of Liquids, 1, 93 (1968).

"Structure of Simple Liquids by X-Ray Diffraction," Chapter in Physics of Simple Liquids," C. J. Pings, editors H.A.V. Temperley et al., North-Holland Publishing Company, Amsterdam, in press.

"Analysis of Scattering Data for Mixtures of Amorphous Solids or Liquids," C. J. Pings and J. Waser, J. Chem. Phys., 48, 3016 (1968).

"The Polarizability of an Argon Atom in Solid Argon," B. L. Smith and C. J. Pings, J. Chem. Phys., 48, 2387 (1968).

"Refractive Index and Lorentz-Lorenz Function of Liquid and Gaseous Argon," R. K. Teague and C. J. Pings, J. Chem. Phys., in press.

"On Counting Graphs of Interest in Statistical Mechanics Including Non-Additivity Effects," A. H. Larsen and C. J. Pings, J. Chem. Phys., in press.

"Experimental Study of the Shape of the Coexistence Curve of Argon Near the Critical State," R. K. Teague and C. J. Pings, Phys. Rev. Letters, 26A, 496 (1968).

"AFOSR Program on Liquid Structure," Final Technical Report, AFOSR-67-2512.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of this program has been experimental and theoretical studies of the chemistry and physics of liquids, study of forces and configurations in condensed matter at the molecular level, and quantitative experiments in the general critical region. The basic underlying objectives are to test the validity of existing theories and models of behavior of the liquid state, to obtain better quantitative information about the energy of interaction between molecules, and to obtain basic information for those phenomena where at the present time theory seems to be missing altogether. The central theme of the project has been the direct determination of liquid structure by means of X-Ray diffraction.

During the period covered by this contract, progress toward these objectives can be summarized by the following. The structure of liquid gallium was determined at seven different temperatures, including four in the supercooled region, with the conclusion that this supercooled liquid is quite normal in its structural aspects. There were suggestions of a probable gallium dimer in the liquid phase. Our most extensive structural study so far has been on liquid argon for which we recently reported the X-ray scattering function and the radial distribution function at thirteen different thermodynamic states selected on a systematic temperature-density grid. This permitted for the first time an inspection of the variation of the structure with independent variations of temperature and density. Using these data, a systematic study was also undertaken of the coordination number and its variation with the density of the fluid. With the basic diffraction data it was also possible to make the computations of the direct correlation function, a very important quantity appearing in many recent theoretical characterizations of the liquid state. The hypothesized short-range character of this direct correlation function was substantiated for all thirteen states of argon which were studied.

The computed direct correlation functions and the radial distribution functions were used to test the validity of basic hypotheses underlying the derivations of the Percus-Yevick and convoluted-hypernetted-chain integral equations. These equations have been the two most prominently used theories for describing the liquid state in recent years. Comparison with our experimental data revealed that there are definitely systematic density dependent defects in both theories.

A new method was developed for obtaining the intermolecular potential function directly from X-ray diffraction data on moderately dense gases. This new technique has taken on added significance as it has become apparent during the last two years that the much used Lennard-Jones potential is grossly incorrect in detail. The new method was improved and strengthened considerably by a demonstration that a number of the coefficients in the density expansion of the radial distribution function can be computed directly from the Fourier transform of specific functions of the experimentally accessible X-ray scattering data.

An extensive experimental study of the absorption of sound near the consolute point of the nitrobenzene-isoctane system was completed. This led to the first conclusive confirmation of the functional correctness of the Fixman theory. A separate theoretical analysis led to a simplification and symmetrization of the Fixman theory for the viscosity of critical mixtures.

An extensive mapping has been completed of the Lorentz-Lorenz function for argon through a range of gaseous, liquid and solid states, with the unexpected conclusion that this primitive theory, though not perfect, is remarkably good.

Some new statistical mechanical counting theorems have been derived. These are applicable to the density expansions of the compressibility factor and the radial distribution function; results previously existing in the literature have been generalized to account for systems of arbitrary composition and for non-additivity effects in the intermolecular potential functions.

Dr. D. L. Ball

COMPLETED PROJECT SUMMARY

1. TITLE : Reactions of Free Radicals

2. PRINCIPAL INVESTIGATOR: Prof William A. Pryor
Department of Chemistry
Louisiana State University
Baton Rouge, Louisiana

3. INCLUSIVE DATES: 1 October 1963 - 31 October 1967

4. GRANT NOS: AF-AFOSR-540-64; AF-AFOSR-540-66

5. COSTS AND FY SOURCES: $25,778 FY63; $29,856 FY66

6. SENIOR RESEARCH PERSONNEL: Dr. N. Carroll
Dr. Umberto Tonellato
Dr. E. Ciuffarin

7. JUNIOR RESEARCH PERSONNEL: Richard W. Henderson
Tzu-Lee Huang

8. PUBLICATIONS:

"Hydrogen Secondary Isotope Effects on the Radical Polymerization of Styrene," W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, J. Am. Chem. Soc., 88, 1199 (1966).

"Nucleophilic Displacements at Sulfur. III. The Exchange of Oxygen-18 Between Sodium Thiosulfate and Water," W. A. Pryor and U. Tonellato, J. Am. Chem. Soc., 89, 3379 (1967).

"Use of Tritiated Hydrogen Sulfide as a Radical Scavenger in Liquid-Phase Radiolysis," W. A. Pryor and U. Tonellato, in preparation.

"Rates Constants for Hydrogen Abstraction by Methyl Radicals in the Liquid Phase," W. A. Pryor, U. Tonellato, D. L. Fuller and S. M. Jumonville, to be submitted.

"The Kinetics of Polymerization of Pentafluorostyrene," W. A. Pryor and Tzu-Lee Huang, to be submitted.

"Reactions of Free Radicals," Final Technical Report, AFOSR-67-2386.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

During the period of this grant, research was initiated in these laboratories in three areas of free radical chemistry In addition, a project not involving radicals which was begun some years ago with AEC support was completed under AFOSR support.

1. Vinyl Polymerization

(a) The radical polymerization of styrene was used as a model free radical reaction on which to evaluate hydrogen secondary kinetic isotope effects. Secondary isotope effects have been measured for many ionic reactions but for very few radical reactions. Isotope effects on radical re-

reactions are useful in elucidating the structure of the transition state in radical reactions and for evaluating differences in bonding in the transition state in radical and ionic reactions. By measuring the isotope effect for both deuterium and tritium substituted styrenes, the isotope effect for all of the hydrogens in the activated complex could be calculated.

(b) The kinetics of polymerization of pentafluorostyrene were examined. This research included the study of: rates of polymerization under precipitating and non-precipitating conditions, transfer to organic hydrogen donors, copolymerization, and the measurement of cross-termination rate constant ratios in copolymerization.

2. Hydrogen Sulfide as a Radical Scavenger in Gamma Radiolysis

Solutions of organic solvents containing from 2 to 5 mole % tritiated hydrogen sulfide were subjected to gamma radiation. This was done to demonstrate that H_2S-t can be used to scavenge the free radicals produced by irradiation of organic materials. During the course of work, other laboratories published accounts of the use of H_2S as a scavenger in gas phase and solid phase radiations. The limited experiments by Pryor and his coworkers showed that H_2S promises to be a convenient and reliable scavenger in the liquid phase.

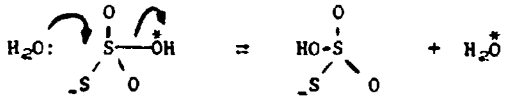
3. Reactions of Methyl Radicals

In 1950, Edwards and Mayo, in a classical study, measured the rate of hydrogen abstraction by the methyl radical from eight hydrogen donors in the liquid phase. These data are widely quoted and they have been used to characterize the methyl radical in solution. In addition, since the rate constants for hydrogen abstraction by the methyl radical have been reported for nearly 100 donors in the gas phase, Edward's and Mayo's data have been used to demonstrate the effect of phase change on the relative rate of reaction of radicals with hydrogen donors. Pryor has repeated the Edwards and Mayo study using modern gas chromatographic techniques. To date, rate constants for some 20 organic donors have been obtained. Eventually, it is hoped to obtain a large collection of rate data reflecting the influence of donor structure on the rate of hydrogen transfer to methyl radicals in the liquid phase.

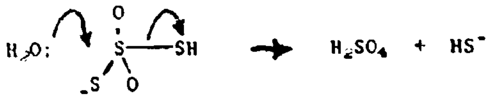
4. Exchange of O-18 Between Thiosulfate and Water.

The mechanism of this exchange reaction was studied. Pryor finds that it is an SN2 reaction by water on the central sulfur of $HO-SO_2-S^-$. As such, the mechanism is analogous to the A-2 hydrolysis of organic esters. This conclusion is supported by the rate law, the entropy of activation, and the solvent isotope effect. One of the fascinating features is the comparison of this oxygen exchange reaction with a disproportionation of thiosulfate which was also studied.

O-18 exchange:



disproportionation:



The second reaction is 10^{12} slower than the first and has a 40 kcal/mole higher activation energy. A mechanism for this interesting O-18 reaction was proposed.

Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Organometallic Synthesis of Reactive Intermediates

2. PRINCIPAL INVESTIGATOR: Dr. Dietmar Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts

3. INCLUSIVE DATES: 1 October 1963 - 9 October 1967

4. GRANT NOS: AF-AFOSR-502-64; AF-AFOSR-502-66

5. COSTS AND FY SOURCE: $46,603 FY64; $54,144 FY66

6. SENIOR RESEARCH PERSONNEL: Dr. L. J. Todd
Dr. G. Singh
Dr. R. J. Cross
Dr. B. Prokai
Dr. R. Suzuki

7. JUNIOR RESEARCH PERSONNEL: J. M. Burlitch
J. Y. -P. Mui
H. D. Simmons, Jr.
M. E. Gordon
R. J. Minasz
R. Damrauer
S. S. Washburne
K. V. Darragh
F. M. Armbrecht, Jr.
V. Mai
H. Dertouzos
R. M. Turkel

8. PUBLICATIONS:

"Concerning the Mechanism of the Reaction of Phenyl(trihalomethyl)-mercurials with Olefins," D. Seyferth and J. M. Burlitch, J. Am. Chem. Soc., 86, 2730 (1964).

"Dihalomethylenation of Protonic Acids with Phenyl(trihalomethyl)-mercury Compounds," D. Seyferth, J.Y.-P. Mui and L. J. Todd, J. Am. Chem. Soc., 86, 2961 (1964).

"Phenyl(dihalomethyl) mercury Compounds. The Reaction of Organotin and Organosilicon Hydrides with Halomethylmercury Compounds." D. Seyferth, H. D. Simmons, Jr., and L. J. Todd, J. Organometal. Chem., 2,282(1964).

"A New Method of Dihalocarbene Generation Based on Trihalomethyl-metal Compounds," D. Seyferth, J.Y.-P. Mui, M. E. Gordon, and J. M. Burlitch, J. Am.Chem. Soc., 87, 681 (1965).

"Synthesis of Monohalocyclopropanes and 1-Haloolefins via Phenyl (dihalomethyl) mercury Compounds," D. Seyferth, H. D. Simmons, Jr., and G. Singh, J. Organometal. Chem., 3, 337 (1965).

"Halomethyl-Metal Compounds. II. The Preparation of gem-Dihalocyclopropanes by the Reaction of Phenyl(trihalomethyl) mercury Compounds with Olefins," D. Seyferth, J. M. Burlitch, R. J. Minasz, J.Y.-P.Mui, H. D. Simmons Jr., A.J.-H. Treiber, and S. R. Dowd, J. Am. Chem. Soc., 87, 4259(1965).

"A Novel Cleavage of Carbodiimides by Phenyl(bromodichloromethyl) Mercury," D. Seyferth and R. Damrauer, Tetrahedron Letters, 189(1966).

"CCl_2 Insertion into Tetraalkylsilicon and -tin Compounds via Phenyl (bromodichloromethyl) mercury." D. Seyferth and S. S. Washburne, J. Organometal. Chem., 5, 389(1966).

"The Insertion of Halocarbenes into the Mercury-Halogen Bond," M. E. Gordon, K. V. Darragh, and D. Seyferth, J. Am. Chem. Soc., 88, 1831 (1966).

"Halomethyl-Metal Compounds. VI. Phenyl(dihalomethyl) mercury Compounds: Their Preparation nd Some Cleavage Reactions," D. Seyferth and H. D. Simmons, Jr., J. Organometal. Chem., 6, 306(1966).

"Halogenated Organotin Compounds as CX_2 Transfer Agents," D. Seyferth, F. M. Armbrecht, Jr., B. Prokai, and R. J. Cross, J. Organometal. Chem., 6, 573 (1966).

"Halomethyl-Metal Compounds. VII. The reaction of Phenyl (bromodichloromethyl) mercury with Carboxylic Acids," D. Seyferth and J. Y.-P. Mui, J. Am. Chem. Soc., 88, 4672 (1966).

"Halomethyl-Metal Compounds. IX. The Reaction of Phenyl(bromodichloromethyl) mercury with Alcohols," D. Seyferth, A. Mai, J.Y.-P. Mui and K. V. Darragh. J. Org. Chem., 8, 29(1967).

"Halomethyl-Metal Compounds. X. The Reaction of Organosilicon, Organogermanium and Organotin Hydrides with Phenyl(trihalomethyl) mercury Compounds," D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, Jr., J. Organometal. Chem., 7, 405 (1967).

"Halomethyl-Metal Compounds. XII. The Action of Sodium Iodide on Phenyl (trihalomethyl) mercury Compounds. A New Method of Dihalocarbene Generation," D. Seyferth, M. E. Gordon, J Y.-P. Mui, and J. M. Burlitch, J. Am. Chem. Soc., 89, 959 (1967).

"CX_2 Insertion into the Silicon-Mercury and Germanium-Mercury Bonds," D. Seyferth, R. J. Cross, and B. Prokai, J. Organometal Chem., 7, P20 (1967).

"Insertion of CCl_2 into the Silicon-Carbon Bond of Silacyclobutanes," D. Seyferth, R. Damrauer, and S. S. Washburne, J. Am. Chem. Soc., 89, 1538 (1967).

"The Reaction of Phenyl(trihalomethyl) mercurials with Hexamethylditin. The First Case of Dihalocarbene Insertion into a Metal-Metal Bond to Give a Stable MCX_2M System," D. Seyferth and F. M. Armbrecht, Jr., J. Am. Chem. Soc., 89, 2790 (1967).

"Halomethyl-Metal Compounds. XIII. The Preparation of gem-Difluorocyclopropanes by Iodide Ion Induced CF_2 Transfer from Trimethyl (trifluoromethyl) tin," D. Seyferth, H. Dertouzos, R. Suzuki, and J.Y.-P Mui, J. Org. Chem., 32, 2980 (1967).

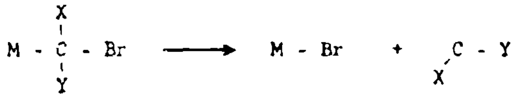
"Halomethyl-Metal Compounds. XIV. The Mechanisms of the Phenyl(bromodichloromethyl) mercury-Olefin Reaction," D. Seyferth, J.Y.-P Mui, and J. M. Burlitch, J. Am. Chem. Soc., 89, 4953 (1967).

"The Chemistry of Halomethyl-Mercury Compounds. Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research. IX. Organometallic Compounds," D. Seyferth, pp89-135, Robert A. Welch Foundation, Houston, Texas (1966).

"Organometallic Synthesis of Reactive Intermediates," Final Report AFOSR-68-0157.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The general area of the research was the generation of DIVALENT CARBON INTERMEDIATES through α-elimination reactions from ORGANOMETALLIC PRECURSORS.



$$M-\overset{X}{\underset{Y}{C}}-Br \longrightarrow M-Br + \dot{C}(X)-Y$$

Such reagent systems are of great value since they allow the generation and transfer to substrate of CARBENE under very mild conditions in the virtual absence of complicating side reactions. This has allowed Dr. Seyferth and his coworkers to study in some detail the chemistry of carbenes and has allowed them to carry out carbene reactions which had never been observed before because alternate carbene generating systems were incompatible with the products formed.

Among carbene transfer systems investigated by Dr. Seyferth's group are the following. The divalent carbon species generated is in brackets.

$PhHgCCl_3$ [CCl_2], $PhHgCCl_2Br$ [CCl_2], $PhHgCClBr_2$ [$CClBr$],

$PhHgCBr_3$ [CBr_2], $PhHgCHCl_2$ [$CHCl$], $PhHgCHBr_2$ [$CHBr$],

$PhHgCHClBr$ [$CHCl$], [$Ph_2Hg + ICH_2HgI$] [CH_2],

$Hg(CH_2Br)_2$ [CH_2], [$PhHgCCl_3 + NaI$] [CCl_2],

Me_3SnCF_3 [CF_2], [$Me_3SnCF_3 + NaI$] [CF_2].

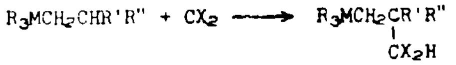
Among the reactions of carbenes studied were the following:

a) olefin + $CX_2 \longrightarrow$ cyclopropane

b) $RCO_2H + CX_2 \longrightarrow RCO_2CX_2H$

c) $RN{=}C{=}NR + CX_2 \longrightarrow RN{=}CX_2 + RN{\equiv}C$

d)



$$R_3MCH_2CHR'R'' + CX_2 \longrightarrow R_3MCH_2\underset{CX_2H}{C}R'R''$$

(M = Si and Sn)

e) $RHgCl + CX_2 \longrightarrow RHgCX_2Cl$

f) $R_3SnCl + CX_2 \longrightarrow R_3SnCX_2Cl$

g) $ROH + CX_2 \longrightarrow ROCX_2H$

h) $HCl + CX_2 \longrightarrow HCX_2Cl$

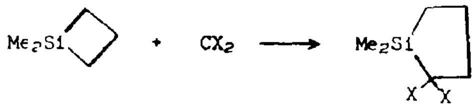
i) $R_3MH + CX_2 \longrightarrow R_3MCX_2H$

(M = Si and Ge)

j) $(Me_3M)_2Hg + CX_2 \longrightarrow Me_3MCX_2HgMMe_3$

(M = Si and Ge)

k)



l) $Me_3Sn\text{-}SnMe_3 + CX_2 \longrightarrow Me_3SnCX_2SnMe_3$

Mechanism studies relating to reactions a, b, g, h, i and j were carried out, in greatest detail for reactions a and i. Among the notable "firsts" in this list are the following:

(a) the first CX_2 insertion into a metal-metal bond (reactions j and l).

(b) the first CX_2 insertion into a strained, cycloaliphatic ring, with ring expansion (reaction k).

(c) the first *bona fide* CX_2 insertion into a metal-halogen bond (reactions e and f).

(d) the first CX_2 insertion into the O-H bond of carboxylic acids (reaction b).

(e) noteworthy is the cyclopropanation of very unreactive (to CX_2 from other sources) olefins or olefins which are very sensitive to nucleophilic attack, such as acrylonitrile, vinylsilanes, vinyl acetate, tetrachloroethylene, etc.

(f) noteworthy also is the Me_3SnCF_3 + NaI reagent system which represents the mildest CF_2 generating system to date and which transfers CF_2 to olefins in high yield.

The $PhHgCX_3$ reagents whose chemistry Dr. Seyferth's group has developed under this grant have been finding increasing use by others in organic synthesis, particularly in the preparation of cyclopropanes. One of these reagents, $PhHgCCl_3$, has found its way into the Eastman catalog. During his travels Dr. Seyferth has noted industrial interest in these mercury reagents which apparently are useful the adding CX_2 to C=C bonds in polymers from 1,3-dienes.

Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Photochemistry of Azo Compounds and Studies in Unimolecular Reactions

2. PRINCIPAL INVESTIGATOR: Dr. Colin Steel
Department of Chemistry
Brandeis University
Waltham, Massachusetts

3. INCLUSIVE DATES: 1 January 1964 - 31 December 1967

4. GRANT NOS: AF-AFOSR-583-64; AF-AFOSR-583-66

5. COSTS AND FY SOURCE: $44,828 FY64; $53,262 FY66

6. SENIOR RESEARCH PERSONNEL: Dr. T. F. Thomas
Dr. G. S. Milne

7. JUNIOR RESEARCH PERSONNAL: M. L. Arin
C. I. Sutin

8. PUBLICATIONS:

"Photoinitiation of Unimolecular Reactions. The Photolysis of 2,3-Diazabicyclo [2.2.1] hept-2-ene," T. F. Thomas and C. Steel, J. Am. Chem. Soc., <u>87</u>, 5390 (1965).

"The Florescence of Cyclic Azo Compounds: Determination of Singlet Lifetimes," C. Steel and T. F. Thomas, Chem. Comm. 900 (1966).

"Distribution and Exchange of Excess Vibrational Energy Produced in the Photolysis of 2, 3-Diazabicyclo [2.2.1] hept-2-ene," T. F. Thomas, C. I. Sutin and C. Steel, J. Am. Chem. Soc., <u>89</u>, 5107 (1967).

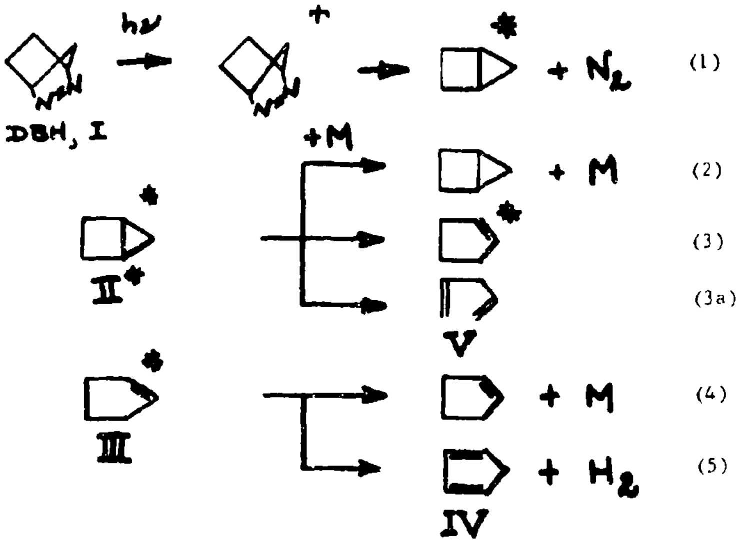
"Primary Processes in the Photochemistry of Bicyclic Azo Compounds," B. S. Solomon, T. F. Thomas and C. Steel, J. Am. Chem. Soc., <u>90</u>, 2249 (1968).

"Gas Phase Oxidation of Photochemically Generated Isopropyl Radicals," G. S. Milne and C. Steel, J. Phys. Chem., to be published (paper presented at Natick Symposium on Photochemistry and Radiation Chemistry, April, 1968).

"Primary Processes in the Photochemistry of Azo and Realted Compounds and Studies in Unimolecular Reactions," Final Technical Report, AFOSR

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

1. Photochemical Initiation of Unimolecular Reactions - The first object of this research was to see if vibrationally excited molecules could be produced photochemically. The following system was studied. 2, 3-diazabicyclo -[2.2.1] hept -2-ene is abbreviated as DBH.



Since the thermal unimolecular reactions of  and  had previously been studied we had knowledge of the unimolecular parameters for these molecules. Furthermore since 3, 3a and 4 are a linked sequence of unimolecular reactions all initiated by 1, they therefore provide a more stringent test of theory than a system which simply initiates one reaction. By studying the pressure dependences of II - V we were able to arrive at a fairly good estimate of E_{mp}, the average excess energy acquired by II* as a result of the photochemical act (E_{mp} = 76.6 kcal for λ_{irr} = 3341 Å). Varying the irradiating wavelength varied E_{mp} in the predicted manner.

These studies lead to the construction of a model by which DBH photodissociates and this model can be used to study vibrational energy transfer by "inert" molecules M.

2. Primary Processes in the Photochemistry of Cyclic Azo Compounds - The studies outlined above required greater knowledge of the processes which precede and compete with photochemical dissociation. We therefore studied the photochemistry of DBH and DBO. (2,3-diazabicyclo.(2,2,2)-2-octene) The primary processes can be represented by the reactions shown below where Azo$^+$ represents the (n, *) excited singlet state of the azo compound.


DBO

$$\text{Azo} + h\nu_a \xrightarrow{I_{abs}} \text{Azo}^+ \qquad (6)$$

$$\text{Azo}^+ \xrightarrow{k_f} \text{Azo} + h\nu_f \text{(fluorescence)} \qquad (7)$$

$$\text{Azo}^+ \xrightarrow{k_q} N_2 + \text{hydrocarbons (dissociation)} \qquad (8)$$

$$\text{Azo}^+ + X \xrightarrow{k_q} \text{Azo} + X \text{ (physical quenching)} \qquad (9)$$

$$\text{Azo}^+ + X \xrightarrow{k_q'} N_2 + \text{hydrocarbons (collision induced dissociation)} \qquad (10)$$

Both DBO and DBH fluoresce, this is the first reported fluorescence of aliphatic azo compounds. Becuase of the high fluorescence yeild of DBO a flash excitation technique was used to measure the lifetime of DBO$^+$ directly. The measured value (1.0×10^{-6} sec) was in good agreement with the calculated value (0.4×10^{-6} sec). DBH$^+$ is quenched mainly by collision induced dissociation. On the other hand in the case of DBO$^+$ physical quenching is the major process. In the latter case our results agree well with those of Hammond on the singlet quenching of aromatic compounds, which suggests that a common mechanism might be operative, but as yet the details of this mechanism are not at all clear.

3. The Gas Phase Oxidation of Photochemically Quenched Alkyl Radicals - The major products in the photodecomposition of azoisopropaneoxygen mixtures are acetone and isopropanol. Other products are isopropylhydroperoxide, Previous work would have suggested that the acetone and isopropanol arose either by disproportionation of two alkoxy radicals or by

$$C_3H_7O_2\cdot \rightarrow \text{acetone} + \cdot OH \qquad (11)$$

$$C_3H_7O_2\cdot + \cdot OH \rightarrow \text{isopropanol} + O_2 \qquad (12)$$

However, analysis showed that neither of these schemes could be correct. Instead, we suggest the mechanism:

$$C_3H_7O\cdot + O_2 \rightarrow \text{acetone} + \cdot HO_2 \qquad (13)$$

$$C_3H_7O\cdot + HO_2\cdot \rightarrow \text{isopropanol} + O_2 \qquad (14)$$

$$C_3H_7O_2\cdot + HO_2\cdot \rightarrow \text{hydroperoxide} + O_2 \qquad (15)$$

$$C_3H_7O\cdot + \text{hydroperoxide} \rightarrow \text{isopropanol} + C_3H_7O_2\cdot \qquad (16)$$

This scheme accounts for the variation in the rates of formation of acetone and isopropanol as the reaction proceeds. It also accounts for the formation of hydroperoxide, which goes through a maximum.

Dr. D. L. Ball

COMPLETED PROJECT SUMMARY

1. TITLE: Rates of Exchange of Solvent Molecules with Paramagnetic Ions

2. PRINCIPAL INVESTIGATORS: Dr. Thomas R. Stengle
Department of Chemistry
University of Massachusetts
Amherst, Mass.

Dr. Cooper H. Langford
Department of Chemistry
Amherst College
Amherst, Mass.

3. INCLUSIVE DATES: 1 January 1963 - 31 August 1967

4. GRANT NO: AF-AFOSR-212-63; AF-AFOSR-212-65

5. COSTS AND FY SOURCE: $26,200 FY63; $20,600 FY65

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL:
John S. Babiec, Jr.
Lawrence S. Frankel
David K. Ravage
Max Eisenberg
Salvatore R. DiNardi

8. PUBLICATIONS:

"The Outer Coordination Sphere. I. Nuclear Magnetic Relaxation Time Effects Produced by Paramagnetic Ions with Nonlabile Inner Coordination Spheres," T. R. Stengle and C. H. Langford, J. Phys. Chem. 69, 3299 (1965).

"A Study of Preferential Solvation Utilizing Nuclear Magnetic Resonance," L. S. Frankel, T. R. Stengle, and C. H. Langford, Chemical Communications, 393 (1965).

"Kinetics of Exchange of DMF Between the Coordination Sphere of Co(II) and Ni(II) and the Bulk Solvent Utilizing ^{17}O Nuclear Magnetic Resonance," J. S. Babiec, T. R. Stengle, and C. H. Langford, Inorg. Chem., 5, 1362 (1966).

"$MnSO_4$ Association and Sulphate Chelation: A Solvent NMR Study," L. S. Frankel, T. R. Stengle, and C. H. Langford, Inorg. Nucl. Chem., 29, 243 (1967).

"The Uses of Nuclear Magnetic Resonance in the Study of Ligand Substitution Processes," T. R. Stengle and C. H. Langford, Coordination Chemistry Reviews, 2, 349 (1967).

"Acetonitrile Exchange Rates in Solutions of Nickel (II) Ions by Nuclear Magnetic Resonance," D. K. Ravage, T. R. Stengle and C. H. Langford, Inorg. Chem., 6, 1252 (1967).

"Kinetic Order with Respect to Solvent: Acid Hydrolysis and Preferential Solvation of the Reineckate Ion," Cooper H. Langford and John F. White, Can. J. Chem., 45, 3049 (1967).

"A Nuclear Magnetic Resonance Investigation of Paramagnetic Relaxation in Viscous Solutions," Laurence S. Frankel, J. Phys. Chem., 72, 736 (1968).

"Rates of Exchange of Solvent Molecules with Paramagnetic Ions," Final Technical Report, AFOSR-67-2387.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this work has been the elucidation of the factors which determine the rate of solvent exchange (and ligand substitution) reactions with transition metal ions in solution. In many octahedral complexes it has become apparent that the reaction is mainly dissociative in mechanism, and that it is relatively independent of the entering group. Hence the composition of the second coordination sphere plays an important role in the reaction rate. It was therefore necessary to work out procedures which will solve this problem.

Solvent Exchange Processes: The research effort was divided between two areas, one of which is the measurement of solvent exchange rates with paramagnetic transition metal ions. In particular there is a need for data in non-hydrogen bonded solvents. Drs. Stengle and Langford examined the reaction of ^{17}O labeled dimethylformamide with several metal ions and worked out reaction rates and activation parameters. The exchange of acetonitrile with Ni(II) was also studied in some detail. One might expect to find a correlation of the rate data with solvent properties, however, no simple interpretation has emerged. It seems that many factors must be taken into account in any attempt at a mechanistic interpretation of the rate data. The extant data do lend considerable support to the idea that the mechanism is primarily dissociative, but the intimate details of the reaction are not clear at this time.

Preferential Solvation Studies: Drs. Stengle and Langford have been engaged in a program directed toward the development of techniques for the study of the second coordination sphere (first solvation shell) of metal complexes. Ion pairing with non-labile Cr(III) complexes was investigated. This was based on the effect which ion pair formation has on the relaxation time of the anion. A similar technique was used to study the solvation of neutral complexes in mixed solvents. If the complex is paramagnetic, its effect on the solvent spectrum can be used to prove the solvation shell; if the complex is diamagnetic, the chemical shift of the central metal nucleus can often be utilized as a probe. This shift is extremely sensitive to the immediate environment of the metal atom. These methods can also be applied to the first coordination sphere. For example, the composition of the ligand sphere in a Co(II) -H_2O-dimethylformamide system can easily be derived from the relaxation time of the solvent protons and independently from the solvent contact shift. A combination of such methods has recently been used to study the change of the composition of the solvation sphere of a metal ion upon ion pair formation.

A total of three techniques have been brought to bear on the preferential solvation problem. When the complex is diamagnetic, the chemical shift of the metal nucleus can be used. With paramagnetic solutes, both the relaxation time and contact shift of the solvent can be used as a probe.

Dr. A . J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: A Study of Solvated and Trapped Electrons

2. PRINCIPAL INVESTIGATOR: Prof M.C.R.Symons
Department of Chemistry
University of Leicester
Leicester, England

3. INCLUSIVE DATES: 1 January 1962 - 31 December 1967

4. GRANT NO: AF-EOAR 62-64, AF-EOAR 64-80

5. COSTS AND FY SOURCE: $7,700 FY62; $13,500 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. R. Catterall, Dr. W. Cronenwett

7. JUNIOR RESEARCH PERSONNEL: Mr. J. Tipping

8. PUBLICATIONS:

"Effect of Added Electrolyte on the Electron Spin Resonance Spectra of Solutions of Metals in Ammonia," R. Catterall, J. Corset and M.C.R. Symons, J. Chem. Phys., 38, 272 (1963).

"Unstable Intermediates. Part XXII. Solvated Electrons: The Effect of Added Electrolytes on the Electron Spin Resonance Absorption of Solutions of the Alkali Metals in Liquid Ammonia," R. Catterall and M.C.R. Symons, J. Chem. Soc., 4342 (1964).

"Unstable Intermediates. Part XXIV. Solvated Electrons: A Confined Model," M.C.R. Symons, J. Chem. Soc., 4357 (1964).

"Electron Spin Resonance Studies of the Onset of Metallic Character in Metal Ammonia Solutions," R. Catterall, J. Chem. Phys., 43, 2262 (1965).

"Unstable Intermediates. Part XL. Solvated Electrons: Electron-Cation Interactions in Potassium - Amine Solutions," R. Catterall, M.C.R. Symons and J. W. Tipping, J. Chem. Soc., 1529 (1966).

"Unstable Intermediates. Part XXXIV. Solvated Electrons: A Model for the Spin-paired Species in Liquid Ammonia" R. Catterall and M.C.R. Symons, J. Chem. Soc., 13 (1966).

"Unstable Intermediates. Part XXXIII, Solvated Electrons: ESR of Solutions of Potassium in Ethylamine," R. Catterall and M.C.R. Symons, J. Chem. Soc., 6656 (1965).

"Unstable Intermediates. Part XXXI. Solvated Electrons: Solutions of Europium in Ammonia," R. Catterall and M.C.R. Symons, J. Chem. Soc., 3763 (1965).

"Unstable Intermediates. Part XLIV. Solvated Electrons: Solutions of the Alkali Metals, Including Sodium in Amines, by Use of ESR and Optical Spectroscopy," R. Catterall, M.C.R. Symons, and J. W. Tipping, J. Chem. Soc., 1234 (1967).

"Metals in Non-Metallic Solvents," Final Technical Report, AFOSR-68-0842

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research performed fell into four somewhat overlapping divisions: (i) the study of the diamagnetic species in metal ammonia solutions, (ii) the study of the species and equilibria in metal amine solutions, (iii) the study of the structure of the nonconducting paramagnetic species in metal amine solutions, and (iv) the study of the interactions of paramagnetic and diamagnetic species in mixed ammonia and amine solutions.

The models proposed for the diamagnetic species include the metal dimer $(M_2)_s$, the ion cluster $(M_s^+e_s^-)_2$, the metal anions $e_s^-M^+e_s$ and M_s^-, and the solvated electron pair $(e_2^{2-})_s$. An examination of molar volume, optical absorption, spin lifetime, and the properties of europium solutions led to the conclusion that the most satisfactory model is the solvated electron pair.

The similarity between metal ammonia solutions and metal amine solutions suggested that a study of the amine solution species might illuminate the processes in ammonia solutions. The potassium-ethylamine system was studied. Optical absorption bands are found at 14,800 cm^{-1}, 12,500 cm^{-1}, and E.S.R. measurements indicate a singlet characteristic of the solvated electron and a pair of quartets characteristic in intensity and splitting of the naturally occurring potassium isotopes.

Potassium was dissolved in ethylamine, propylamine, isopropylamine, and n-butylamine to study the effect of the alkyl group on the equilibrium. The atomic character of the "solvated metal atoms" increases rapidly with increasing alkyl group bulk as well as with temperature; this was formerly thought to be due to a decrease in the overall bonding between the first shell of solvent molecules and the cation. However, the current model, which also explains the two outer lines of the quartet being broader than the two inner lines, is that M_s is composed of two species, one being almost a free atom and the other being an ion-pair. The equilibrium between these two is affected by temperature and solvent.

Of the alkali metals only sodium fails to dissolve in primary amines and no hyperfine splitting has ever been previously observed. Sodium will, however, dissolve in ammonia-amine mixtures and hyperfine splittings were observed. Solutions were studied over a wide ammonia concentration range. Lithium, dissolved in amines, produces quite different E.S.R. spectra to those of the other alkali metals. A model which explains the data for all the alkali metals in amines has been proposed.

Finally, two other related studies have been made, metals in glasses and metals in hexamethylphosphoramide. An obvious experiment for elucidating the structure of the solvation shell is that of freezing the metal solution to a rigid glass. Extensive attempts have been made to freeze metal ammonia solutions but without success. Additionally metal solutions have been made in mixed solvents known to freeze to glasses but again without success. In each case the glasses remain blue but the narrow E.S.R. singlet vanishes and a much broader line characteristic of colloidal metal appears instead.

LtCol E. T. Walford

COMPLETED PROJECT SUMMARY

1. TITLE: Reaction Rate Studies of Gaseous Unimolecular Isomerizations

2. PRINCIPAL INVESTIGATOR: Frederick D. Tabbutt
Reed College
Portland, Oregon

3. INCLUSIVE DATES: 2 October 1962 - 31 August 1967

4. GRANT NOS: AFOSR-119-63; AFOSR-119-65

5. COSTS AND FY SOURCE: $22,460 FY63; $23,153 FY65

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: James Luyten
Kaye Smith Ladd
Edward Waage
Michael Moran

8. PUBLICATIONS:

"The Isomerization of Cyclobutane at Moderately High Pressures" (to be submitted to J. Phys. Chem.)

"Reaction Rate Studies of Gaseous Unmolecular Isomerizations," Final Report, AFOSR-67-2449.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project sought evidence for biradical intermediates in the classical unimolecular thermal, isomerizations of cyclopropane and cyclobutane. These intermediates have been proposed to explain the geometric isomerizations of these compounds which occur concurrently with the permanent ring opening isomerizations. They have not been detected previously in these reactions. Based on the hypothesis that the intermediates do exist but are too short-lived to have been detected previously, a technique was developed to allow these reactions to be studied quantitatively up to pressures of 300 atmospheres. It was hoped that at high enough pressures the intermediate could be engaged in a collision resulting in either a reaction or a deactivation, either one of which might produce a new product.

The cyclopropane system showed no evidence of any intermediate which was longer lived than 10^{-13} seconds and reactive or deactivatable.

The cyclobutane reaction produced ethyl cyclobutane which was not found at low pressures. The ethyl cyclobutane can be explained with a mechanism involving a tetramethylene radical or a mechanism involving an excited state ethylene. The latter is in agreement with the correlation diagram predictions of Woodward and Hoffman. High pressure reactions of ethylene alone produce no measurable cyclobutane, despite the fact it should be detectable based on thermodynamic predictions. This is also in agreement with the Woodward-Hoffman correlation diagram for the cyclobutane system. The existence of tetramethylene is neither proven nor disproven. However, its occurrence is indicated because the first order rate contants of this study compare favorably with those calculated from the data obtained by others at low pressure. The decomposition of cyclobutene, then, is apparently not affected seriously by other reactions.

D. W. Elliott

COMPLETE PROJECT SUMMARY

1. TITLE: Solvent Isotope Effects for Trideuteromethanol vs. Methanol

2. PRINCIPAL INVESTIGATOR: Edward R. Thornton
Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania

3. INCLUSIVE DATES: 1 June 1963 - 31 October 1967

4. GRANT NOS: AF-AFOSR-431-63; AF-AFOSR-431-65

5. COSTS AND FY SOURCES: $30,000 FY62; $33,850 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. Keith C. C. Bancroft
Dr. Peter Smith
Dr. King Auyang

7. JUNIOR RESEARCH PERSONNEL: Paul Heim
Gino Frisone

8. PUBLICATIONS:

"Isotope Effects for Solvolysis of *t*-Butyl Chloride and *t*-Butyl-d_9 Chloride in Solvent Mixtures of Constant Ionizing Power," G. J. Frisone and E. R. Thornton, J. Am. Chem. Soc., **86**, 1900 (1964).

"Solvolysis Mechanisms. β-Deuterium Isotope Effects for t-Butyl Chloride Solvolysis at Constant Ionizing Power and Effect of Structure of Reactant SN 1 Transition State Geometry," G. J. Frisone and E. R. Thurton, J. Am. Chem. Soc., **90**, 1211.

"Solvent Isotope Effects for Trideuteromethenol vs Methanol," Final Technical Report, AFOSR-67-2791.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research was undertaken in order to test competitive solvent isotope effects as a new and powerful tool for studying mechanisms of solvolysis reactions. Among the most basic questions about the mechanisms was the extent of solvent participation in the rate-determining step, especially in cases where a carbonium ion intermediate may be formed. Dr. Thornton and his research group developed analytical methods for precise isotope effect studies of the solvolysis of alkyl halides in CD_3OH-CH_3OH mixtures, determining the isotope effect for product formation by competition. The products of solvolysis were isolated from the relatively large volume of solvent, without isotope fractionation, using gas chromatography and special collectors cooled with liquid nitrogen. These products can then be analyzed for the ratio of CD_3 to CH_3 groups present by high precision mass spectrometric measurements. Precise isotope effect data have not as yet been obtained.

Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Carbonium Ion Radicals and Oxy Radicals

2. PRINCIPAL INVESTIGATOR: Dr. Teddy G. Traylor
Department of Chemistry
University of California, San Diego
La Jolla, California

3. INCLUSIVE DATES: 1 September 1963 - 31 March 1968

4. GRANT NO: AF-AFOSR-514-64; AF-AFOSR-514-66

5. COSTS AND FY SOURCE: $36,615 FY64; $61,749 FY66

6. SENIOR RESEARCH PERSONNEL: Dr. Arnold Factor
Dr. Thomas Tidwell
Dr. Judith Ware
Dr. John Mangravite
Dr. Hansruedi Kiefer

7. JUNIOR RESEARCH PERSONNEL: George Jurch
Crystal Lin

8. PUBLICATIONS:

"Radical-Ionic Reaction Mechanisms. Homolysis of the Carbonium Ion t-Butyl Tropeniumperacetate," G. R. Jurch, Jr. and T. G. Traylor, J. Am. Chem. Soc., 88, 5228 (1966).

"Resonance Stabilization of α-Ferrocenyl Carbonium Ions," J. C. Ware and T. G. Traylor, Tetrahedron Letters, No. 18, 1295 (1965).

"The Chemistry of Metallocenes. I. Carbonium Ion Stabilization by the Ferrocenyl Group," T. G. Traylor and J. C. Ware, J. Am. Chem. Soc., 89, 2304 (1967).

"Nucleophilic Substitution on Ferrocenylmethyl Chloride," Thomas T. Tidwell and T. G. Traylor, J. Am. Chem. Soc., 88, 3442 (1966).

"Di-t-Butyl Hyponitrite. A Convenient Source of t-Butoxy Radicals," Hansruedi Kiefer and T. G. Traylor, Tetrahedron Letters, No. 49, 6163 (1966).

"Cage Reactions of t-Butoxy Radicals. Effects of Viscosity and of Intervening Molecules," Hansruedi Kiefer and T. G. Traylor, J. Am. Chem. Soc., 89, 6667 (1967).

"Mechanisms of Electrophilic Substitution in Metallocenes: The Inside-Outside Relationship," John A. Mangravite and T. G. Traylor, Tetrahedron Letters, No. 45, 4461 (1967).

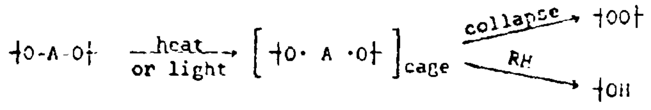
"Carbon-Metal Hyperconjugation in Metallocenes. Hydrogen Exchange in Phenylferrocene," John A. Mangravite and T. G. Traylor, Tetrahedron Letters, No. 45, 4457 (1967).

"Carbonium Ion Radicals and Oxy Radicals," Final Report AFOSR-68-2089

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

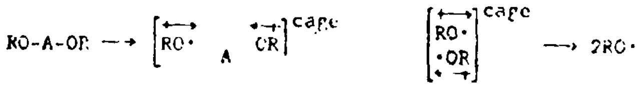
I. Cage reactions of oxy radicals

t-Butoxy radical pairs from three different precursors were generated and the cage collapse, as a function of viscosity in hydrocarbon solvents, was studied.



(1)

The results obtained indicate that there is some force in addition to solvent viscosity (diffusion) which is holding the radicals together. Dr. Traylor suggests that dipolar radicals such as RO·, R_2N· etc. are held together by dipole-dipole interactions in hydrocarbon solvents whereas CH_3· radicals are not.



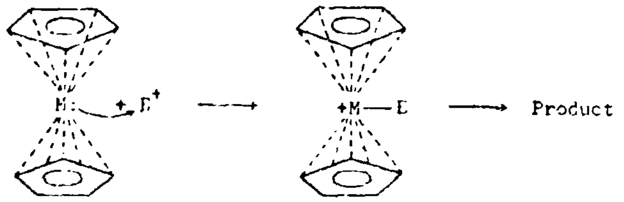
(2)

This conclusion then predicts that cage behavior will depend upon radical structure, solvent viscosity and solvent structure. This offers some explanation for the finding that the theoretical diffusion equation, which states that amount of cage escape should be linear when plotted against the reciprocal of viscosity, does not adequately describe the behavior of t-butoxy radicals.

It was also discovered in this work that hyponitrites, well known to be dangerously explosive, may be very safe, medium temperature initiators if the alkyl group is tertiary. Thus, the easily prepared di-t-butylhyponitrite is a useful initiator in the range 25 to 80° and is about as safe to handle as benzoly peroxide.

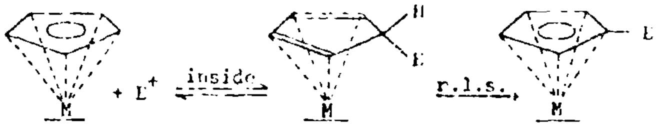
II. Metallocene Reactions

Ring and side chain reactions in metallocenes (particularly ferrocene) were studied. Contrary to popular interpretations which attributed the high reactivity of ferrocenes toward electrophiles to direct attack on the metal, Traylor and his staff have concluded that such metallocene reactions are explicable in terms of two known phenomena: (1) electrophilic cleavage of carbon-metal bonds, and (2) carbon-metal hyperconjugation. Thus, direct interaction of electrophile with the metal atom as in equation (3) is not an important part of electrophilic substitution or side chain reactions.



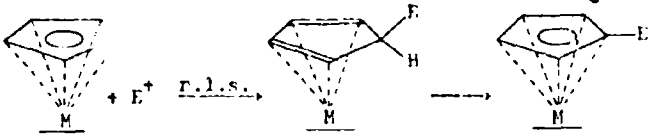
(3)

For electrophilic substitutions two mechanisms have been proposed: an "inside attack" mechanism, and an "outside attack" mechanism. In the more facile inside attack process the electrophile directly breaks the carbon-metal bond with retention of configuration.



(4)

In the slower outside attack mechanism the electrophile breaks the carbon-metal bond with the less favorable inversion of configuration.

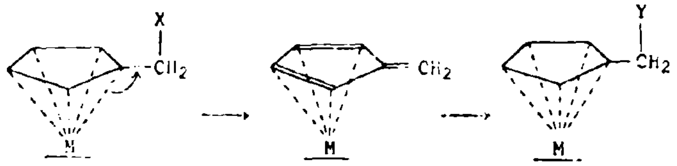


(5)

Strong electrophiles such as $CH_3\dot{C}O$ take path (5) and weak electrophiles such as $Hg(OAc)_2$ take path (4).

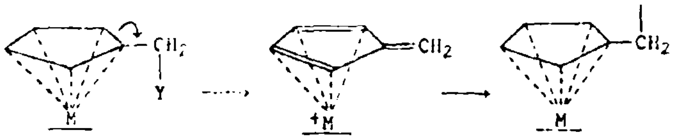
There are correspondingly two solovolysis mechanisms for α-metallocenylalkyl halides, a trans (corresponding to inside) and a cis (corresponding to outside) mechanism.

trans



(6)

cis



(7)

Such trans and cis hyperconjugative accelerations are well known in other organometallic chemical reactions.

These two proposals clarify some paradoxes which existed in metallocene chemistry and make predictions of rates and stereochemistries of such reactions more reliable.

Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. **TITLE:** Concentration Fluctuations in the Vicinity of the Critical Point

2. PRINCIPAL INVESTIGATORS: Dr. Peter Debye
Dr. Benjamin Widom*
Department of Chemistry
Cornell University
Ithaca, New York

3. INCLUSIVE DATES: 1 October 1966 - 31 December 1967

4. GRANT NO: AF-AFOSR-1253-67

5. COST AND FY SOURCE: $18,009 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. Robert T. Jacobsen
Dr. Claude C. Gravatt, Jr.
Dr. Yalman Balta

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Electric Field Effect on Critical Opalescence. II. Relaxation Times of Concentration Fluctuations," P. Debye, C. C. Gravatt, and M. Ieda, J. Chem. Phys., 46, 2352 (1967).

"Measurement of Relaxation Times of Concentration Fluctuations by the Electric Field Effect on Critical Opalescence," C. C. Gravatt, Phys. Rev. Letters, 18, 948 (1967).

"The Direct Visual Observation of Concentration Flucuations in a Critical Mixture," P. Debye and R. T. Jacobsen (in press).

"Elastic Scattering of Light Near the Critical Temperature: I. Methanol-Cyclohexane," Y. Balta and C. C. Gravatt (in press).

"Concentration Flucuations in the Vicinity of the Critical Point," Final Technical Report, AFOSR-67-2300.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The direct visual observation of the concentration fluctuations in a critical mixture of polystyrene in cyclohexane by means of phase contrast microscopy has been accomplished. This work also showed some promise as to obtaining a measure of the persistence lengths and relaxation times in critical solutions.

The scattering function for a distribution of Gaussian polymer coils can be inverted by a Mellon transformation by a method similar to that of Riseman. This will yield the molecular weight distribution as an integral over scattered intensity as a function of the parameter n = ks, where

$$k = \frac{2\pi}{\lambda} \quad \text{and } s = 2 \sin \tfrac{1}{2} \theta .$$

Here λ is the wavelength and θ the scattering angle. The experimental intensity function must be integrated from $n = 0$ to $h = \infty$. The proposed method involved using visible light scattering for the region in which h is small and small angle x-ray scattering for the large h region. The light scattering data can be routinely extrapolated to zero while the x-ray data can be analytically continued to infinity in a manner similar to that of Schmidt.

An investigation was made of the light scattering properties of the methanol-cyclohexane binary system when the system was in the one phase region above the critical solution temperature, T_c, and when the system was in the two phase region below T_c. Measurements were made down the critical isochore for $T > T_c$ and along the methanol rich side of the co-existance curve for $T < T_c$. A modification of the Ornstein-Zernike-Debye theory of light scattering was found to be in qualitative agreement with the results for $T < T_c$. The Debye parameter "ℓ" was 14.5±0.5Å above T_c and 10.4± 1.0Å below T. The temperature coefficient, "γ", of the osmotic pressure derivative was approximately 1.0 both above and below T_c. The ratio of the extrapolated zero angle inverse intensity at any ΔT below T_c to that quantity at the same ΔT above T_c was 3.6. The persistence length for fluctuations below T_c as determined by the Debye theory was of the same order of magnitude as the thickness of the binary interface.

Dr. D. L. Ball

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*Served as principal investigator to complete the effort following the death of Prof. Debye.

COMPLETED PROJECT SUMMARY

1. TITLE: Unimolecular Decomposition of Cyclobutane Derivatives at High Pressure

2. PRINCIPAL INVESTIGATORS: Dr. David J. Wilson
Dr. Winston D. Walters
Department of Chemistry
The University of Rochester
Rochester, New York 14627

3. INCLUSIVE DATES: 1 January 1964 - 31 May 1968

4. GRANT NOS: AF-AFOSR-575-64; AF-AFOSR-575-66

5. COSTS AND FY SOURCE: $24,734 FY64; $26,006 FY66

6. SENIOR RESEARCH PERSONNEL: Dr. James Aspden
Dr. N. A. Kawaja

7. JUNIOR RESEARCH PERSONNEL: Mr. Joseph Reardon
Mr. Lefford Lowden

8. PUBLICATIONS:

"Unimolecular Decomposition of Cyclobutane Derivatives," Final Technical Report, AFOSR

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Theoretical work in the field of unimolecular reactions raises some doubt whether or not high pressure limits to unimolecular rates do exist. The objective of this work was to study the unimolecular decomposition of some alkyl-substituted cyclobutanes at pressures as high as 200 atmospheres, using nitrogen as a diluent gas, in an attempt to determine if the proposed limits actually exist.

The expression given by transition state theory for the high-pressure limit of a unimolecular reaction is $k_{\infty} = \frac{kT}{h} \exp(-\Delta G^{\ddagger}/RT)$ where ΔG is the molar free energy of activation and the other symbols on the right hand side have their usual significance. Application of standard thermodynamic formulas then yields

$$-RT\left(\partial \log k_{\infty} - \partial P\right)_T = \Delta V^{\ddagger},$$

where $V^{\ddagger}$ is the increase in molar volume of reactant in going from its normal thermal state to the transition state. The validity of the second formula depends upon the validity of the interpretation of $\Delta G^{\ddagger}$ as a bona fide free energy change, which is the fundamental postulate of transition state theory. This is the only theoretical expression which predicts a pressure dependence of k_{oo} for unimolecular reactions.

The thermal decomposition of ethylcyclobutane, previously investigated at low and moderate pressures by Walters and his coworkers, was studied at high pressures. Small partial pressures (20-50mmHg) of ethylcyclobutane were mixed with from 100 to 4000 p.s.i. of oxygen-free nitrogen and pyrolyzed at approximately 410°C. Analyses were carried out on a Varian Aerograph 600D chromatograph with flame ionization detection; this instrument received samples directly from the stainless steel reaction vessel, and several samples were taken during each reaction run. This procedure markedly increased the precision over that obtained by the previously used technique of separating the condensibles from the ethylene and nitrogen and then injecting into an off-line chromatograph.

The rate constant was found to be represented by

$$k=4.80\times10^{-5}\,\mathrm{sec}^{-1}-1.85\times10^{-9}\,\frac{\mathrm{sec}^{-1}}{\mathrm{p.s.i.}}\,P,$$

where P is the total pressure in p.s.i. This yields a volume of activation of $+32$ ml/mole, not unreasonable for a bond-breaking reaction in which the reactant molecules are freely rotating in the gas phase, and indicating that the transition state undergoes significant bond lengthening as compared to normal molecules. The uncertainty in this volume of activation is indicated by its standard deviation, 3 ml/mole.

Assessement of Results

The original objective of this work was to search for a theoretically predicted departure of the high pressure limit of a unimolecular reaction rate constant from a constant pressure-independent value. Despite serious experimental problems, the search was successful, and the predicted decrease of the rate constant was observed and verified. Measurements of this sort can provide kineticists with a new type of information about the nature of the transition state in unimolecular gas reactions.

LtCol L. D. Whipple

COMPLETED PROJECT SUMMARY

1. TITLE: Research on Chemical Reactions of Secondary Electrons

2. PRINCIPAL INVESTIGATOR: Dr. Paul Y. Feng
IIT Research Institute
Chicago, Illinois

3. INCLUSIVE DATES: 1 September 1961 - 31 March 1967

4. CONTRACT NO: AF49(638)-1104

5. COSTS AND FY SOURCES: $60,223 FY62; $60,836 FY64

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: Y. H. Kim
J. Lounsbury
F. Vetrovec
J. Wurmel

8. PUBLICATIONS:

"Nature of the Interaction of Secondary Electrons with Chemical Systems," Final Technical Report, AFOSR-68-0941.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary effort expended during the course of this program has been directed toward development of the procedures and actual experiments for studies involving the interaction of low energy electrons with simple organic compounds, principally n-hexane. Both photoelectric and thermionic sources were used; the electrons were accelerated by means of electrostatic fields built in the irradiation vessel, and analysis of the products obtained was carried out using mass spectrometry and gas chromatography. Other experiments which have been performed included irradiation by low energy protons obtained by slowing down higher energy protons from a van de Graaff generator, as well as preliminary experiments using the recoil nuclei formed by neutron capture processes. Results show that although low energy electrons in the sub-KeV range and protons in the near MeV range have comparable velocities and comparable LET values, the nature of the chemical processes induced by the interaction of these two kinds of radiation may nevertheless differ from each other. Several possible alternative explanations for this phenomenon have been examined and the most plausible one appears to be a concept based on ionic reaction mechanisms for some of the products and the relative total ionization cross sections of these radiations at such energy ranges.

Dr. A. Weissler

APPENDIX

DIRECTORATE OF CHEMICAL SCIENCES
AFOSR-OAR Arlington, Va. 22209
Area Code 202, OXford 45337

NOTE: To Principal Investigators July 1, 1968

Become familiar with the terms of your grant or contract and the AFOSR brochure. Grants for Basic Research is part of the legal agreement signed by your institution in the case of grants, and Contracts for Basic Research outlines the terms of the contract.

1. STATUS REPORTS

The Directorate of Chemical Sciences has additional administrative requirements. It is necessary that we keep in tune with your problems, activities and productivity - so we can answer those who ask, "how are those tax dollars being spent?" We require a status report therefore six months after your start date and each six months thereafter for the period of the AFOSR research support.

Write a short (one, two or more page) discussion about your research progress, equipment status, and personnel problems; emphasize any changes so as to keep us informed. If your trips, papers delivered, and honors received are important, tell us.

Include a cumulative list of papers (from the beginning of your research effort, published or in preparation) with journal references (star those reprint titles which you have sent us).

Your AFOSR Chemistry staff administrator plays a major role in selecting the one investigator (and his research program) from among many new outstanding investigators clamoring for funds each year. He is also administrator for about 30 others who feel their research is more important than yours. He must continually select and then sell basic research to the Department of Defense and the Air Force. When you identify results of your research relevant to our mission - tell us!

The status report is a golden opportunity for you to infect your AFOSR Chemistry Directorate administrator with the importance of your research and to present him with your concern, your dedication and your enthusiasm for your research. Photographs also help us tell your chemistry research story.

2. MANUSCRIPTS FOR PUBLICATION

Send us a copy when you submit it for publication.

3. REPRINTS

Send us 25 copies of each reprint and one copy of Form DD1473 for each set of reprints. A brief specific abstract and list of key words are required for the storage and retrieval of information about your researches at the Defense Documentation Center (DDC).

4. ACKNOWLEDGEMENT

If you forget to include the acknowledgement "Research sponsored by AFOSR (SRC) - OAR, USAF, Grant (or Contract) No.______________," what should we do? Only remember those who remember us?

5. FINAL SCIENTIFIC REPORT AND COMPLETED PROJECT SUMMARY

The legal agreement signed by your institution requires (within 30 days after the expiration of your grant or contract) that you submit a copy of the completed Form DD1473 and 25 copies of a final scientific report which contains a chronological bibliography of all publications produced or anticipated with journal references when known.

With the final scientific report include a Completed Project Summary of the scientific significance of your four (plus) year research accomplishments; include a 200-500 word abstract of these accomplishments; include a list of all the senior (post docs) and junior (graduate) research people who assisted you; and as cited above include a chronological bibliography of all publications with available references. Citations of papers appearing in scientific journals may be referenced in lieu of a detailed account of the same work.

Please bind one additional copy of your final report with one set of reprints and/or (papers) for our Chemistry Office use.

6. PHOTOGRAPHS

If you have a story of research accomplishment that lends itself to portrayal by photographs or charts and can include copies of originals for our office use, these items will aid us greatly in telling your research story and in our continuing effort to obtain funds for basic research in chemistry. They will aid us in preparing the Chemistry Program Review (AFOSR-OAR), a report to our reviewers and a report to the taxpayers whose funds you have used.

May your researches be successful and your resources sufficient,

The Directorate of Chemical Sciences
AFOSR-OAR-USAF

DIRECTORATE OF CHEMICAL SCIENCES

AFOSR-OAR Arlington, Va. 22209
Area Code 202, OXford 45337

NOTE: To Proposers September 1, 1969

New fundamental chemistry in areas of immediate or potential interest to the Air Force is the objective of the investigations sponsored by the Directorate of Chemical Sciences. Congressional appropriations of tax funds via the Department of Defense and the Office of Aerospace Research are used for this purpose.

Our support is provided in the form of grants or contracts to investigators in academic institutions, research institutes and industrial organizations engaged in basic chemical research. It is the general practice of the Directorate of Chemical Sciences to support a particular research effort for a four year term. If the investigator wishes to apply for a further term of support, his renewal request is treated as a new proposal and is given the same evaluation procedure as an entirely new effort.

It is necessary that the research supported by this directorate, in cooperation with the principal investigator's institution, be a distinct, definable area of the investigator's research interests with minimum overlap with the research supported by other agencies. In some cases the Directorate of Chemical Sciences prefers to be the sole source of outside support for a given investigator.

Because of the keen competition, our support is awarded on a highly selective basis; this applies to both sole support and distinct area support for the investigator. The criteria for research awards include: first, the significance of the science proposed; second, cost to the government; and third, the enthusiasm and dedication which the investigator himself has for the proposed research.

The proposal should contain a statement about the principal investigator's total workload, including teaching, other research and sources of support, and particularly the portion of his efforts which will be devoted to the proposed research. (A minimum of 25% of his time is expected.) Plans for extended leave or prospective sabbaticals should be included in the proposal. One primary purpose of a research proposal is to aid in the selection of an outstanding principal investigator who will have a personal commitment to research on significant chemical problems -- problems which are also of scientific interest to the Air Force.

The truly productive scientist urgently needs the time to reflect on his program and its ultimate meaning. Too often the energies of the established investigator are sapped by extraneous demands on time and thought. Young, new investigators frequently sacrifice long range quality for immediate mediocre results and data collection. The tendency is all too frequent to exploit familiar fashionable and sure-fire areas of research to the exclusion of precarious, high risk but potentially valuable high pay-off research. The Directorate of Chemical Sciences four year policy goes far to eliminate this temptation. In addition, the administration and reporting requirements are as simple and direct as possible.

Proposal budgets should show the total cost of the proposed program. One budget column should show funds requested of AFOSR and a second should show the contributions being made by the institution. Too few budgets outline the many cost-sharing contributions that the institution, particularly a university, is making or will make to proposed research. For example, the investigator's salaries, stipends for research assistants, or special equipment paid for by the university should be included.

Unofficial proposals of inquiry are entertained at any time. Official proposals should be submitted during November and December or in May and June.

An abstract describing the proposed research, between 150 and 200 words in length, must accompany each proposal on a separate page.

The AFOSR mission encompasses basic research only. Applied research is not supported directly by this part of the Air Force. The Air Force, however, is faced with many applied chemical problems: new materials to withstand extremes of temperature and other environmental conditions; lubrication at high vacuum and low temperatures; the chemistry of corrosion, fatigue and crack propagation alloys; high strength and other special glasses; electrochemical power systems; propulsion; non-conventional and advanced photographic systems; sensitive methods of detection and analysis. These are examples of applied Air Force problems. The best way to attack these problems is to do the fundamental researches first. Relevant basic research is given priority.

Research and Purpose*

I doubt if anyone has given more constructive thought to the role of basic research in this country than has Alan Waterman, nor with more results. Yet his introduction of the term "free basic research" into the discussion ("The changing environment of science," 1 Jan., p. 13) could do a disservice to science and scientists. There are three points I want to make.

1) The problem arises from the oft-stated desire of university scientists for "free" funds to do research with. This is nonsense. Money is something that is given in exchange for goods or services. There are no "free" funds legally available to scientists or to anyone else. It is not logical, nor will it long remain economically useful, to urge the allocation of federal appropriations to scientists without the requirement of accountability.

2) What makes research basic is not the objective or lack of one. As Allen Astin has stated it, basic research is "characterized only by the intensity or depth of the inquiry" (in Symposium on Basic Research, D. Wolfle, Ed., AAAS, 1959 p. 144). Research upon the structure of matter, the cure of cancer, the mechanism of photosynthesis, the development of lubricants, can be basic or not to the degree that it is done well, that new concepts are developed and their correctness established, and that new avenues of study are opened up. The idea that quality of endeavor is the important and distinguishing characteristic is not limited to science. It is expressed in everyday terms in an old song: "It ain't what you do, it's the way that you do it, that's what gets results" (Oliver and Young, Copyright 1939, Leeds Music, New York).

3) Is it important to have an understood and clearly stated objective for a research endeavor? I believe it is. Waterman cites Archimedes, Galileo, Newton, Jenner, and Pasteur, noting that each worked upon problems of technological importance. He could have come much further into the present. It would be no compliment to Calvin to say that his work on photosynthesis did not have a clearly defined objective, or to Woodward, or to Ziegler, or to the Nobel prize winners of the coming years. It has been my experience that all research workers of great ability have clearly defined objectives, and that they will expound them at the drop of a hat. It is the ineffective research worker who often has no well-defined objective and who speaks obscurely of obtaining basic information, of "contributing to knowledge."

Some time ago, I suggested a statement that summarizes the points I am trying to make: "It is no handicap to good research to have a purpose in mind."

Sam R. Hoover
2017 Hillyer Place, N. W.
Washington, D. C. 20009

*<u>Science</u>, p. 1523, March 26, 1965

THE FUTURE OF CHEMICAL SCIENCE

G. S. Hammond
Chemistry Department
California Institute of Technology

Norris Lecture, October 15,1968

I have chosen the wording of my title intentionally. Some few people suggest that natural science as a whole has nearly run its course and will within a few decades cease to exist as an explicit part of intellectual and functional human activity. Personally, I do not believe that this is so and will proceed under the assumption the science will continue. This restrictive assumption still leaves ample grounds for discussion of the changes that may occur in the character of science. Although I am tempted to philosophize about the whole of this many faceted subject, including the current trend toward throwing the scientists out along with the politicians, I will try to stick to consideration of what may happen to that part of science known as chemistry.

An abridged dictionary defines chemistry as, "A science that deals with the composition, structure and properties of substances and of the transformations that they undergo." This is a gloriously broad mandate. Even if problems of nuclear structure and transformations are arbitrarily removed and put into physics, the residue of structure and change studies appears to have enough breadth and centrality in science to remain a part of the action for some time to come.

However, we should not parlay the fact that chemistry does occupy a central location within science into the conclusion that chemistry as such must retain its identity. Chemistry does enter other scientific and technological fields such as biology, geology, physics, engineering, medicine, agriculture and so on. This fact means that chemistry could disappear as an explicit discipline and become absorbed elsewhere. If this should occur, chemical research would still be done by people who consider themselves primarily as biologists, geologists, engineers and so forth. Consequently, I predict that "chemical science" may have a longer effective lifetime than "chemistry."

I hope that I will not be regarded as irretrievably provincial if I admit that I do not welcome the disappearance of chemistry. If it happens, I can probably stand the strain. The elements of chemistry would probably still be being taught as a basic subject, like trigonometry, which many people need to enter active fields of science. If the debacle came tomorrow, I might be able to land a job in some prep school or, alternatively, I might even make the grade as an engineer having some special expertise in chemistry. Although my survival probably doesn't rest upon the survival of chemistry, I have been worried enough to expend some thought on ways of extending the useful lifetime of the science. I would like to share with you some of the rather amorphous conclusions that I have reached.

Chemistry today faces some grievous problems. The image of the field has become relatively dull, even in the minds of many chemists. Current methods of teaching chemistry are under severe attack, even by other scientists and engineers; and statements of general directions of chemical research often should like resolutions to continue doing the same things over and over again.

A clear symptom of a problem is found in the great frequency with which chemists say, "It is impossible to tell the lay public what chemistry is all about, because it is too complex." I don't buy this assertion. After all, high energy physics and molecular biology are also exceedingly complex if one looks at the details of research programs in the fields, and yet, physicists and biologists have been somewhat successful in giving the public real empathy for their work. Part of the reason for their success comes from their ability to identify noble and profound objectives of their fields. These objectives are described clearly and little emphasis is placed on details of current work in the most successful public presentations. Chemists, on the other hand, seem to have a terrible time in resisting the temptation to wade through all the gorey details of their research even when they speak to the Chamber of Commerce. Not surprisingly, chemists are no longer intensively sought as speakers by such groups.

I'm distressed by the repeated insistence that chemistry is too complex for public discussion. Has the science degenerated to a welter of detail devoid of any describable grand purposes? Despite evidence to the contrary, I think that this is not the case. The Westheimer report provided powerful evidence that chemistry has done well during the past two decades and has prospects for sensational gains in the immediate future. The real problem lies in the disinclination of chemists to talk or even think very much beyond their personal plans for next week.

We must face one certain fact. Many chemical research laboratories, especially those in academic institutions, do not produce much that is of immediate value in any practical way. There is no shame in this, because new materials for industry, medicine and so on are successfully sought in countless industrial laboratories around the country. The so-called "pure" research laboratories have two principal purposes: to educate young scientists and to study basic principles of science. Tying together these two functions seems like a most appropriate marriage of purposes. The scheme might even work if it were not for the hypocrisy and mythology surrounding that inspiring phrase "basic principles." How can a mass of details that is so complex as to be totally incomprehensible even to most of the people in the field be regarded as a basic principle? What on earth are basic principles anyway? Detailed inquiry of many chemists indicates that their own basic principles are an unbelievable array of miscellaneous ideas and techniques. Most commonly, basic principles turn out to be those notions that first gave a particular individual some feeling of security about chemistry.

I believe that there are some concepts in chemistry that genuinely merit the name of basic principles. These are for the most part simple ideas that can be used over and over again in many different contexts. For example, the idea that the energetic changes accompanying chemical reactions can be related in a straightforward way to the energy relationships of classical mechanics, the notion that the principles of wave mechanics can be applied to the many particles that make up a molecule, and the idea that there are only two kinds of elementary reactions, (unimolecular and biomolecular), all seem worthy of being called basic principles. I don't even care to worry about the longevity of these generalizations, as long as they are an important part of the thinking of many chemists, they serve the purpose of basic principles.

In addition to having some set of ideas to use as basic principles, any scientist must have some facts and some techniques for applying the principles and facts. Most basic research deals with supplying facts and working out the details of application of the principles. This inherently nonglamorous work can be a lot of fun as a form of game playing, and I see nothing wrong with a chemist enjoying the games that he plays in his professional life. However, the attempt to elevate useful game playing to the status of a holy mission for basic principles is arrant nonsense.

I don't feel like a traitor to my kind for having stated facts that are now being pointed out by critics of all science. Unless we are reasonably honest with ourselves, we deserve the kind of rejection by the public that is now occurring. We need to do an honest review of what it is that scientific research does offer to the society. The blithe assumption that there is bound to be a lot of useful fallout has some merit, but I think that we can do much better. In particular I think that chemistry can survive among the sciences and earn support of the society by its contribution to intellectual life and technological advancement. To accomplish this chemists must shape up and come out of their dream worlds.

We must first realize that chemistry has become highly conservative. The traditional subdivisions of the field are those that were established in the 19th century, the lines of demarcation in our undergraduate curricula were drawn many years ago. and we frequently see elegance evaluated more highly than innovation. Some of our games have become so stylized that the chief objective of research problems seems to be to wrap them up more neatly than was done with last year's version of the same problem. Such behavior is characteristic of an old and settled society.

To me, one of the most significant things to happen in chemistry in recent years was the description of the fields of chemistry found in the Westheimer report. The three principal fields were chemical structure, chemical dynamics and chemical synthesis; other fields were defined to facilitate description of some of the important outreaching parts of the field. This was like a breath of fresh air. With such terms we can talk about the directions of chemistry. It makes a lot of sense to say that the past 40 years have been a golden age of theoretical and experimetal structural chemistry. By comparison, chemical dynamics, the study of chemical reactions and reactivity has had a spotty record. A great deal has been done to develop useful models for reaction mechanisms and there has been a good deal of progress in methodology for monitoring reaction rates, especially those of very fast reactions. However, it seems to me that theory has lagged terribly. The transition state theory has provided little more than a useful conceptual basis for discussion of reaction rates and presentation of experimetal results in parametric form. I for one am rather bored with the repeating exercise of taking another reaction and sorting out the steps in its mechanism, or assembling mountains of kinetic data for the rates of reaction of series of closely related compounds to build semiempirical theories of relative reactivity. I hasten to say that I have tremendous respect for semiempirical theory in general, but I do see the frontiers in the field of relative reactivities being pushed back by microscopic increments.

The history has not really been the result of incompetence, but of practical limitations. However, at the present time, some of those limitations are removed so we should push ahead with enthusiasm rather than dawdling around with the old fun and games. Methods are now available for study of the simplest reactions in molecular beams, we are beginning to realize the great power of studying kinetic behavior of all kinds of energetically hot systems, and new theory is in the making. I could easily devote my entire talk to the theme that the golden age of chemical dynamics is here. However, I will only assert the fact and encourage other chemists to share in my enthusiasm for a coming good time.

During the past 25 years, synthesis, the most sophisticated and creative branch of chemistry has come of age. Led by R. B. Woodward, synthetic chemists have demonstrated that applied chemical dynamics can be a beautifully systematic field. The future of synthesis must surely be great, but it seems to me that no part of chemistry is more in need of a general review of objectives.

The current problem in synthesis is instructive. Overwhelming competence, sophistication and ingenuity are seen in the field, but it is very hard to state impressive objectives or to cite large numbers of new principles emerging from most current work in synthesis. I believe that the field needs new objectives. At the present time two objectives seem dominant: (1) synthesis of natural products, and (2) synthesis of unusual molecules of interest to structural chemists and chemical dynamicists. The first goal is losing its glamour since Woodward has clearly demonstrated that man can make any molecule made by nature, with the possible exception of the biological macromolecules. Synthesis of exotic molecules of theoretical interest provides a more viable goal but may be running down. Furthermore, making exotic new compounds because of their theoretical interest in chemistry is part of a cyclic process that does little to lead chemistry outside of itself.

During the past few decades, chemistry has been largely acquisitive and self-propagating. The principal thrust of theory has involved adaptation of the methods of particle physics for use in chemical structural problems. The process has been wonderfully successful but unfortunately has tended to divert the attentions of chemists from expansive activity. Consequently, we have been burned badly. The greatest advances in biochemistry and solid state chemistry have been made by biologists and physicists, not by chemists. I recall with some humiliation the attitude of most chemists, including myself, toward biochemistry 20 years ago. The field was generally regarded as grubby, nonquantitative and quite unfit for the attention of the scholarly folks in the proper chemical fraternity. I hope that something has been learned, but see some evidence that only the first lesson has really penetrated. To be sure, chemists are now turning to problems of molecular biology in large numbers. However, there seems to be a continuing tendency to eschew other obvious areas for expansion such as solid state science, materials science and the incorporation of chemical changes in engineered systems. If one listens carefully to the discouraging comments of chemists about materials science, he must be struck with the similarity to the gloomy and patronizing views expressed about biochemistry in the 1940's.

Let me elaborate a couple of examples very briefly. I believe that the most fundamental and lasting objective of synthesis is not production of new compounds, but production of properties. Historically this was the strongest motivation for evolution of synthesis of natural products. Furthermore, the historical mission has been wonderfully fulfilled. Synthesis has produced compounds having an almost unbelievable range of physiological properties. A similar thing has occurred in the field of synthetic polymers where some kinds of physical properties have been sought and found. I see nothing demeaning about the idea of asking what other properties people can use, trying to construct theoretical models relating structure to properties and thus creating a wealth of new and challenging synthetic problems. A few years ago Little published a suggestion of a structure that he believed would lead to an organic semiconductor. Here was a clear challenge to the synthetic chemist. The fact that his particular structure is a bizarre synthetic problem is of no real import. The logical procedure would be marriage of Little's theoretical model with realistic consideration of synthetic capability to produce target structures that can be made and tested.

My final sally is reserved for my own field of chemical dynamics. It is fun to study chemical reactivity and attempt to construct self-consistent theories from the results. But what use is it all? Are chemical reactions only useful for making more new chemicals? This is surely an important part of applied chemical dynamics but we are in real trouble if it is the only one. I think there is a tremendous future for the use of chemical reactions in systems that are part mechanical, part electrical and part chemical. The idea is not new; the automobile is an example of such a system. However, the automobile is a shame to the chemists. It is a marvel of mechanical engineering but the chemical part of the system is just about as crude as lighting a fire. I conceive of a future when delicately controlled chemical reactions will be incorporated in many kinds of systems involved in such diverse functions as energy management and information transfer and storage. To be sure, the path to these new engineered systems is no better marked than was the path to modern pharmaceutical chemistry in the late 19th century, but I see no reason to expect that we will not ultimately enjoy similar success.

Advertisement of such immodest objectives may seem like a frightening risk, but to me it seems small in comparison with the danger in continuation of our pose as people dedicated only to ourselves and our own intellectual games. As a matter of fact, the best defense against pressure to devote all our efforts to short range work having little chance of generalization is to put careful thought into enunciation of the long range prospects for chemistry. Speaking only for myself, I enjoy the action because guessing about the future is inherently interesting and because I gain a feeling of greater relevance about my own chemistry.

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The review provides a record of research in progress together with illustrative achievements resulting from the basic research program of the Directorate of Chemical Sciences, AFOSR (OAR). There are three main sections in the review. The first section is devoted to research high lights under the headings of Chemical Instrumentation and Techniques, Chemical Structure and Properties, Chemical Energetics, Theoretical Chemistry, and Chemical Synthesis and Dynamics. The second section contains summaries of program statistics. The third section consists of factual summaries of each project completed during fiscal year 1968.

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