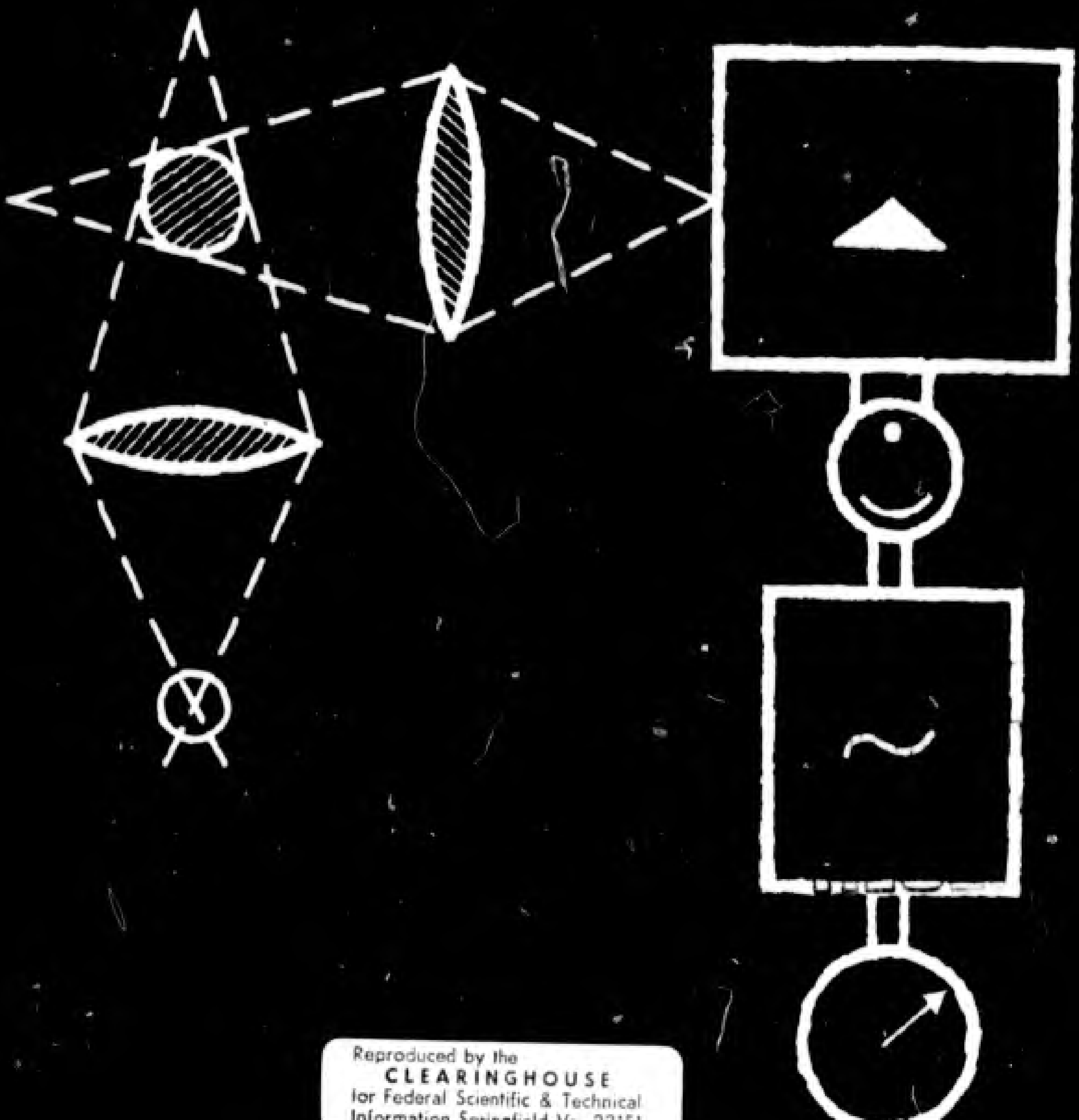
AFOSR 69-3129TR

# 15th annual CHEMISTRY program review



AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Office of Aerospace Research ⋆ United States Air Force
Fiscal Year 1969

## THE COVER

One of the articles on chemical methods titled, "Methods of Trace Element Analysis," includes a brief description of the work of Dr. James D. Winefordner of the University of Florida. The cover of the book is an artist's concept of a simple diagram of the flame fluorescence analysis instrumentation developed by Dr. Winefordner.

Qualified requestors may obtain additional copies from the Defense Documentation Center (DDC). All others should apply to the Clearinghouse for Federal Scientific and Technical Information (CFSTI).

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AFOSR 69-3129TR
January 1970

# 15th Annual Chemistry Program Review

## Fiscal Year 1969

Dr. Donald L. Ball, Scientific Editor
Lt. Col. L. D. Whipple, Managing Editor

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DIRECTORATE OF CHEMICAL SCIENCES
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
OFFICE OF AEROSPACE RESEARCH, USAF
Arlington, Virginia 22209

DEPARTMENT OF THE AIR FORCE
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (OAR)
1400 WILSON BOULEVARD
ARLINGTON, VIRGINIA 22209

February 10, 1970

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

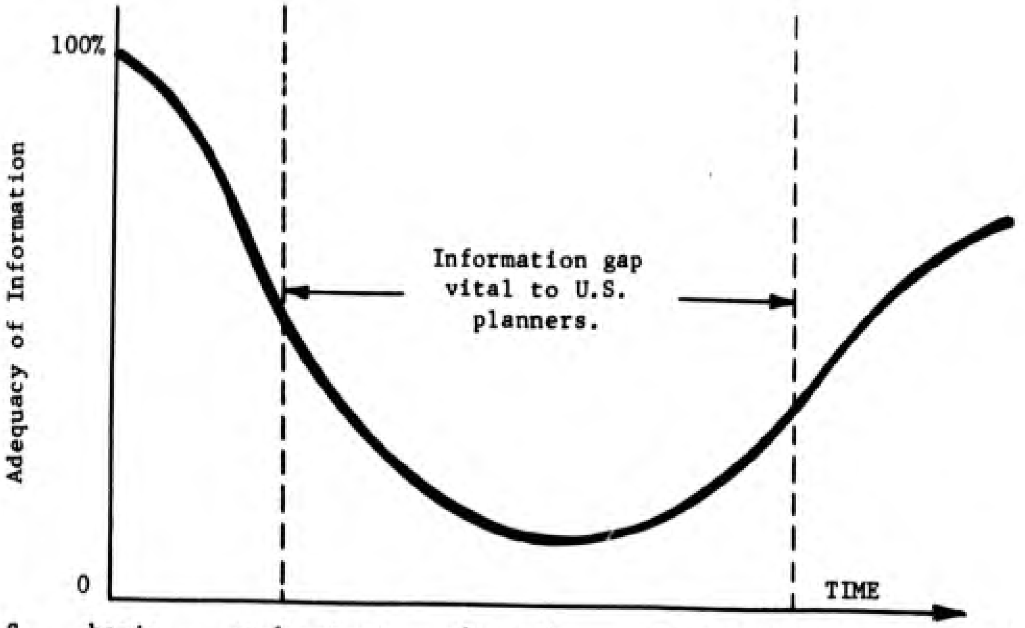
As of now we--the United States of America--have not yet lost our technological superiority in national security. It is equally true that we could well do so over the next decade. According to Dr. John Foster, the "chief scientist" of the Department of Defense, our best intelligence estimates show that Soviet spending for defense-related research and development is expanding at an annual rate of 10 percent. By way of contrast, the United States effort, increasing at just 4 percent yearly, may be lost as a result of the general sentiment to reduce military budgets.

The loss of our technological superiority may very well imperil our future national security for this reason: our adversaries operate behind a veil of secrecy. We are much more vulnerable than they to technological surprise. That is, they can develop a weapon over a period of time with a high assurance that we will not find out about it (Fig. 1). When we do, it may be too late to catch up if we are caught with our technological and scientific pants down. The only way to guarantee American security in the face of this situation, where our intentions are well publicized and immediately available to Soviet decision-makers, is to "get there first" in the research and development field.

In light of the above, I should like to call to your attention Mr. Daddario's remarks concerning Sec. 203 of the FY 70 Military Authorization Act--quoted from the Congressional Record in our appendix--and paraphrasing the last line of Sam Hoover's letter and our note to proposers (see Appendix),

"relevancy is no handicap to superior scientific research."

Amos G Horney
AMOS G. HORNEY
Director of Chemical Sciences



| | | | | | |
|---|---|---|---|---|---|
| U.S. R&D cycle | basic research (6.1) | exploratory development (6.2) | advanced development (6.3) | engineering development (6.4) | operational system development |
| Soviet counterpart (approx) | theoretical: academic (15-year lead), industry (10-year lead) | | applied (5-7-year lead) | design: development and experimental verification | system test: qualification<br>state acceptance |

Fig. 1. Information gap concerning Soviet weapon system development.[1]

Reference:

1. "The Future Role of USAF Scientific Advisory Board," Lt. Col. H. A. Steiner, Air University Review, XXI-1, 65 (1969).

AFOSR

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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

In addition to the technical staff of the Directorate of Chemical Sciences, many others assisted in preparing this review. The Directorate is particularly grateful to Dr. Sam R. Hoover who granted permission to include his writing in the Appendix. Special thanks are due Mrs. Jerry Dillard, Mrs. Lucille Tarbert, and Mrs. Wanda Clemenhaga for their many hours devoted to typing the drafts and final copy. The editors and authors are grateful also to Mrs. Amos Horney for the arduous task of proofreading. The cover was prepared by Mr. Charles P. Shealy, Presentations Division, Office of Information, OAR.

# CONTENTS

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# INTRODUCTION

The objective of this review is to present to you a picture of the AFOSR Chemistry Program by discussing potential for the future, status of the present, and events and efforts of the past.

The review is presented in three general sections. The first section includes five articles which emphasize "the methods of chemical science." This unifying theme was chosen because of the broad and vital application of methods across the spectrum of chemical research. In addition, instrumentation and methods provide not only long-range contributions through their use in support of research, but potential shorter range contributions through their early application in instrumentation for use in Air Force military operations.

The second section of the book presents statistics and information pertaining to the current AFOSR Chemistry Program. The third section of the book contains summaries of the research efforts that were completed during Fiscal Year 1969.

The dynamic nature of the program can be seen by comparing this review with previous editions. Fiscal Year 1970 already promises many opportunities to reflect this dynamic nature. We look forward to describing the results of these opportunities in our next edition.

# THE METHODS OF CHEMICAL SCIENCE

# THE CHEMICAL LASER - A NEW TOOL FOR CHEMICAL KINETICS

By Dr. Donald L. Ball

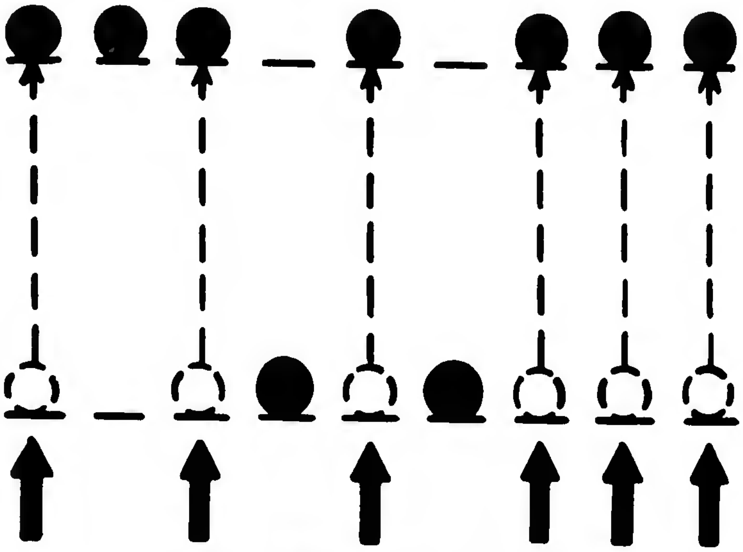
Both the science and the technology of lasers have gained enormous advances in recent years. Vigorous basic and applied research programs on the subject are in progress,world-wide. There are numerous present and potential laser applications--some specifically oriented to defense needs, but others of more general commercial interest. However, for the purpose of the present article, our interest will be restricted to a particular sort of application for a particular sort of laser. This is in keeping with the unifying theme of the 15th Annual Chemistry Program Review--"the methods of chemical science." The paragraphs to follow will trace recent progress with the chemical laser, a particular variety which was first discovered in the University of California laboratory of Prof. George C. Pimentel under sponsorship by the Directorate of Chemical Sciences, AFOSR. Stress will be given to the special exploitation of chemical lasers in unraveling the complex microscopic events of chemical kinetics. Particularly detailed information on molecular collisions and kinetic rate constants is, in some cases, rendered more readily measured or, in other cases, rendered measurable for the first time.

The chemical laser was the subject of an earlier account by Dr. W. L. Ruigh in the 11th Annual Chemistry Program Review for FY 1965. However, there has been a great deal of significant achievement in Prof. Pimentel's laboratory since the first discoveries in 1964. There has been, of course, considerable significant research in many other laboratories, but for the present we are restricting our discussion to the continuing AFOSR program.

Recently, in St. Louis, on 22-24 May 1969, was held the "2nd Conference on Chemical and Molecular Lasers" under the support of the U. S. Army Missile Command and AFOSR (Directorate of Engineering Sciences). Four papers presented at the conference were authored (or co-authored) by Prof. Pimentel. In one of these, entitled "The Significance of Chemical Lasers in Chemistry," he stated: "In the Berkeley laboratories alone, we have observed...laser emission from 36 different reactions of five distinct types...." It seems, therefore, a fitting time to review the progress achieved with particular reference to the use of the chemical laser as a research tool.

By way of background and a basis for assessment, a brief review is needed of just what a laser is and how it operates. The special characteristics of "chemical" lasers can thus be best identified.

Whether solid, liquid, or gas, a laser emits monochromatic, directional, coherent, and intense radiation following an inversion in the normal population of energy states. This inversion, i.e., occupation of higher energy states than the most stable, requires an input of energy (or "pumping"). The situation is given schematically as follows:



ENERGY INPUT

Light photons of appropriate energy (equal to the difference between the levels) can stimulate relaxation to the lower energy state again with the additional emission of photons of the very same energy (wave length). This is the basis of laser action and the origin of the word (the acronym from light amplification by stimulated emission of radiation). It is necessary also, of course, that the active material be suitably contained in a resonant cavity--bounded by reflective mirrors. After the radiation intensity has built up (following multiple reflections), some means is provided to allow emergence of the laser light from the cavity.

Lasers are available with a variety of emission frequencies. The energy levels, which provide the basis for "lasing," can be differences in electronic states but more commonly they are differences in vibrational energy. The associated transitions are called vibrational/rotational transitions. Ordinarily, a change in vibrational energy is accompanied by a change in rotational energy. For example, a unit decrease in the vibrational quantum number, $V$, (which labels this energy state) may be associated with a unit increase in rotational quantum number, J. This transition--or the reverse associated with light absorption rather than emission--is responsible for the familiar "P branch" in infrared spectra. The "Q and R branches" are due to $\Delta J = 0$ and $\Delta J = +1$, respectively, with $\Delta V = +1$ (on absorption). The transition energy increases, of course, in the sequence P, Q, R. Depending on the nature of the molecular system (and corresponding selection rules) these different "branch" transitions may or may not be observed. For our purposes we will need consider further only the "P" transition. In each of the systems to be described in some detail, all the frequencies observed in emission are attributable to P transitions (with identified values for $V$ and J).

The nature of the energy input (or "pumping") is what truly distinguishes a "chemical" laser. Whereas commonly the energy source is provided by an external, intense flash lamp, in the chemical laser the source is an exothermic chemical reaction. The product of a chemical reaction is a molecule bearing the reaction energy in the form of vibrational excitation. A "population inversion" is produced directly--with the birth of the product. Subsequent emission--in the infrared--by the excited product is the source of the laser light. In the summary equations below, vibrational excitation is identified with the symbol, $\dagger$ .

$$A + B \longrightarrow AB^{\dagger} \qquad \text{(vibrationally excited)}$$

$$AB^{\dagger} \longrightarrow AB + h\nu$$

The basis, then, of the chemical laser is "chemical activation."

For several years, the possibility of a chemical laser was the subject of widespread speculation and search. Then, finally in 1964, a type of "chemical" laser was reported by Prof. Pimentel, based on research by his student, Jerome V. V. Kasper. A more apt term, however, is photodissociation laser; laser action was based on the photolysis of methyl iodide. The emitting species was an electronically excited iodine atom, indicated with the asterisk.

$$CF_3I \xrightarrow{h\nu} I^* + CF_3$$

The subsequent emission is by electronic transition specifically identified as $^2P_{\frac{1}{2}} \longrightarrow {}^2P_{3/2}$. Here the symbol P is the electronic quantum number for orbital angular momentum. The superscript represents electron spin multiplicity. The subscript represents the coupling between spin angular momentum and orbital angular momentum. The transition yields a more weakly coupled state. The symbol P is coincidentally used here. It is not related to transitions in vibrational energy discussed earlier.

The term chemical laser (without the quotation marks) is applicable to another soon-discovered system (also by Kasper in Pimentel's laboratory). This was called the "explosion laser;" the first example reported was based on the reaction of atomic hydrogen and molecular chlorine. A manuscript[1] describing the discovery was soon dispatched. A copy was simultaneously provided for the information of AFOSR. The cover letter (of 21 January 1965)--addressed to Dr. A. G. Horney--is quoted below. It should impart some of the significance then assigned to the discovery.

> "Enclosed please find a manuscript entitled 'HCl Chemical Laser' that Jerry Kasper and I have just mailed off to Physical Review Letters. I know it will interest you--it is the outcome of Jerry's studies of the emission from the $H_2$-$Cl_2$ explosion. As far as we know, it is another prototype laser, the first real chemical laser in the sense that excitation occurs through a chemical reaction: $H + Cl_2 \quad HCl + Cl$. The $CF_3I$ laser involved chemical bond rupture but not a reaction of two or more chemical species."

Research in the field has been vigorously pursued in Prof. Pimentel's laboratory (under continuing AFOSR support) as well as in laboratories elsewhere. Five distinct types of chemical lasers have been reported so far by Pimentel (based, at last count, on 36 different chemical reactions). These types (and dates of discovery) are listed as photodissociation (1964), explosion (or three body, 1964), abstraction (1967), elimination (1968), and photoelimination (1969). We can better see just what these various types are with the aid of the following table.

## TABLE

## TYPES OF CHEMICAL LASERS

| Type (Emitter) | | Example |
|---|---|---|
| Photodissociation (I*) | | $CF_3I \rightarrow I^* (^2P_{\frac{1}{2}}) + CF_3$ |
| Explosion ($HCl^\dagger$, $DCl^\dagger$) | | $H + Cl_2 \rightarrow HCl^\dagger + Cl$ |
| Abstraction ($HF^\dagger$, $DF^\dagger$) | | $F + H_2 \rightarrow HF^\dagger + H$ |
| | or | $F + HR \rightarrow HF^\dagger + R$ |
| Elimination ($HF^\dagger$) | | $CF_3 + CH_3 \rightarrow CF_3\,CH_3^\dagger \rightarrow HF^\dagger + CH_2\,CF_2$ |
| Photoelimination ($HF^\dagger$, $HCl^\dagger$) | | $CH_2CHF \rightarrow CH_2CHF^\dagger$<br>$CH_2CHF^\dagger \rightarrow HF^\dagger + CHCH$ |

It is not appropriate here to expand on the chemistry fundamental to operation of all the laser systems outlined in the Table. In two instances, however, this will be attempted to some detail in order to reveal how laser performance does provide new insight to basic processes in chemical kinetics. The duration and intensity of output pulses is attributed to specific molecules and specific states of vibrational excitation. By adjustments in pressure, temperature and composition variations in laser performance are relatable to the causative kinetic processes. In Prof. Pimentel's words: "A chemical laser under control is a poor man's molecular beam." The further exploration of the examples should reveal just what is meant by these words.

### Explosion Laser

The operation of this system,[2] which was the first encountered, is summarized by the following sequence (for $H_2/Cl_2$).

| | |
|---|---|
| flash initiation | $Cl_2 + h\nu \rightarrow 2\,Cl$ |
| (a) | $Cl + H_2 \xrightarrow{k_a} HCl + H$ |
| (b) | $H + Cl_2 \xrightarrow{k_b} HCl^\dagger + Cl$ |

The final step provides the vibrationally activated species, $HCl^\dagger$, whose subsequent radiative relaxation is the source for lasing. The sequence of steps given is adequate to understand demonstrated effects of initiating flash energy, power, $Cl_2$ pressure, $H_2/Cl_2$ ratio, and total pressure. Similar analysis was made of the isotopically substituted system: $Cl_2$, HD. Kinetic information never before measurable, with considerable impact on theory, is provided.

The chemistry basic to laser operation is described on two simultaneous chain sequences. As before, step (a) is rate determining (slower than (b)).

initiation $Cl_2 + h\nu \longrightarrow 2Cl$

(a) $$Cl + HD \begin{array}{l} \xrightarrow{k_{aH}} HCl + D \\ \xrightarrow[k_{aD}]{} DCl + H \end{array}$$

Separate rate constants are indicated for formations of D and H, respectively. The constant $k_{aH}$ governs formation of unexcited HCl (vibrational ground state) and, in the next rapid step, excited $DCl^{\dagger}$. Similar considerations hold for $k_{aD}$.

(b) $D + Cl_2 \longrightarrow DCl^{\dagger} + Cl$ or $H + Cl_2 \longrightarrow HCl^{\dagger} + Cl$

The two rate constants, $k_{aH}$ and $k_{aD}$, cannot be distinguished by classical methods (stoichiometry of products) because of the final step in the chain reaction. Each unexcited HCl is paired with a deuterium atom which subsequently provides an excited DCl. Similarly, formation of DCl assures formation next of excited HCl. This composite result is best revealed by adding steps (a) and (b). The product of $HD + Cl_2$ in one sequence is $HCl + DCl^{\dagger}$; in the others $HCl^{\dagger} + DCl$. Vibrational excitation is the real label which can, in fact, be identified from laser performance at associated, identified frequencies.

Observed in laser performance were two sets of operating conditions (same temperature and $Cl_2$ pressure but varied $H_2$, $D_2$, and HD pressures) at which $HCl^{\dagger}$ and $DCl^{\dagger}$ emissions occurred with equal intensities. The ratios of HCl of DCl population inversions must have been the same for each set of conditions. The separate concentrations are relatable to the pressures of $H_2$, HD, and $D_2$ and the rate constants of the slow, rate determining steps in their formation $k_a$. The latter is known for $H_2$ and $D_2$. The pressures are also known for two sets of pressures yielding equal laser gains. The ratio $k_{aH}/k_{aD}$ is thus calculated to be 1.9 ± 0.4. This determination assumes particular significance since it disagrees with existing theory, which predicts a value 0.4 - 0.7.

### Abstraction Laser

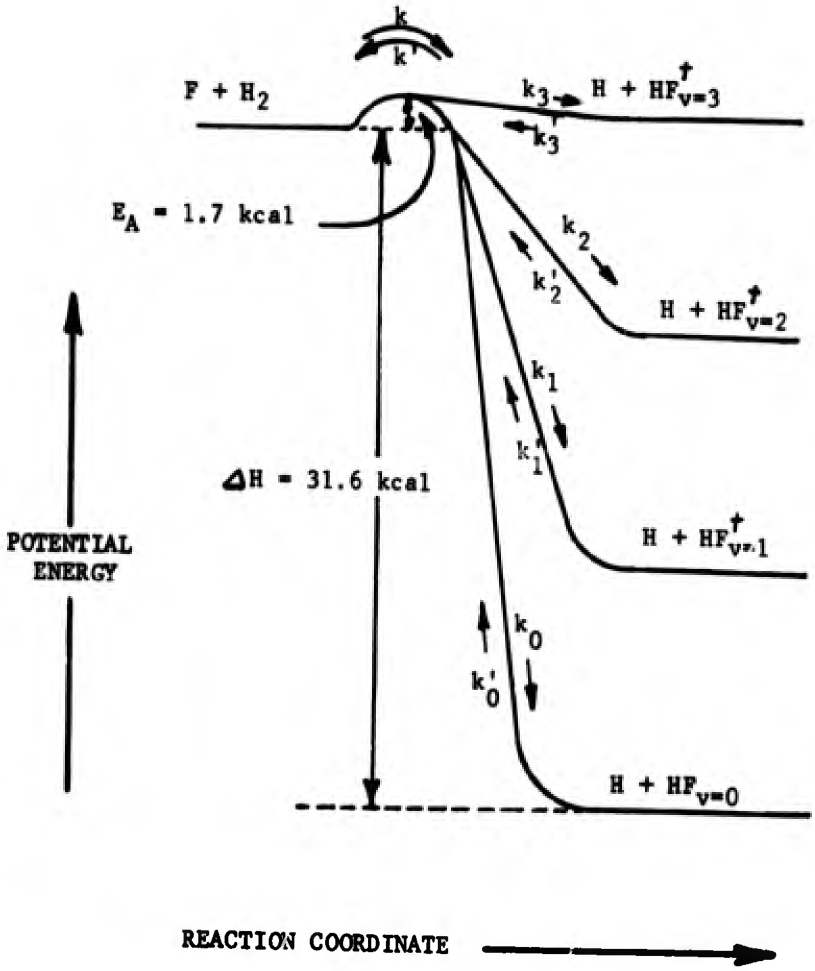
We shall consider in some detail the system $UF_6/H_2$[3].

flash initiation $UF_6 + h\nu \longrightarrow UF_5 + F$

$$F + H_2 \xrightarrow{k} H + HF^{\dagger}$$

The basic reaction of the abstraction laser can lead to products at various levels of vibrational/rotational excitation (identified by vibrational quantum number $V$ for HF). This is given in the figure in terms of the associated potential energy barrier for reaction, $E_a$, and appropriate forward and reverse rate constants, $k$ and $k'$.

$F + H_2 \rightarrow H + HF^{\dagger}$



By determining conditions whereby equal gain (intensity) and equal time delay before emission are displayed for two frequencies, relative densities of two associated energy levels $N_v/N_{v-1}$ are calculable with available theory. It can be shown also that conditions are appropriate for a complete equilibration of rotational energy but no deactivation occurs of vibrational energy by collision. It follows that the population ratio also equals the corresponding rate constant ratio, $k_v/k_{v-1}$. Specifically with $F/H_2$, for example, $k_2/k_1 = 1.38 \pm 0.10$.

Based on the Principle of Microscopic Reversibility, considerable significance is found for the deviation of the rate ratios from unity. A unit value is predicted by many theories of kinetics which presume vibrational degrees of freedom to be equilibrated with all other degrees of freedom in the activated complex (transition state for reaction appropriate to the peak of the potential barrier). The results for HF portend a severe impact on theory. They indicate that vibrational energy is more effective than translational in bringing about this particular endothermic reaction ($H + HF \rightarrow F + H_2$).

In the example cited, the rate of formation was highest for products of the highest vibrational state, $k_v/k_{v-1} > 1$. This is not a general result, however. In some reactions the ratio has been found to be less than unity. This fact has considerable implications that will guide emerging theory and understanding of reactive molecular collisions.

Other laser systems beside the two selected could be analyzed in kinetic terms. Considerably more significant work has been done. No doubt, the most significant remains yet to be done. It is hoped that at least some inkling as to the possibilities has been conveyed. The subject can be taken up again in a future Chemistry Program Review

By way of closing, it may be reiterated that the description provided reveals how laser performance can permit a detailed analysis of underlying processes in chemical kinetics. General understanding is gained applicable in, for example, combustion dynamics and materials synthesis. However, to be more specific, the converse of the research description is also valid. Understanding the basic kinetic processes involved assists discovery, optimization, and interpretation of chemical lasers. Diverse applications in communication, reconnaissance, and other areas await new laser systems of varied output frequencies, higher operating efficiencies, increased power, and increased power to weight ratios. Some of these new systems will be "chemical lasers."

References:

1. "HCl Chemical Laser," J. V. V. Kasper and G. C. Pimentel, Phys. Rev. Letters, 14, 352 (1965).

2. "The Hydrogen-Chlorine Explosion Laser: II. DCl," P. H. Corneil and G. C. Pimentel, J. Chem. Phys., 49, 1379 (1968).

3. "Vibrational Energy Distribution Through Chemical Laser Studies: I. Fluorine Atoms plus Hydrogen or Methane," J. H. Parker and G. C. Pimentel, J. Chem. Phys., 51, 91 (1969).

# KINETIC METHODS OF ANALYSIS

By Denton W. Elliott

In the Air Force's world-wide operations of carrying out its missions in reconnaissance, surveillance, communications, navigation, and weapons delivery, it is required to have continuous monitoring of all its functional systems. It must be alert to excessive engine wear, to defects in its electrical circuitry, to impurities in its cabin environment, to the hazards encountered in the atmosphere as well as on the ground, and to any possible material or structural failures. To combat or prevent these problem areas, and to evaluate and establish performance specifications, new and improved analytical instrumentation and techniques are needed.

At Purdue University, Professors Dale Margerum and Harry Pardue have been working in a unique area in which kinetics are employed as a means of making chemical analyses. The following discussion should give one some insight as to the importance of this field of research to analytical chemistry and consequently to the various problems of the Air Force.

In the world of chemical analysis, the conventional approach involves the making of a measurement of some physical property of the chemical system at equilibrium and relating this measurement to chemical composition. If the system of interest is not at equilibrium, then conditions are adjusted to drive it to equilibrium in the shortest possible time. An alternative approach to analysis involves the measurement of the rate at which a reaction approaches equilibrium. This approach is generally referred to as the "kinetic" or "reaction rate" or "non-equilibrium" method. The use of non-equilibrium conditions permits many analytical determinations which are not possible under equilibrium conditions.

Interest and activity in research related to the applications of kinetics for quantitative chemical analysis has recently had a significant growth. These interests have been varied but have been directed at either (1) complete understanding of the chemical systems involved in the analyses, or (2) the development of instrumentation for improving the measurement step.

What types of problems are handled by the kinetic methods? One of the approaches may be entitled the "Organic Functional Group." In this approach, advantage is taken of differences in reaction rates of the same functional group in different organic molecules. These differences in reaction rates have been utilized in the selective determination of mixtures of these compounds. An example is the determination of primary and secondary alcohols based upon differences in rates of reaction with acetic anhydride. Amines, diazonium compounds and sugars are included in the functional groups and types of compounds that have been determined.

Another approach is that of enzymatic reactions. Enzymes are large molecules which cause reactions which are thermodynamically favorable, but would otherwise be very slow, to proceed at appreciable rates under rather mild conditions of temperature and pH. Enzymes are important and useful for analytical purposes in many ways. They show real promise as selective reagents for organic analyses because of their inherent specificity for specific reactions or groups of reactions.

The determination of the concentrations or activities of the enzymes themselves is important in many areas, including fundamental enzymology and clinical diagnosis of disease. Rates of many enzyme reactions are changed markedly by the additions of small concentrations of other species such as metal ions or anions. As such, the enzyme reaction can act as a sensitive monitor for the concentration of these inhibitors and activators. An enzymatic reaction example is shown when damage occurs to tissue of certain organs in the body, and enzymes held within the cell walls of the tissue are released into the bloodstream. Detection of the elevated levels of the enzymes can provide a useful tool in the diagnosis of the organ in which damage has occurred such as heart or liver. Since enzyme activity is defined as a reaction rate, there is no choice but to use a kinetic method.

A most promising area for the application of kinetics in analysis is the determination of trace constituents using catalytic reactions. Sensitivities into the nanogram region are easily possible with rather simple procedures. These reactions may divide into catalytic oxidation-reduction reactions and ligand exchange reactions.

Some oxidation-reduction reactions which are thermodynamically favorable proceed at extremely slow rates in the absence of any catalyst. But, upon the addition of trace quantities of a catalyst, a reaction may proceed at any appreciable rate which, under controlled conditions, is a simple function of the amount of catalyst added. Typical sensitivities for the catalytic species are in the range of $10^{-7}$ to $10^{-9}$ g/ml.

One of the most widely used reactions of this type is the oxidation of Arsenic (III) by Cerium IV as catalyzed by iodide. This reaction is sensitive to iodide reactions to 10 parts per billion. There is no interference from chloride or bromide. This reaction has been used extensively for the determination of traces of iodide in body fluids, and useful in detecting thyroid gland malfunction.

One of the more interesting recent developments in the application of kinetics in analysis is the use of ligand exchange reactions for trace analysis. Professor Dale Margerum discovered and exploited this method under AFOSR sponsorship. The method is based on the measurement of the exchange rate between triethylene-tetraaminenickel (II) (Nitrein) and ethylenediaminotetroacetocuprate (II) (Cutrein). The rate of exchange to produce NiEDTA and Cutrein is catalyzed by trace quantities of ligand. Any metal ion which complexes EDTA makes it ineffective as a catalyst and therefore will inhibit the reaction. Furthermore, any other agent which complexes the metal ion more strongly than EDTA will release EDTA and will effectively enhance the reaction rate. Therefore, this reaction scheme can be used for the determination of a variety of metal ions and anions.

At this point it should be noted that kinetics have been used in analytical chemistry for a long time. Kolthoff and Sandell (J. Am. Chem. Soc., 56, 1426 (1934)) reported a catalytic method for microdetermination of iodide 35 years ago. Biochemists have long been using enzyme kinetics for the determination of both substrates and enzymes. However, the development and application of kinetic methods have lagged behind other areas of analytical chemistry. There are several reasons why the area has not developed rapidly, but they are not to be belabored at this stage. Rather, we should look where the advances are being made.

For a view of the advances, we point again to Professor Margerum and his cohorts at Purdue University. They have developed a method for differential kinetic analysis of the metallic elements. The metal ions are first complexed with trans-1, 2-diaminocyclohexane-N, N, $N^1$, $N^1$-tetraacetate (CyDTA)--

a strong 1:1 complexing agent--and then their rate of conversion to a new complex is measured. For example, alkaline earth mixtures react with lead to give the lead complex:

$$Pb^{+2} + \begin{array}{l}(Mg\ CyDTA^{-2})\\(Ca\ CyDTA^{-2})\\(Sr\ CyDTA^{-2})\\(Ba\ CyDTA^{-2})\end{array} \longrightarrow Pb\ CyDTA^{-2} + \begin{array}{l}(Mg^{+2}\\(Ca^{+2}\\(Sr^{+2}\\(Ba^{+2}\end{array}$$

These reactions are fast (few milliseconds to a few seconds) and are followed with a stopped flow spectrometer. The resulting signal of per cent transmittance versus time is sampled many times to obtain data points. The resulting series of simultaneous equations is solved for the concentrations of $Mg^{+2}$, $Ca^{+2}$, $Sr^{+2}$, and $Ba^{+2}$ in the sample. More than thirty (30) metal ions have been tested with rate constants varying by $10^{12}$ so that mixtures of metal ions are readily analyzed. The adjacent rare earth ions also have sufficiently different rate constants to permit their determination.

Because the data in kinetic experiments vary with time, it is almost imperative that the data collecting and processing steps be automated to eliminate the need for constant attention from the chemist. Dr. Harry Purdue and Dr. Margerum of the Purdue Chemistry Department have combined their efforts to develop such a system. Both analog and digital instrument systems have been developed which automatically collect and process the data to generate numerical values of the concentration of the species being determined (see Fig. 1). These and other instrumental developments are being utilized to perform kinetic studies and analyses with operational simplicity and reliability not previously obtained.

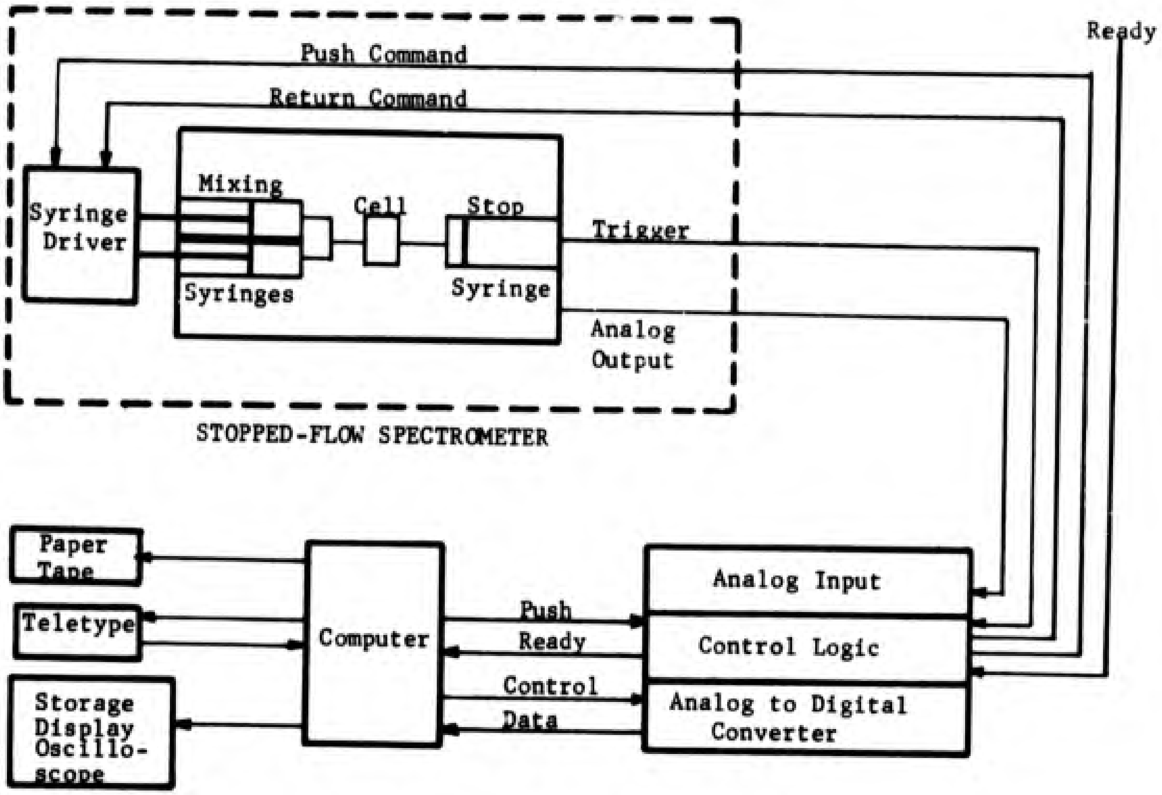


Fig. 1. Stopped-Flow Spectrometer/Computer System.

In this system the stopped-flow spectrometer combination is interfaced to a Hewlett-Packard 2115A computer for on-line operation with fast reactions. The present capability of the operation is as follows:

(1) Time range for reactions: milliseconds to minutes.
(2) Data presentation from the computer in three forms: (a) On teletype, (b) On paper tape, (c) On storage display scope.
(3) Data can be collected and transferred as percentage transmittance versus time or as absorbance versus time. Data points can be taken at pre-determined intervals and can be programmed to sample at different rates.
(4) Smoothing and ensemble averaging of data is possible.
(5) First-order rate constants with their standard deviation can be calculated on-line.

By having the computer in direct communication with the experiment from start to finish, with electronic instrumentation instead of an operator as the link between computer and experiment, removes that part of the human element which can be both boring and painfully time-consuming. A detailed evaluation can be carried out in minutes or even seconds, where routinely it would require hours or maybe days by other means. This savings in time alone provides the scientist with feedback information rapidly enough to allow modification of experiments for optimized measurements.

Bibliography:

J. B. Pausch and D. W. Margerum, Analytical Chemistry, 41, 226, (1969).

Margerum, Pausch, Nyssen, and Smith, Analytical Chemistry, 41, 233, (1969).

H. L. Pardue in Advances of Analytical Chemistry and Instrumentation, 7, 141, Wiley, New York (1969).

H. L. Pardue in Record of Chemical Progress, 27, No. 3, 151,(1966).

P. A. Rodriguez and H. L. Pardue, Analytical Chemistry, 41, 1369, (1969).

D. W. Margerum and R. K. Steinhaus, Analytical Chemistry, 37, 222, (1965).

# PHOTOIONIZATION AND PHOTOELECTRON SPECTROSCOPY

By Dr. Anthony J. Matuszko

Research investigations supported by the Directorate of Chemical Sciences at the University of Texas and the University of Wisconsin utilizing photoelectron spectroscopy and other photoionization techniques are providing fundamental information about chemical substances useful in many areas of Air Force interest, particularly in the materials area. The results obtained in these two independent, yet related, studies will provide detailed and precise chemical bonding and structural information pertinent to the synthesis of new thermally stable and radiation-resistant materials for use in high speed aircraft and guided missiles. Additionally, this research will provide basic information pertaining to the effects of high energy radiation on radiation shields, polymeric materials, clothing, rocket fuels, etc.

Several new techniques which have come into laboratory use during the past twenty years have revolutionized methods applied to studying chemical and physical properties and reactivity of chemical compounds. During these years, nuclear magnetic resonance, electron spin resonance, and gas chromatography were among the new tools to come into prominent use in the leading chemical research laboratories around the world. Chemists were beginning to understand "why" as well as "how" chemical substances behave as they do, as they probed deeper and deeper into the mysteries of chemical behavior.

Although not as yet achieving the notoriety or versatility of the instrumentation mentioned above, photoelectron spectroscopy is a new technique for studying molecular properties which came into being during the nineteen sixties. As described by Al-Joboury and Turner (J. Chem. Soc. 5141 (1963)), photoelectron spectroscopy involves the measurement of the kinetic energy distribution of the ejected electrons following photoionization of a sample molecule. The empirical data about ionization potentials (energy required to remove an electron from an atom or molecule) and relative transition probabilities obtained from the kinetic energy distribution of the ejected electrons can then provide information concerning the types of bonding present and the energies of bonding, anti-bonding and non-bonding electrons in the molecule. Applying Koopmans' theorem (Von T. Koopmans, Physica, 1, 104 (1933)), which states that the energy required to remove an electron from a molecule can be equated approximately to the energy of the molecular orbital from which the electrons came, comparisons of experimental data with molecular orbital calculations provide useful extensions of theoretical information about molecular structure.

The basic principle involved in photoelectron spectroscopy can be traced back sixty five years to Einstein's description of the photoelectron effect. When a sufficiently energetic photon of light, somewhere in the vacuum ultraviolet region (500-2000 angstrom wavelength) interacts with a gaseous molecule, the incident radiation is absorbed and an electron ejected. The energy of the electron ejected in the photoionization process is equal to the energy of the photon $h\nu$ ($h$ = a constant; $\nu$ = frequency of incident radiation), minus the energy required to remove the electron from the molecule. The energy needed to detach the electron from the molecule (ionization potential) can be calculated, knowing the kinetic energy of the electron and the energy of the photon beam. The most commonly used photon source is a helium resonance lamp which emits photons in the 21.22 electron volt or 584 angstrom wavelength region.

At the University of Texas, Dr. Michael Dewar has been using photoelectron spectroscopy in his combined experimental and theoretical approaches to determining the properties of a variety of organic molecules. Experimental data is used to check on the validity of theoretical approaches. The theoretical calculations should then make it possible to predict properties of new substances, or even set the framework for the synthesis of materials having desirable properties. In studying the behavior of large aromatic molecules, knowledge of the ionization potentials was vital to the development of the theory. Since only a few reliable values were reported for compounds other than benzene derivatives, Dewar and his research group built a low resolution photoelectron spectrometer (retarding grid type) and measured ionization potentials for over 100 compounds, including the interesting new organometallic complex shown in Fig. 1.

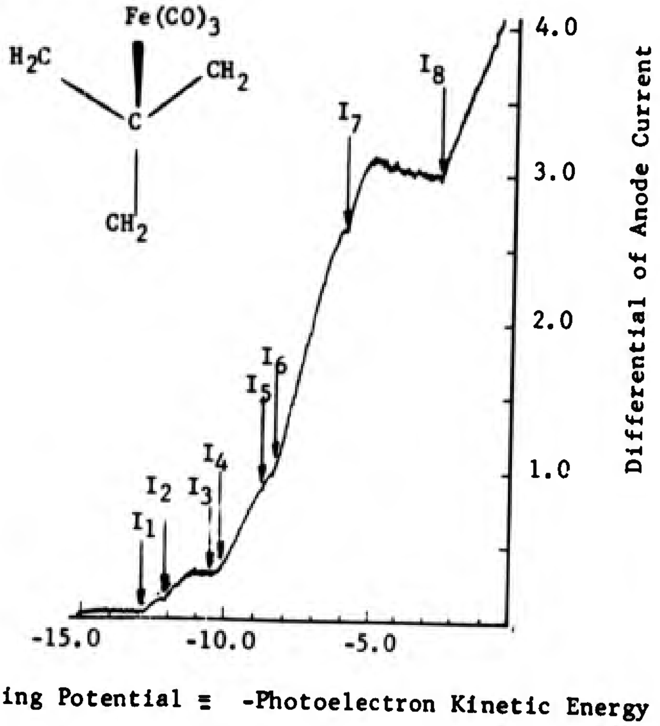


FIG. 1. Photoelectron spectrum of trimethylenemethaneiron tricarbonyl ($p = 0.032$ mm). Excitation source was 584 Å (21.22 eV) resonance line of helium.

(M.J.S. Dewar and S. D. Worley, J. Chem. Phys., 51, No. 4, 1672 (15 Aug 1969). The results were interpreted in terms of molecular orbital theory and theoretical values were calculated by a MINDO method (modified intermediate neglect of differential overlap). The observed ionization potentials showed a remarkably close relationship to the calculated molecular orbital energies over the whole range of ionization potentials studied. The parameters used for these molecular orbital calculations were the same as those previously used by Dewar and his associates for obtaining theoretical values for heats of formation of organic molecules which checked very closely with experimental values. Due to this unexpected turn of events, Dr. Dewar proceeded to construct a high resolution photoelectron spectrometer (with an electrostatic velocity analyzer) which would give more precise ionization potentials, particularly the energy needed to remove the second, third, fourth, etc. electrons from a molecule ($I_2$, $I_3$, $I_4$, etc. shown in Fig. 1). This data could then be used to obtain more detailed information about molecular orbital energies and to adjust molecular orbital parameters for even better calculated values for molecular properties. The high resolution photoelectron spectrometer is nearly completed and should be in operation the first quarter of 1970.

At the University of Wisconsin, Dr. James Taylor is doing a related study. He is combining photoionization and mass spectrometric detection with photoelectron spectroscopy measurements to determine properties of chemical substances and the kinetics and mechanisms of their fragmentation processes. The University's Physical Science Laboratory synchrotron facility provides a continuum of high intensity photon light energy uniquely suited for this work. Electrons from a particle accelerator of the synchrotron are shot into a storage ring where they are made to circulate at about 32 million times per second (99.999% the speed of light). Traveling at such high speeds the electrons give off extremely intense light in the soft x-ray and vacuum ultraviolet regions (wavelengths of 50-2000 angstroms). With an appropriate wavelength isolation device or monochromator, a high concentration of photons in the desired wavelength region can be focused on a sample of material under study. The energy associated with dislodging an electron from a molecule can be determined (by photoelectron spectroscopy), or the manner in which the molecule breaks up (photoionizes) into fragments may be measured with a mass spectrometer. During the first year of this investigation considerable data has been obtained on photoionization and fragmentation patterns of a number of aromatic compounds and olefins. Initial results show identical photoionization spectra for different olefins studied. This suggests that fragmentation of the olefins proceeds from the same precursor ion - a result which has implications in the combustion of hydrocarbon fuels and the decomposition of organic coatings if this initial assumption holds true. Interpretation of the accumulated experimental data and further experimentation, including photoelectron spectroscopy measurements, are currently in process. The initial results and interpretations will be published in the early part of 1970.

Combinations of new experimental techniques and refinement of theory are providing much needed information about the properties and behavior of molecular substances. Although we are still a long way off from being able to depend on theory alone, investigations such as those supported by AFOSR at the Universities of Texas and Wisconsin bring us closer to the day when an aerospace scientist or engineer may be able to formulate the properties needed in a new material, put the data into a computer, and come up with a chemical structure to fulfill these requirements.

# METHODS OF TRACE ELEMENT ANALYSIS

By Dr. William L. Ruigh

The theme of this section of the annual review is "Methods of Chemical Science." To illustrate this topic we will use analytical chemistry and the AFOSR project headed by Dr. J. D. Winefordner in the Department of Chemistry at the University of Florida, Gainesville. This basic research effort is not only an excellent illustration of modern scientific chemical progress but also has already contributed and is further expected to improve markedly the Air Force Spectrometric Oil Analysis Program which deals with the prediction and prevention of aircraft engine failures (and sharply reduces maintenance costs) through the periodic analysis of engine oil for trace wear metals.

Dr. Winefordner's research is in the area of analytical chemistry and was initially a study of a new gas chromatographic detector relevant to the detection of toxic gases. After about a year the project was very much expanded as the result of a new proposal and personal visits by members of the AFOSR chemistry staff and now includes Winefordner's work in flame photometry. The AFOSR grant since then has supported all of Winefordner's research with the exception of a small project on the fluorometric analysis of drugs. Winefordner's work illustrates well the complexity and sophistication of todays analytical chemistry contrasted with the older methods.

Forty years ago the analyst's primary tools were the balance, crucible, buret and combustion tube, supplemented for special analysis with the gas buret, the hand operated colorimeter, a crude device for the electro deposition of metals such as copper and a spark spectrograph for metals and alloys.

The development in recent years has been in theory, in techniques, and in instrumentation. The three categories are not mutually exclusive. Thus, the various forms of chromatography, adsorption, ion exchange, liquid-adsorbed liquid, paper and thin film are all primarily examples of new techniques. In addition, instrumentation in the form of mechanized fraction cutters can be used. An example of almost pure instrumentation is the mass spectrograph, although its use to unravel complex organic structures (which is really not analytical chemistry) involves a considerable knowledge of organic theory. An example of an advance due primarily to new theories of atomic and molecular structure is nuclear magnetic resonance spectroscopy. It must be noted that without the introduction of a commercial instrument, progress in the area would have been much slower.

The spectacular change in analytical chemistry has been for the most part caused by a markedly increased application of chemical theory and by the adoption of sophisticated electrical instrumentation starting with the potentiometric titrimeter, the glass electrode pH meter, and the polarograph in the early thirties. This shift of analytical chemistry to electrical instrumentation is illustrated by the recent publication of a book, "Electronics for Scientists" by Malmstadt, Enke and Toren. All three are analytical chemists (incidentally, the first two authors have had AFOSR support).

The workhorses in the new age of analytical chemistry have been the vastly improved ultraviolet, visible and infrared spectrometers dependent on photosensitive electrical detectors of high stability, sensitivity and reliability. Also of considerable utility are the beta and gamma ray spectrometers for the analysis of radioactive materials and the technique for the analysis of trace amounts of materials known as neutron activation analysis. In addition, x-ray and electron beam methods using diffraction and fluorescence are of specialized value in trace analysis, the analysis of micro phase separations in alloys, and, more recently, photoelectron spectroscopy for organic materials and Auger electron emission for surfaces.

The next group of methods is flame and spark spectrophotometric analyses. Flame emission, flame absorption and the new flame fluorescent analysis developed primarily by Winefordner are examples (see Fig. 1).

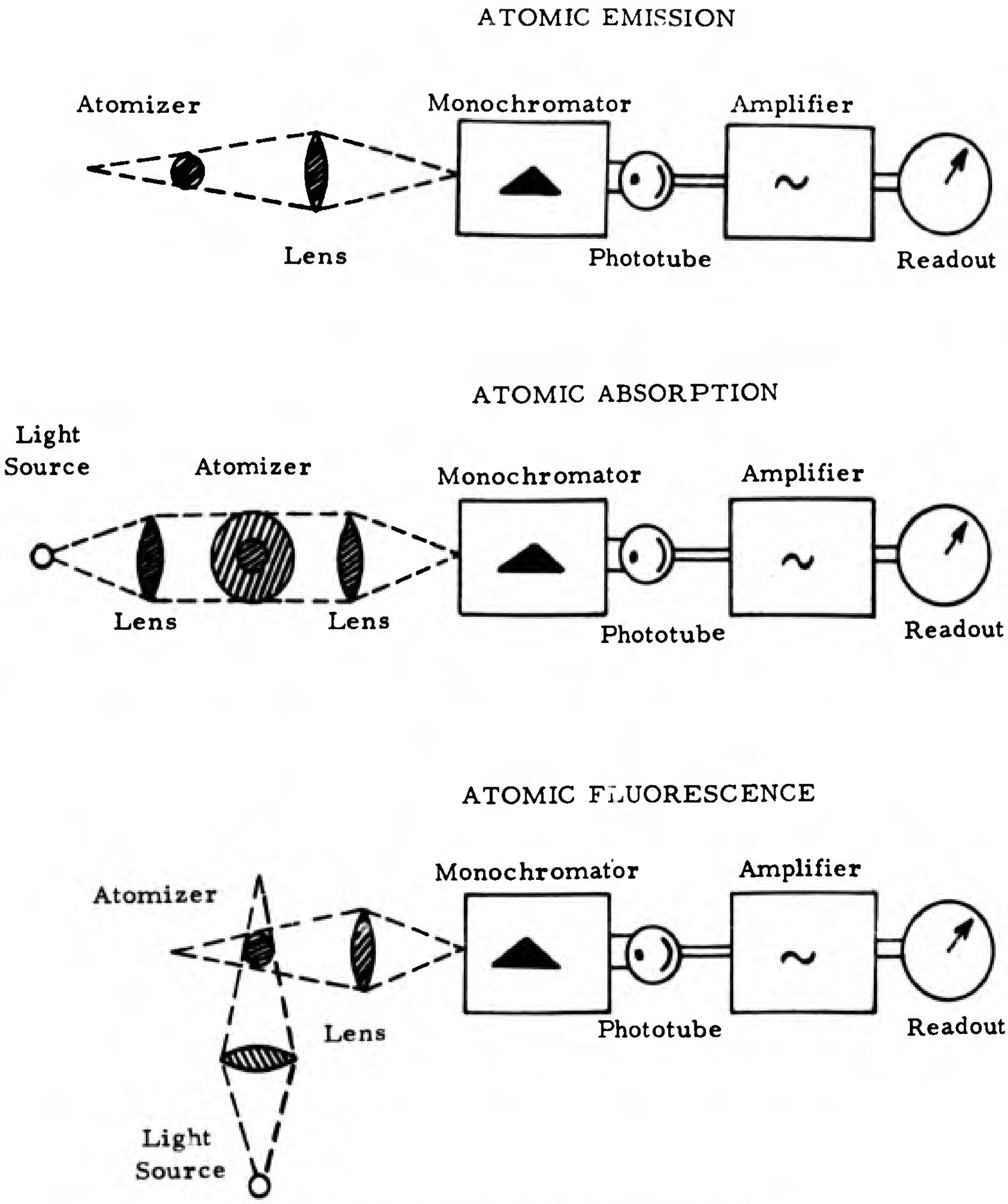


Fig. 1. Spectrophotometric Analysis Instrumentation.

The first of these methods, flame emission spectrometric analysis, was originally developed for the analysis of sodium, potassium, calcium, and magnesium in soil extracts, biological materials, and boiler waters. Later it was found applicable to a number of other elements including the rare earths. In all three methods the flame serves to vaporize the sample, usually introduced as a spray in the gas. (Beside the flame this function can be accomplished by a spark or more recently by electrical heating of a sample boat.) In emission flame (or spark) spectroscopy the atoms (and/or molecules) in their ground state are thermally agitated and reach higher energy or excited states by collision. On returning to the ground state the light emitted by radiation and passed through a spectrometer is measured for analysis. In atomic absorption analysis an external (usually resonant monochromatic) light source is employed to excite the thermally ground state atoms in the flame. The difference, source light minus passed light, is measured with the sample present. (Source light measured without sample is the flame alone.) The second flame analysis method to arrive rather belatedly on the analytical scene was the rather recent flame atomic absorption spectrometric analysis. The adoption of this method was probably triggered by two major factors, the success of infrared absorption analysis, particularly for organic analysis, and again the introduction of stable, sensitive commercial flame atomic absorption instruments. A recent development in this area is the announcement late in 1969 of a commercial, combined simultaneous absorption-emission spectrophotometer. This instrument permits the choice of method best suited to particular elements in a single multi-element analytical determination. So far we have considered the first two methods of flame spectrometric analysis. The third and latest method is flame fluorescence analysis first discovered and developed by Winefordner. The phenomenon of flame fluorescence has been studied, primarily by physicists, for a number of years and its use as an analytical tool for chemical analysis even suggested at a spectroscopy symposium by Alkemade in 1962. With the relative recession in interest in the nuclear field there has been a great upsurge of research by physicists as well as chemists in quantum theory, electronic atomic and molecular energy levels, energy transfer lifetimes of excited states and radiation phenomenon, particularly since the advent of the laser. All these topics have been essential in the development of flame spectroscopy and Winefordner has published mathematical equations to calculate (with the aid of a large computer) the limiting detectable atomic concentrations by all three flame spectrometric methods. The formula contains, in addition to the values derived from a knowledge of the excited atomic states, a considerable number of more empirical factors relating to the light source, flame, spectrometer, phototube, and amplifier system. These formulas are not so much useful to give absolute results but to disentangle the multitude of complex physical and chemical factors involved and to guide intelligently the evolution of an analytical system and then to predict the choice of method to analyze a complex mixture.

Winefordner's project was originally chosen by AFOSR for its scientific excellence and its relevance to the trace analysis requirements of the Air Force. It has been closely coordinated with the Air Force, Army, Navy, and DoD SOAP (Spectrometric Oil Analysis Program) programs.

The Spectrometric Oil Analysis Program is the trace analysis of wear metals in oils, particularly jet engine oils. From the increase in the pattern of the trace metal concentration of about ten elements in the oil at fixed time periods, the need for overhaul or removal of an engine can be determined. It has frequently predicted and prevented the catastrophic failure of engines which may result in airplane crashes, particularly with single engine fighters.

Table I at the end of this paper gives a comparison of the detection limits of elements of interest in the SOAP program by the various flame and graphite spectrometric methods. The last three columns indicate the limits of detection when the sample is vaporized in an electrically heated graphite sample boat instead of by the conventional flame. For some elements such as cadmium and zinc, the atomic fluorescent method is about 1000 times as sensitive as the flame absorption procedure. The complexity of Winefordner's research necessary to compile this table is illustrated by some of the titles in the references.

## TABLE I

## COMPARISON OF DETECTION LIMITS OF ELEMENTS

| | AAF | AEF | AFF | AAG[b] | AEG[b] | AFG[b] |
|---|---|---|---|---|---|---|
| Al (5-77)[e] | 0.1 | 0.01 | --- | 0.05 | --- | --- |
| Ba | 0.05 | 0.002 | --- | --- | 0.01 | --- |
| Be | 0.002 | 0.10 | 0.02 | --- | --- | --- |
| B | 6.0 | 3.0 | --- | --- | 1.5 | --- |
| Cd | 0.001 | 2.0 | 0.000001 | 0.0002 | --- | 0.00002 |
| Co | 0.005 | 0.05 | 0.01 | --- | 0.03 | --- |
| Cr (10-50)[e] | 0.005 | 0.003 | 0.05 | --- | 0.001 | --- |
| Cu (3-72)[e] | 0.005 | 0.01 | 0.001 | 0.001 | --- | 0.05 |
| Fe (15-130)[e] | 0.005 | 0.05 | 0.008 | 0.002 | --- | 0.3 |
| Pb (10)[e] | 0.03 | 0.2 | 0.01 | 0.001 | --- | 0.003 |
| Mg (2-34)[e] | 0.0003 | 0.005 | 0.001 | --- | --- | 0.0003 |
| Mn | 0.002 | 0.005 | 0.006 | 0.0008 | 0.004 | --- |
| Mo | 0.03 | 0.1 | --- | --- | --- | --- |
| Ni | 0.003 | 0.03 | 0.003 | 0.007 | 0.01 | --- |
| Si | 0.1 | 5.0 | --- | --- | --- | --- |
| Ag (3-14)[e] | 0.005 | 0.02 | 0.0001 | 0.00008 | --- | 0.0002 |
| Na | 0.002 | 0.0001 | --- | 0.0007 | --- | --- |
| Sn (5-29)[e] | 0.02 | 0.3 | 0.05 | 0.02 | --- | --- |
| Ti | 0.1 | 0.2 | --- | --- | --- | --- |
| V | 0.02 | 0.01 | --- | --- | --- | --- |
| Zn (3)[e] | 0.002 | --- | 0.00004 | 0.00008 | 0.5 | 0.000004 |

a. AAF = Atomic Absorption, Flame AAG = Atomic Absorption, Graphite
AEF = Atomic Emission, Flame AEG = Atomic Emission, Graphite
AFF = Atomic Fluorescence, Flame AFG = Atomic Fluorescence, Graphite

b. Limits of detection (mg/ml) are the best available in the literature and from this program. Most results are for aqueous solutions.

c. Data is based on 10 μl samples.

d. An estimate of the limit of detection in oil can be made by multiplying each result in the table by ∼10.

e. SOAP threshold limits are in parts per million.

Bibliography:

"Use of a Continuous Source in Flame Fluorescence Spectrometry," Claude Veillon, J. M. Mansfield, M. L. Parsons, and J. D. Winefordner, 38, 204 (1966).

"On the Influence of the Flame Temperature in Atomic Emission and Atomic Absorption Flame Spectrometry," Leo de Galan and J. D. Winefordner, 38, 1412 (1966).

"Derivation of General Expressions for Quantum and Power Efficiencies for Atomic Fluorescence in a Hot Gas with Emphasis on Atomic Fluorescence Flame Spectrometry," W. J. McCarthy, M. L. Parsons, and J. D. Winefordner, Spectrochim. Acta., 238, 25 (1967).

"The Selection of Optimum Conditions for Spectrochemical Methods: III. Comparison of the Sensitivity of Atomic Fluorescence, Atomic Absorption, and Atomic Emission Flame Spectrometry," M. L. Parsons, W. J. McCarthy, and J. D. Winefordner, J. Chem. Ed., 44, 214 (1967).

"Atomic Fluorescence Flame Spectrometry," J. D. Winefordner, and J. M. Mansfield, Appl. Spectr. Reviews, 7, 1 (1967).

"Several High Sensitivity Radio-Frequency Detectors For Permanent Gas Analysis," H. P. Williams and J. D. Winefordner, J. Gas. Chromatog., 6, 11 (1968).

"An Evaluation of Atomic Fluorescence Flame Spectrometry for the Determination of Wear Metals in Jet Engine Lubricating Oils," R. Smith, C. M. Stafford and J. D. Winefordner, Canadian Spectroscopy, 14, 2 (1969).

# ELECTROCHEMICAL METHODS

By Lt. Col. L. D. Whipple

Air Force operations have placed new demands on technology to provide electrochemical power sources that have increased reliability, lighter weight, longer life, and higher power. Communications, often under very adverse conditions, are the heart of command, control, and information transfer. Continual and dependable operation of these communications, regardless of the situation, depends on the batteries or fuel cells that provide the primary, auxiliary, or emergency power.

Communications with remotely located facilities, such as near-earth satellites or forward battle zone navigational devices, depend on power sources which will operate for long periods of time with no maintenance. Communications with downed aircrew personnel present a variety of extreme requirements. In this case the power supply must withstand such conditions as the shock of bailout or crash landing, the affects of being submerged in water, the extreme cold temperature of the arctic or the hot humid environment of the tropical jungle. In any case, the power source is the vital link to successful rescue operations. An improved portable power source needed for air rescue work is a current problem as expressed in a requirement for technology entitled, "High Capacity Batteries for Survival Radios," prepared by the Air Force Aeronautical Systems Division. Other electrochemical power source requirements are expressed by the Air Force Systems Command laboratories in their Technical Objective Documents.

A better base of fundamental knowledge is needed. A study by the Institute of Defense Analyses states that battery technology is "founded almost entirely on practical and empirical arts rather than on exact science."[1] It further points out that there must be a "long-range program set up and followed to keep advancing the state of the art to match the demands of electrochemical power."

Air Force interests in electrochemical methods include not only those applicable to power sources, but fundamental knowledge and control of corrosion as well. Corrosion of equipment in the varied environments of world-wide operations costs indeterminable amounts of money, manpower, and equipment.

As a result of Air Force interests and the underlying need for more fundamental knowledge, the Directorate of Chemical Sciences of AFOSR has, for the past four years, emphasized the area of electrochemistry. A review of the program was presented in the 13th Annual Chemistry Program Review. The purpose of this paper is to review two efforts in the program that emphasize new electrochemical methods being developed and used. Both these efforts relate to a better understanding of the kinetics and mechanisms of reactions at the electrode-electrolyte interface (the electrical double layer). One of the goals of the AFOSR program is to assist in providing a theoretical basis from which technology may advance. Activities to acquire this base for technology are confronted with many limitations. The measurement of the absolute potential difference across the electrical double layer has historically been an ellusive parameter limited by the lack of instrumentation of sufficient minute accuracy and precision. Another limitation has been the inability to expeditiously handle the large amounts of data required to provide the statistical basis for further development of applicable theories. The two efforts discussed here attack the frontiers of these limitations and thereby provide substance toward reaching the AFOSR program goal.

The first of the efforts to be discussed is that of Dr. Robert deLevie of Georgetown University who is contributing to the fundamental knowledge bank by elucidating the role of the electron at the electrode-electrolyte interface. The nature of the hydrated electron has been described by Dr. deLevie in a recent Georgetown University publication.[2] His studies have involved the generation of hydrated electrons by means of photo-emission from dropping mercury electrodes. Unlike electrons expelled from metals into a vacuum, which never return to the electrode unless a field is applied, those expelled from metal into a solution eventually return to the electrode unless there are species in the solution which react quickly with the electrons and trap them in the solution. The currents involved in these mechanisms are extremely small, and special instrumentation was required to detect them. Experimental data collected provide a plot of photocurrent versus the difference in potential between the dropping mercury electrode and the solution. The photocurrents are less than one per cent of the total current in the electrode. Consequently, special techniques are required to discriminate between the photocurrents and the "noise."

Dr. deLevie has developed an instrument for the automatic measurement of the very small photocurrents.[3] Figure 1 shows the major components of the electrical circuitry. Preliminary experiments using various concentrated

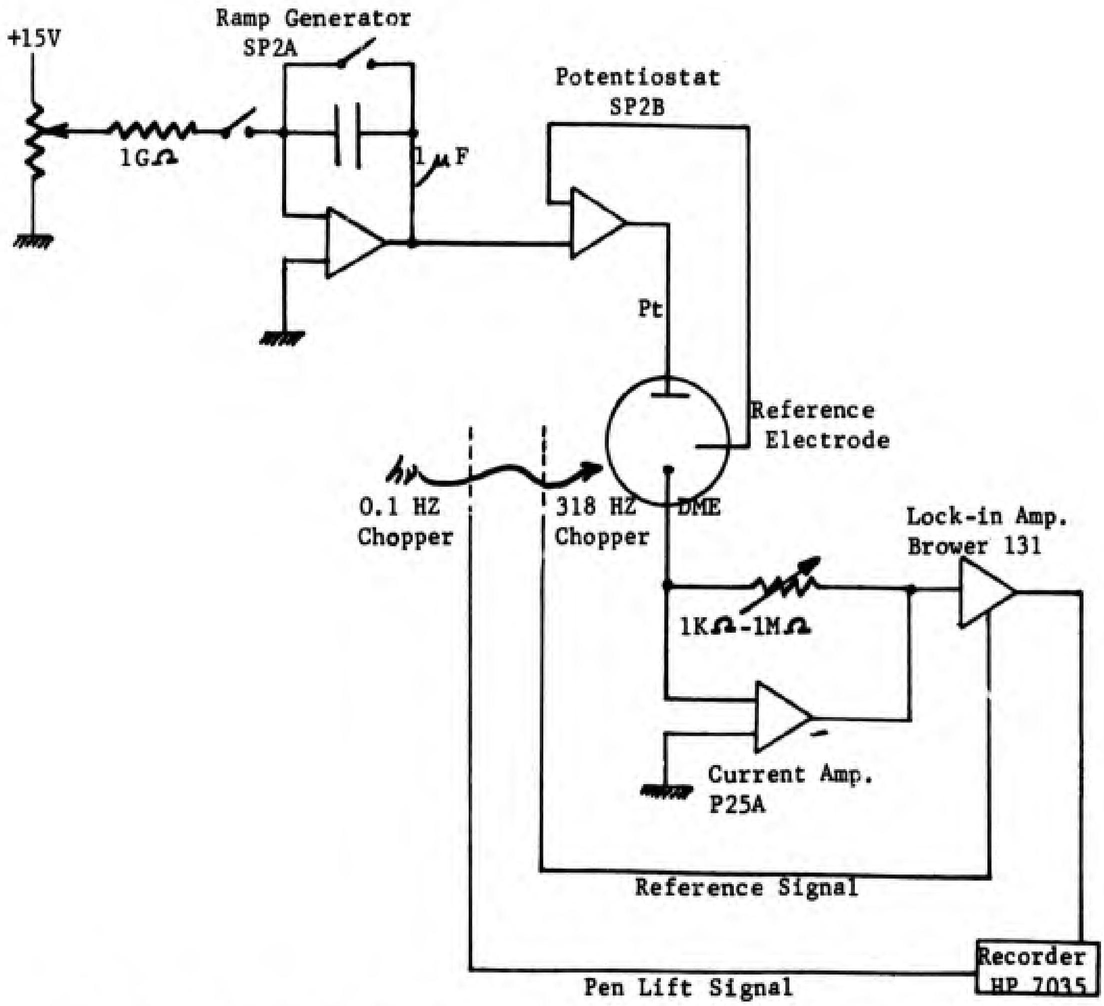


Fig. 1. Electrical Circuit for Automatic Measurement of Photocurrents

(0.5 to 1.0M) aqueous electrolytes, including NaF + $N_2O$, HCl, $KNO_3$, and $KBrO_3$, showed that the overall noise level was always less than one nanoampere. This sensitivity is considered satisfactory in view of the fact that the residual currents, the double layer charging currents, are of the order of one microampere. In addition, the preliminary experiments showed that photocurrents were present prior to the onset of the regular photocurrents in all solutions. They also indicated that Delahay's square root of current versus voltage straight line relationship in HCl, $KNO_3$, and $KBrO_3$ did not hold true at these small photocurrent levels. NaF data obeyed the straight line relationship which suggests that the deviations were related to anion specific absorption. These early experiments also pointed out that the initially developed instrument was unable to maintain a comparable performance level in solutions of less than 0.1M concentration. This inability was eliminated by further modifications of the instrument.

The sensitivity and precision of this instrumental technique enabled Dr. deLevie to decide that electron tunneling is indeed the reason for the observed potential-dependence of the photocurrents and that Heyrovsky's explanation for the generation of photocurrents via charge transfer interaction of solvent molecules was incorrect.

The highly precise and sensitive instrumentation and the encouraging results indicate that the way may be open towards the primary goal of establishing a scale of single electrode potentials. Further work will attempt to develop an ultrafast electrochemical measurement technique using photo-generation of hydrated electrons.

The second effort to be discussed in the paper also involves the critical electrode-electrolyte interface which is being investigated in a different manner by Dr. David M. Mohilner of Colorado State University. He is studying the mechanism of adsorption of organic molecules in order to further elucidate and develop the theory of the electrical double layer. In electrode processes, adsorbed organic molecules may act either as electroinactive or as electroactive species. Therefore, to describe the charge-transfer kinetics involved, an understanding of adsorption is necessary. Two major parameters of the electrical double layer are interfacial tension (electrocapillary data) and differential capacitance from which the important charge density may be determined. The typically used graphical thermodynamic analyses of these data have been relatively inaccurate, often equivocal, and long and tedious processes. Dr. Mohilner has developed digital computer techniques for differentiating the interfacial tension versus voltage data and for integrating the capacitance versus voltage data. From these computerized calculations, charge density on the electrode is obtained with sufficient speed that it is feasible to use the results to monitor the experiments in progress. Thus, a central role in his work is the digital computer analysis of the adsorption equilibrium data.

Dr. Mohilner has made significant improvements in instrumentation used in making electrocapillary measurements. The modifications of the capillary electrometer included drawing a heavy-walled fine capillary, insetting an optically flat viewing window into the wall of the electrometer cell, using a 120X stereomicroscope, and developing an improved pressure adjusting system. The reproducibility of measurement obtained is of the order of $\pm$ 0.02 to $\pm$ 0.05 dyne/cm. This is nearly one order of magnitude improvement over previous instruments. This means that changes in interfacial tension can be measured approximately ten times more accurately than the best by the sessile drop method which serves as the basis of calibration of capillary electrometers.

In order to achieve the goal to develop methods of elucidating the mechanism of adsorption of organic molecules by analysis of adsorption kinetics, it is necessary first to derive the theoretical rate equations for adsorption kinetics corresponding to various established adsorption equilibrium curves. Dr. Mohilner, working with Dr. P. Delahay in 1962, developed the equations of neutral organic molecules that obeyed the logarithmic Temkin curve.[4] This curve is only an approximation and work is now in progress to derive the rate equations necessary to test the data on the basis of more realistic curves such as the Frumkin and virial curves. Dr. Mohilner has developed a new adsorption equilibrium approach which appears to be general enough to include the treatment of adsorbed ionic species as well as neutral organic molecules.[5]

The efforts of Dr. deLevie and Dr. Mohilner are but examples of the extent of the electrochemistry efforts supported by AFOSR. However, they are examples of significant forward motion being attained in the field of electrochemical instrumentation and techniques.

References:

1. "A DOD Research Program for Electrochemical Sciences with Applications to Energy Storage and Conversion," Institute for Defense Analyses, G. C. Szego, Chairman, Study S-208, December 1965.

2. "The Hydrated Electron - A Charged Empty Space in Water," Research Bulletin, Georgetown University Science Center, Vol. VI, No. 2, March 1969, R. deLevie.

3. "Instrument for the Automatic Measurement of the Electrode Admittance," R. deLevie and A. A. Husovsky, J. Electroanal. Chem., 20, 181 (1969).

4. P. Delahay and D. M. Mohilner, J. Phys. Chem., 66, 959 (1962); J. Am. Chem. Soc. 84, 4247 (1962).

5. "Double Layer Effects - In the Kinetics of Heterogeneous Electron Exchange Reactions," David M. Mohilner, J. Phys. Chem., in press.

# CHEMISTRY PROGRAM STATISTICS AND INFORMATION

## FY 1969 CHEMISTRY PROGRAM STATISTICS

(30 June 1969)

| | Number | Amount, Thousands |
|---|---|---|
| New Projects | 16 | $ 830 |
| Renewals | 56 | 2,590 |
| Continuing Projects | 47 | |
| Completed Projects | 25 | |
| TOTAL | 144 | |
| Active Projects, 30 June 1969 | 119* | |
| Monies Committed During FY 69 (for 86.3 Project Years) | | 3,420** |
| Cost per Project-Year | | $ 39.6 |

* In addition, the Directorate of Chemical Sciences administers two ARPA projects and one THEMIS project.

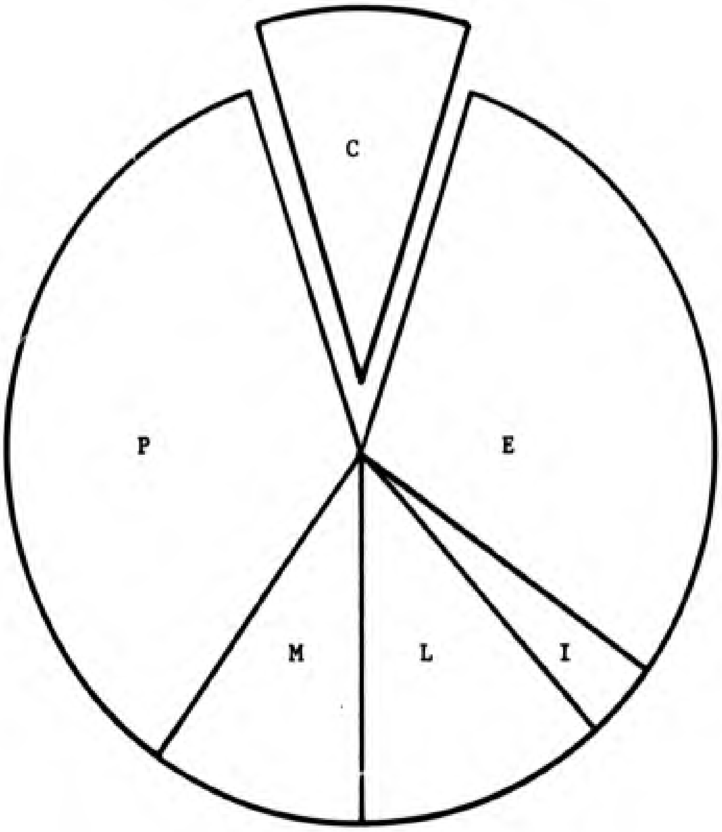
** A distinction is made between the FY 69 "program" and the FY 69 "budget." For administrative reasons, some research efforts in the FY 69 program are funded with FY 68 money; similarly, some FY 69 money is used to fund part of the FY 70 program.

## FY 1969, PROPOSAL DATA

| | |
|---|---|
| New Proposals Received | 201 |
| Renewal Proposals Received | 58 |
| TOTAL | 259 |
| New Proposals Declined, Withdrawn, or Transferred | 176 |
| New Proposals Funded | 25 |
| Percent Funded | 12% |
| Renewal Proposals Funded | 58 |
| Overall Percent Declined | 68% |
| Overall Percent Funded | 32% |

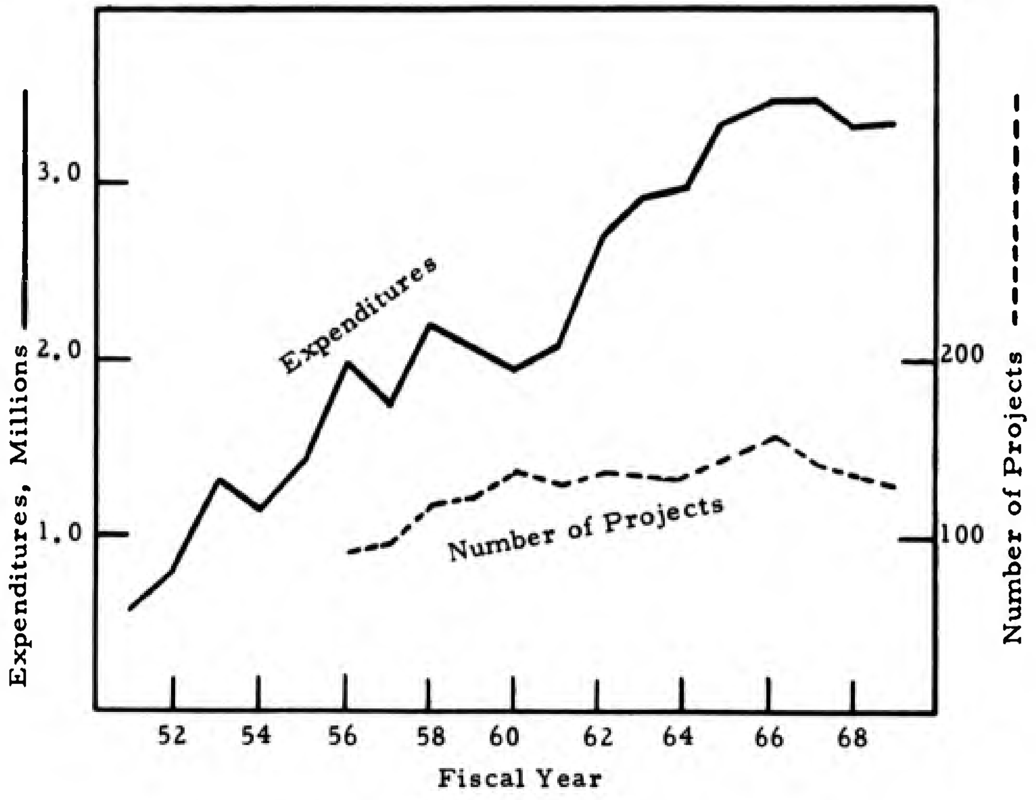
AFOSR FY69 BUDGET

| Directorate | Symbol | Amount, Thousands | Percent |
|---|---|---|---|
| Chemical Sciences | C | $ 3,338 | 10.1 |
| Engineering Sciences | E | 10,050 | 30.3 |
| Information Sciences | I | 1,050 | 3.2 |
| Life Sciences | L | 3,690 | 11.1 |
| Mathematical Sciences | M | 3,209 | 9.7 |
| Physical Sciences | P | 11,847 | 35.6 |
| | | $ 33,184 | 100.0 |



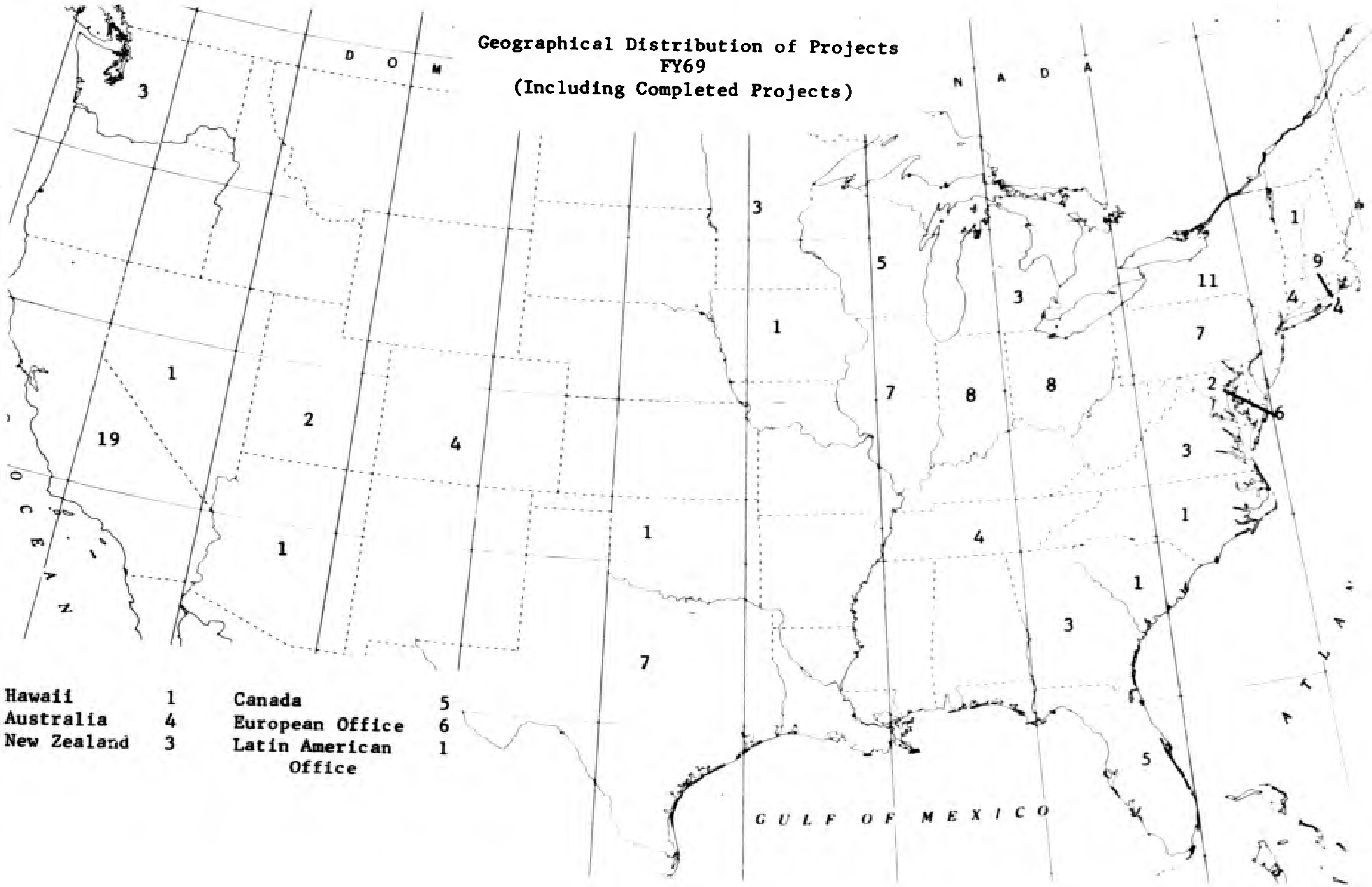
## CHEMISTRY BUDGET

| FY | Expenditures ( Thousands) | FY | Expenditures ( Thousands) |
|---|---|---|---|
| 51 | $ 596 | 61 | $2,086 |
| 52 | 835 | 62 | 2,700 |
| 53 | 1,310 | 63 | 2,922 |
| 54 | 1,150 | 64 | 2,959 |
| 55 | 1,451 | 65 | 3,356 |
| 56 | 1,976 | 66 | 3,475 |
| 57 | 1,732 | 67 | 3,480 |
| 58 | 2,205 | 68 | 3,329 |
| 59 | 2,066 | 69 | 3,338 |
| 60 | 1,964 | 70 ( Est.) | 3,250 |



NOTE: A comparison of the two plots indicates the rising cost of basic research in chemistry.

## Geographical Distribution of Projects
FY69
(Including Completed Projects)



| | | | |
|---|---|---|---|
| Hawaii | 1 | Canada | 5 |
| Australia | 4 | European Office | 6 |
| New Zealand | 3 | Latin American Office | 1 |

## SYMPOSIA

An important part of activities by the Directorate of Chemical Sciences to publicize and stimulate areas of research of interest to the Air Force is the support of symposia. The following list includes symposia sponsored by the Directorate during FY 68 and FY 69:

The Gordon Research Conference on Inorganic Chemistry
New Hampton, New Hampshire
7-11 August 1967

The Gordon Research Conference on High Temperature Chemistry
Crystal Mountain, Washington
29 July - 2 August 1968

The Gordon Research Conference on Inorganic Chemistry
New Hampton, New Hampshire
5 - 9 August 1968

Second International Liquid Crystal Conference
Kent State University, Kent, Ohio
12 - 16 August 1968

Sixth International Symposium on the Reactivity of Solids
General Electric Research and Development Center
Schenectady, New York
25 - 30 August 1968

Fifth International Congress of Photobiology
Dartmouth College, Hanover, New Hampshire
26 - 31 August 1968

# PUBLICATIONS RECEIVED DURING FY 1969 ON PROJECTS EXPIRED DURING PRIOR YEARS

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

"1,3-Asymmetric Induction in Stereospecific Addition Polymer, T. J. Leitereg and D. J. Cram, J. Am. Chem. Soc., 90, 4011 (1968).

"Studies in Stereochemistry. XXXVIII. Open-chain Versus Cyclic Models for 1,3-Asymmetric Induction in Addition Reactions," T. J. Leitereg and D. J. Cram, J. Am. Chem. Soc., 90, 4019 (1968).

Crosby, G. A.
University of New Mexico
Albuquerque, New Mexico
AF-AFOSR-269-65

"Spectroscopic Studies of Ruthenium (I) Complexes. Assignment of the Luminescence," D. M. Klassen and G. A. Crosby, J. Chem. Phys., 48, 1853 (1968).

Dahl, L. F.
University of Wisconsin
Madison, Wisconsin
AF-AFOSR-518-66

"Organometallic Sulfur Complexes. XII. Structure of a Hexameric Mercaptocobalt Carbonyl Sulfide Complex," C. H. Wei and L. F. Dahl, J. Am. Chem. Soc., 90, 3977 (1968).

Dannhauser, W.
State University of New York
Buffalo, New York
AF-AFOSR-271-63

"Dielectric Relaxation in Isometric Octyl Alcohols," W. Dannhauser, J. Chem. Phys., 48, 1918 (1968).

"Dielectric Study of Intermolecular Association in Isometric Octyl Alcohols," W. Dannhauser, J. Chem. Phys., 48, 1911 (1968).

Fraenkel, G. K.
Columbia University
New York, New York
AF-AFOSR-285-67

"The Photolysis of Alkyl Nitrites in Alcoholic Media," S. Shih, R. J. Pritchett, J. M. Riveros, Tetrahedron Letters, 47, 4897 (1968).

House, H. O.
Massachusetts Institute of Technology
Cambridge, Massachusetts
AF-AFOSR-573-66

"Perhydroindan Derivatives. IX. The Diels-Alder Reaction with 7-Methylindene Derivatives," H. O. House and F. J. Sauter, J. Org. Chem., 33, 957 (1968).

Hylleraas, E. A.
University of Oslo
Oslo, Norway
AF-EOAR-33-66

"On the Convergence Properties of the $1/Z$ Expansions as Furnished by Variational Perturbation Theory Calculations," J. Midtdal, K. Aashamar and G. Lyslo, Physica Norvegica, 3, 11 (1968).

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

"The Relative Nucleophilicity of Some Common Nucleophiles Toward Sulfinyl Sulfur. The Nucleophile Catalyzed Hydrolysis of Aryl Sulfinyl Sulfones," J. L. Kice and G. Guaraldi, J. Am. Chem. Soc., 90, 4076 (1968).

Kolthoff, I. M.
University of Minnesota
Minneapolis, Minnesota
AF-AFOSR-28-65

"Electronic Absorption Spectra of Ion Pairs Composed of Substituted Amine Picrates in Acetonitrile," M. K. Chantooni, Jr. and I. M. Kolthoff, J. Am. Chem. Soc., 90, 3005 (1968).

Kwiatek, J.
U. S. Industrial Chemicals Co.
Cincinnati, Ohio
AF-49(638)01214

"Catalytic Hydrogenation and Hydrogenolysis by Pentacyanocobaltate (II)," J. Kwiatek and J. K. Seyler, Advances in Chemistry Series, Homogeneous Catalysis, Am. Chem. Soc. (1968).

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

"Ionizing Photolysis of Methane," C. A. Jensen and W. F. Libby, J. Chem. Phys., 49, 2831 (1968).

"Intramolecular Electrostatic Electron Traps," J. P. Mittal and W. F. Libby, Nature, 220, 1027 (1968).

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

"Nonplanar Cyclobutane Evidence for a Conformationally Controlled Classic Mechanism in the Deamination of Cis-and Trans-3-isopropylcyclobutylamine," I. Lillien and R. A. Doughty, J. Org. Chem., 33, 3841 (1968).

MacDonald, D. J.
University of Nevada
Reno, Nevada
AF-AFOSR-994-66

"Kinetics and Mechanism of Acid Hydrolysis of Ethylenebisbiguanide-Palladium(II)Ion," D. J. MacDonald, J. Inorg. Nucl. Chem., 30, 1971 (1968)

"Ionization Constants of Squaric Acid," D. J. MacDonald, J. Org. Chem., 33, 4559 (1968).

McDonald, R. L.
University of Hawaii
Honolulu, Hawaii
AF-AFOSR-983-65

"Solvation of Extracted Complex Metal Acids. IV. The $HAuCl_4$-Nitrobenzene System," S. L. Law and R. L. McDonald, J. Phys. Chem., 72, 1617 (1968).

Margerum, J. D.
Hughes Research Laboratories
Malibu, California
AF-49(638)01264

"Photopolymerization Studies. II. Imaging and Optical Fixing," J. D. Margerum, L. J. Miller and J. B. Rust, Photo. Sci. and Eng., 12, 177 (1968).

Murray, R. W.
University of North Carolina
Chapel Hill, North Carolina
AF-AFOSR-584-66

"Optically Transparent Thin Layer Electrodes Ninhydrin Reduction in an Infrared Transparent Cell," W. R. Heineman, J. N. Burnett and R. W. Murray, Analytical Chemistry, 40, 1974 (1968).

Pings, C. J.
California Institute of Technology
Pasadena, California
AF-49(638)01273

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

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

"Structure of Liquids. VIII. On X-Ray Diffraction Study of Liquid Mercury-Gallium Systems," R. W. Coputi, C. J. Pings and S. E. Rodriguez, Phys. and Chem. of Liquids, 1, 1 (1968).

Skell, P. S.
Pennsylvania State University
University Park, Pennsylvania
AF-AFOSR-1038-66

"Stereochemical Course of the Free-Radical Addition of Hydrogen Bromide to 1-Chloro-4-t-Butylcyclohexene," P. D. Readio and P. S. Skell, J. Org. Chem., 31, 753 (1966).

Steele, W. A.
Pennsylvania State University
University Park, Pennsylvania
AF-AFOSR-118-63

"Physical Properties of Fluid Methane and Deuteromethane. Theory," A. F. Grigor and W. A. Steele, J. Chem. Phys., 48, 1038 (1968).

"Physical Properties of Fluid Methane and Deuteromethane. Experimental," A. F. Grigor and W. A. Steele, J. Chem. Phys., 48, 1032 (1968).

Stengle, T. R.
University of Massachusetts
Amherst, Massachusetts
AF-AFOSR-212-65

"Preferential Solvation of Co$^{++}$ and Ni$^{++}$ Ions in Mixed Solvents. N.M.R. Methods," L. S. Frankel, T. R. Stengle and C. H. Langford, Canadian J. of Chem., 46, 3183 (1968).

Tobolsky, A. V.
Princeton University
Princeton, New Jersey
AF-49(638)00974

"The Dissociation Energy of the Tetrasulfide Linkage," I. Kende, T. L. Pickering and A. V. Tobolsky, J. Am. Chem. Soc., 87, 5582 (1965).

DIRECTORATE OF CHEMICAL SCIENCES
AFOSR ARLINGTON, VA.
RESEARCH EFFORTS
As of 1 July 1969
(Alphabetical by Principal Investigator)

| | |
|---|---|
| Physical Adsorption of Vapors<br>W4 (870) 60/1097-66 | Arthur W. Adamson<br>Department of Chemistry<br>University of Southern Calif.<br>Los Angeles, California |
| Chemical Electronic Structure Theory<br>B4 (969) 39/1625 | Leland C. Allen<br>Department of Chemistry<br>Princeton University<br>Princeton, New Jersey |
| Studies on the Kinetics and Mechanism of Electrode Processes in Molten Salt Media<br>W1 (570) 38/69-1780 | A. J. Arvia and<br>J. J. Podesta<br>Department of Chemistry<br>La Plata University<br>Buenos Aires, Argentina |
| Kinetic Spectroscopy of Chemically Active Systems<br>E4 (170) 60/1703 | Edward J. Bair<br>Department of Chemistry<br>Indiana University<br>Bloomington, Indiana |
| Chemiluminescence and Chemionization in Flames<br>B1 (1070) 38/70-1872 | Kyle D. Bayes<br>Department of Chemistry<br>University of California<br>Los Angeles, California |
| Microwave Spectroscopy of Boron Compounds<br>R5 (1070) 37/67-0849B | Robert A. Beaudet<br>Department of Chemistry<br>University of Southern Calif.<br>Los Angeles, California |
| Electrolytic Reduction of Organic Compounds<br>W4 (1269) 62/67-0822A | Robert A. Benkeser<br>Department of Chemistry<br>Purdue University<br>Lafayette, Indiana |
| Chemistry of Strained Olefins<br>M4 (969) 62/68-1358 | Jerome A. Berson<br>Department of Chemistry<br>University of Wisconsin<br>Madison, Wisconsin |
| Some Thermochemical Studies by Mass Spectrometry<br>R4 (869) 10/68-1356 | D. R. Bidinosti<br>Department of Chemistry<br>University of Western Ontario<br>London, Ontario, Canada |

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|---|---|
| Theoretical Studies on the Structure of Inorganic and Organometallic Compounds<br>M5 (871) 39/70-1862 | J. E. Bloor<br>Department of Chemistry<br>University of Tennessee<br>Knoxville, Tennessee |
| The Solvolytic Reactivity of Pi-Complexed Compounds<br>M4 (170) 62/67-0991A | Robert S. Bly, Jr.<br>Department of Chemistry<br>University of South Carolina<br>Columbia, South Carolina |
| Theoretical and Experimental Analysis of Electron Scattering from Atoms and Molecules<br>B4 (1169) 37/1681 | Russell A. Bonham<br>Department of Chemistry<br>Indiana University<br>Bloomington, Indiana |
| Nucleophilic Displacements by Organo-Phosphorus Compounds<br>R5 (270) 62/67-117C | Irving J. Borowitz<br>Department of Chemistry<br>Yeshiva University<br>New York, New York |
| Studies of Liquid Crystals as Related to Electro-Optical and Other Devices<br>E3 (870) 37/0103 | Glenn H. Brown<br>Department of Chemistry<br>Kent State University<br>Kent, Ohio |
| Detector Research Using Liquid Crystals<br>E4 (872) 7921/0021 | |
| Second International Liquid Crystal Conference<br>W2 (869) 60/68-1345 | |
| Electrochemical Studies Using the Rotating Ring Disk Electrode<br>W1 (770) 36/70-1832 | Stanley Bruckenstein<br>Department of Chemistry<br>State University of New York<br>Buffalo, New York |
| Studies in Ring Expansion<br>M7 (1070) 62/67-13 | George L. Buchanan<br>Department of Chemistry<br>University of Glasgow<br>Glasgow, Scotland |
| Kinetics of Atomic Association Reactions Using Flash Photolysis Over a Wide Temperature Range<br>R6 (170) 38/69-1695 A | George Burns<br>Department of Chemistry<br>University of Toronto<br>Toronto, Canada |
| Density of Cryogenic Liquid Mixtures<br>W4 (1269) 37/66-1020C | Frank B. Canfield<br>Department of Chemistry<br>University of Oklahoma<br>Norman, Oklahoma |
| Investigations of Energy Transformation in Luminescent Materials<br>R3 (970) 38/68-1342B | Glenn A. Crosby<br>Department of Chemistry<br>Washington State University<br>Pullman, Washington |

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|---|---|
| Interaction of Molecules with Solid Surfaces<br>B4 (370) 60/68-1388A | A. D. Crowell<br>Department of Chemistry<br>University of Vermont<br>Burlington, Vermont |
| The Single Electrode Potential and the Electrochemistry of the Hydrated Electron<br>W4 (771) 36/68-1344A | Robert deLevie<br>Department of Chemistry<br>Georgetown University<br>Washington, D. C. |
| Organometallic Electrochemistry<br>E2 (1070) 36/69-1694 | Raymond E. Dessy<br>Department of Chemistry<br>Virginia Polytechnic Institute<br>Blacksburg, Virginia |
| Organic Chemical Physics<br>M4 (1269) 39/67-1050B | Michael J.S. Dewar<br>Department of Chemistry<br>University of Texas<br>Austin, Texas |
| Use of Mossbauer Effect in Chemistry<br>E4 (771) 36/67-1236B | James F. Duncan<br>Department of Chemistry<br>Victoria University of Wellington<br>Wellington, New Zealand |
| Double Optical Resonance Spectra of Organic and Inorganic Molecules<br>E2 (171) 37/69-1715 | Thomas M. Dunn<br>Department of Chemistry<br>University of Michigan<br>Ann Arbor, Michigan |
| Reactions of Metallic Ions<br>E4 (1270) 38/1225-67 | Joseph E. Earley<br>Department of Chemistry<br>Georgetown University<br>Washington, D. C. |
| Isotope Study of the Decomposition of Inorganic Peroxides<br>B4 (1069) 10/68-1439 | John O. Edwards<br>Department of Chemistry<br>Brown University<br>Providence, Rhode Island |
| The Chemistry of Particles with Vicinal Non-Bonded Electron Pairs<br>B1 (870) 40/70-1839 | |
| Chemical Dynamics on Crystal Surfaces<br>R2 (970) 38/69-1671A | Gert Ehrlich<br>Coordinated Science Laboratory<br>University of Illinois<br>Urbana, Illinois |
| Relaxation Method Rate Studies<br>R1 (1269) 36/69-1717C | Edward M. Eyring<br>Department of Chemistry<br>University of Utah<br>Salt Lake City, Utah |
| Research on Inorganic Chemical Nomenclature<br>W5 (270) 10/65-0890D | W. Conrad Fernelius<br>National Academy of Sciences<br>Washington, D. C. |

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|---|---|
| High Resolution Raman Spectroscopy<br>E4 (170) 36/67-1092A | William H. Fletcher<br>Department of Chemistry<br>University of Tennessee<br>Knoxville, Tennessee |
| Macromolecules<br>R2 (1070) 37/0058 | Paul J. Flory<br>Department of Chemistry<br>Stanford University<br>Stanford, California |
| Inorganic Diradicals: Carbenoids<br>M2 (1269) 40/0005 | W. B. Fox<br>Inorganic Research<br>Allied Chemical Corporation<br>Morristown, New Jersey |
| Inorganic N.M.R. Spectroscopy<br>E4 (370) 10/68-1567 | R. J. Gillespie<br>Department of Chemistry<br>McMaster University<br>Hamilton, Ontario, Canada |
| X-Ray Adsorption-Edge Fine-Structure Spectrometry of Glass and Glass-Crystal Materials<br>R4 (1269) 37/1670 | G. L. Glen<br>General Research Division<br>Owens-Illinois Technical Center<br>Toledo, Ohio |
| Stereochemical Aspects of Ionization Processes<br>M5 (670) 62/67-847A | Harlan L. Goering<br>Department of Chemistry<br>University of Wisconsin<br>Madison, Wisconsin |
| Photochemically Generated Valence Tautomers<br>B5 (969) 62/67-0837A | Theodore D. Goldfarb and<br>Robert S. Boikess<br>Department of Chemistry<br>State University of New York<br>Stony Brook, L.I., New York |
| X-Ray Crystallographic Methods<br>R4 (270) 37/69-1769 | J. Zanos Gougoutas<br>Department of Chemistry<br>Harvard University<br>Cambridge, Massachusetts |
| Chemistry of Decaborane<br>R5 (1270) 40/910 | Norman N. Greenwood<br>Department of Chemistry<br>King's College<br>University of Newcastle<br>Newcastle-upon-Tyne, England |
| Inorganic Applications of Nuclear Quadrupole Resonance Spectroscopy<br>R4 (169) 10/859-67 | Terry E. Haas<br>Department of Chemistry<br>Tufts University<br>Medford, Massachusetts |
| Gordon Research Conference on Inorganic Chemistry<br>E2 (171) 39/69-1721 | Jack Halpern<br>Gordon Research Conferences<br>University of Rhode Island<br>Kingston, Rhode Island |

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| Transfer of Excitation in Solution<br>B5 (1069) 38/1479 | George S. Hammond<br>Department of Chemistry<br>California Institute of Technology<br>Pasadena, California |
| Kinetic Spectroscopy in the Infrared<br>R4 (769) 36/66-0976C | Robert M. Hexter<br>Clifford W. Hand<br>Carnegie-Mellon University<br>Pittsburgh, Pennsylvania |
| Bibliographic File of Abstracts on Photographic Science<br>W4 (770) 36/70-1837 | Thomas Hill<br>Rochester Institute of Technology<br>69 Plymouth Avenue South<br>Rochester, New York |
| Spectroscopic Studies of Chemical Reactions in the Solid State<br>E5 (1269) 36/67-0907C | I. C. Hisatsune<br>Department of Chemistry<br>Pennsylvania State University<br>University Park, Pennsylvania |
| Inorganic Structure and Spectra<br>R6 (869) 37/1492 | William D. Horrocks, Jr.<br>Department of Chemistry<br>Princeton University<br>Princeton, New Jersey |
| Reaction of Organometallic Intermediates<br>M2 (1269) 62/68-1518 | Herbert O. House<br>Department of Chemistry<br>Massachusetts Institute of Tech.<br>Cambridge, Massachusetts |
| The Nature of Non-Stoichiometric Solids: Structure, Texture, Thermodynamic and Magnetic Properties<br>E1 (870) 37/69-1806 | Bruce G. Hyde<br>Department of Physical Chemistry<br>University of Western Australia<br>Nedlands, W.A., Australia |
| Solid-Non-Stoichiometric Oxide Phases of the Inner and Outer Transition Metals<br>E4 (1269) 60/67-0853A | |
| Far Infrared Studies of the Hydrogen Bond<br>E4.5 (1069) 36/69-1621 | Robert Jakobsen<br>Organic Chemistry Division<br>Battelle Memorial Institute<br>Columbus, Ohio |
| ESR Thermal Decomposition Studies of Nitroaromatic Compounds and Inorganic Salts<br>M4 (870) 40/68-1554A | Edward G. Janzen<br>Department of Chemistry<br>University of Georgia<br>Athens, Georgia |
| The Mechanisms of Substitution Reactions of Niobium Compounds<br>B3 (970) 40/68-1355B | Ronald C. Johnson<br>Department of Chemistry<br>Emory University<br>Atlanta, Georgia |
| The Solution Chemistry of Polyhedral Boron Hydride Ions<br>R5.5 (370) 37/69-1665 | Alexander Kaczmarczyk<br>Department of Chemistry<br>Tufts University<br>Medford, Massachusetts |

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|---|---|
| Calorimetric Studies of Polymers<br>B3 (1070) 37/68-1434B | Frank E. Karasz<br>Polymer Science and Engineering<br>University of Massachusetts<br>Amherst, Massachusetts |
| Effects of High Pressure on Materials: Crystal Chemistry Studies<br>B3 (770) 37/0047 | J. S. Kasper<br>Physical Chemistry Laboratory<br>Research and Development Center<br>General Electric<br>Schenectady, New York |
| Coordination Compounds of the Transition Metals<br>E3 (1269) 40/68-1435A | R. Bruce King<br>Department of Chemistry<br>University of Georgia<br>Athens, Georgia |
| Photo-Induced Redox Reactions<br>B5 (1070) 10/70-1874 | Jay K. Kochi<br>Department of Chemistry<br>Indiana University Foundation<br>Bloomington, Indiana |
| Acid-Base Equilibria and Titrations and Electrochemical Equilibria in Acetonitrile<br>W4 (970) 36/67-1223B | I. M. Kolthoff<br>Department of Chemistry<br>University of Minnesota<br>Minneapolis, Minnesota |
| Electrochemistry of Solids<br>W4 (969) 37/68-1405A | Ferdinand A. Kroger<br>Department of Chemistry<br>University of Southern California<br>Los Angeles, California |
| Vapor Phase Calorimetry<br>W5 (869) 62/67-0810A | John R. Lacher and<br>Joseph D. Park<br>Department of Chemistry<br>University of Colorado<br>Boulder, Colorado |
| Mass Spectrometric, Thermochemical and Related Studies on Series of Inorganic Compounds<br>R4 (970) 38/0005 | Michael F. Lappert<br>Department of Chemistry<br>University of Sussex<br>Falmer, Brighton<br>Sussex, England |
| The AFOSR Program for Space Chemistry at UCLA<br>W3 (1169) 38/67-1255B | Willard F. Libby<br>Department of Chemistry<br>University of California<br>Los Angeles, California |
| Study of $N_2$ A-Triplet-Sigma State Generated by 1849 A Mercury Photosensitization<br>B4.5 (1169) 60/67-765A | Norman N. Lichtin and<br>Morton Z. Hoffman<br>Department of Chemistry<br>Boston University<br>Boston, Massachusetts |

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|---|---|
| NMR and ESR Studies of Solvation and Complex Formation<br>E3 (1170) 60/67-24 | Zeev Luz<br>Department of Chemistry<br>Weizmann Institute of Science<br>Rehovoth, Israel |
| Charge and Energy Transfer in Organic Systems<br>E4 (570) 60/68-1561 | Lawrence E. Lyons<br>Department of Chemistry<br>University of Queensland<br>St. Lucia, Brisbane<br>Australia |
| High Pressure (3-5 Kb.) Inorganic and Organometallic Syntheses<br>R4.5 (869) 10/1519 | Alan G. MacDiarmid<br>Department of Chemistry<br>University of Pennsylvania<br>Philadelphia, Pennsylvania |
| Stable Silicon Compounds<br>R1 (870) 37/70-1836 | |
| Structural Relaxation in Molten Glasses<br>R3 (870) 37/68-1376B | Pedro B. Macedo<br>Department of Chemistry<br>Catholic University of Americ<br>Washington, D. C. |
| Viscosity and Electrical Conductivity of Glasses at Constant Volume<br>R 2 (870) 37/ 70-1856 | John D. Mackenzie<br>Department of Chemistry<br>University of California<br>Los Angeles, California |
| Defect States and Structure of Oxide Glasses<br>R4 (1169) 37/67-0974A | John H. Mackey, Jr.<br>Carnegie-Mellon University<br>Pittsburgh, Pennsylvania |
| Plasma Pinch Flash Photolysis<br>B4 (869) 60/67-980A | Gilbert J. Mains<br>Department of Chemistry<br>University of Detroit<br>Detroit, Michigan |
| Investigation of Photochemistry Related to Polymerization<br>R2 (1269) 40/0043 | J. David Margerum<br>Photochemistry Section<br>Hughes Research Laboratories<br>Malibu, California |
| Study of Kinetic Methods of Chemical Analysis<br>E4 (1070) 36/67-1212B | Dale W. Margerum<br>Harry L. Pardue<br>Department of Chemistry<br>Purdue University<br>Lafayette, Indiana |
| Stable Aqueous Solutions of Gold<br>E2 (871) 40/70-1829 | Donald R. Martin<br>Department of Chemistry<br>The University of Texas<br>Arlington, Texas |
| The Solvent Extraction Behavior of Inorganic Complexes<br>E4.5 (370) 10/68-1387A | Ray L. McDonald<br>Department of Chemistry<br>University of Hawaii<br>Honolulu, Hawaii |

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|---|---|
| The Interaction of Molecular Beams with Atomically Clean Metal Single Crystals which are Chemically Reactive<br>B2 (969) 38/68-1409A | Robert P. Merrill<br>Department of Chemistry<br>University of California<br>Berkeley, California |
| Studies in Stereochemistry<br>M4 (870) 37/67-1188D | Kurt Mislow<br>Department of Chemistry<br>Princeton University<br>Princeton, New Jersey |
| Adsorption of Organic Molecules at Electrodes<br>W2 (1269) 60/68-1451A | David M. Mohilner<br>Department of Chemistry<br>Colorado State University<br>Fort Collins, Colorado |
| Fundamental Studies of Electrochemical Processes<br>E2 (970) 36/69-1625B | Royce W. Murray and<br>Charles N. Reilley<br>Department of Chemistry<br>University of North Carolina<br>Chapel Hill, North Carolina |
| Factors Affecting the Utilization of Research Investigations in Chemistry<br>B2 (1169) 10/0080 | D. O. Myatt<br>Department of Chemistry<br>Science Communication, Inc.<br>McLean, Virginia |
| Structure of Molten Salts and Glasses<br>E4 (170) 10/66-1086A | Norman H. Nachtrieb<br>Department of Chemistry<br>University of Chicago<br>Chicago, Illinois |
| Vibrational Relaxation in the Photochemical Primary Process<br>E2 (1270) 38/69-1682 | W. Albert Noyes, Jr.<br>Department of Chemistry<br>University of Texas<br>Austin, Texas |
| Molecular Interactions and Crystal Structures at Low Temperatures<br>W4 (170) 60/68-1549 | S. C. Nyburg<br>Department of Chemistry<br>University of Toronto<br>Toronto, Canada |
| An Investigation of the Mechanism of the Reaction Between Boron Trifluoride and Nitrogen (III, IV, V) Oxides<br>E4 (570) 10/68-1556 | P. R. Ogle, Jr.<br>Department of Chemistry<br>Otterbein College<br>Westerville, Ohio |
| Vibrational Anharmonicity and Rotation-Vibration Interaction in Polyatomic Molecules<br>E4 (970) 39/67-0570C | John Overend<br>Department of Chemistry<br>University of Minnesota<br>Minneapolis, Minnesota |
| Chemistry of Radiation Protecting Agents<br>B5 (271) 60/68-1417A | John Packer<br>Department of Chemistry<br>University of Auckland<br>Auckland, New Zealand |

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|---|---|
| Photochemical Generation of<br>Divalent Carbon Derivatives<br>M4.5 (869) 62/67-1213A | Albert Padwa<br>Department of Chemistry<br>State University of New York<br>Buffalo, New York |
| Chemistry of Iodoperfluorocycloalkenes<br>M2 (1170) 40/69-1679 | Joseph D. Park<br>Department of Chemistry<br>University of Colorado<br>Boulder, Colorado |
| Kinetics of Ion-Complex Formation in<br>Mixtures of Fused Salts Studied by<br>Ultrasonic Absorption<br>R4 (970) 38/67-1185B | Sergio Petrucci<br>Department of Chemistry<br>Brooklyn Polytechnic Institute<br>Brooklyn, New York |
| Gas Phase Reaction of Atoms,<br>Radicals and Simple Molecules<br>B4 (271) 38/67-1265A | Leon F. Phillips<br>Department of Chemistry<br>University of Canterbury<br>Christchurch, New Zealand |
| Ultrarapid-scan Infrared<br>Spectroscopy<br>E4 (170) 60/68-1536 | George C. Pimentel<br>Department of Chemistry<br>University of California<br>Berkeley, California |
| Chemical Reactions in<br>Frozen Solutions<br>M4.5 (870) 62/66-1102B | Richard E. Pincock<br>Department of Chemistry<br>University of British Columbia<br>Vancouver, Canada |
| AFOSR Program for Research<br>on Liquid Structure<br>B3 (870) 37/68-1382B | C. J. Pings<br>Department of Chemical<br>Engineering<br>California Institute of Technology<br>Pasadena, California |
| Gordon Research Conference on the<br>Chemistry and Physics of Liquids<br>B1 (570) 39/69-1784 | |
| Heteropoly Compounds of<br>Group VB Elements<br>E4 (270) 10/66-1066A | Michael T. Pope<br>Department of Chemistry<br>Georgetown University<br>Washington, D. C. |
| Primary Photoprocesses in<br>Organic Materials<br>B2 (1069) 38/0010 | G. Porter<br>Department of Chemistry<br>Royal Institute of Great Britain<br>London W.1., England |
| Intermolecular Energy Transfer<br>B4 (969) 38/1633 | B. S. Rabinovitch<br>Department of Chemistry<br>University of Washington<br>Seattle, Washington |
| Intermolecular Vibrational Energy Transfer<br>B1 (970) 38/0012 | |

| | |
|---|---|
| Experimental and Theoretical<br>Studies of Matter and Radiation<br>and Their Interaction<br>B1 (1069) 39/69-1663 | Stuart A. Rice<br>Department of Chemistry<br>University of Chicago<br>Chicago, Illinois |
| High-Resolution Spectroscopy of<br>Small Molecules in the Gaseous State<br>E4 (170) 37/1644 | G. Wilse Robinson<br>Department of Chemistry<br>California Institute of Tech.<br>Pasadena, California |
| Photochemical Studies in<br>Atomic Chemistry<br>B2 (1269) 60/68-1493 | John W. Root<br>Department of Chemistry<br>University of California<br>Davis, California |
| Basic Studies of Liquid Crystals<br>Related to Electro-Optical and<br>Other Devices<br>E3 (570) 37/0102 | H. C. Scala<br>Chemical Technology<br>Westinghouse Research Labs<br>Pittsburgh, Pennsylvania |
| Lifetime Spectrometry<br>B4 (770) 38/68-1615A | Edward W. Schlag<br>Department of Chemistry<br>Northwestern University<br>Evanston, Illinois |
| Differential Electrical Double<br>Layer Capacities on Liquid and<br>Solid Electrodes<br>W4 (1269) 60/68-1452 | Gerhard M. Schmid<br>Department of Chemistry<br>University of Florida<br>Gainesville, Florida |
| Hot Atom Chemistry of Oxygen and<br>Nitrogen<br>B5 (1070) 38/70-1867 | Friedrich Schmidt-Bleek<br>Department of Chemistry<br>University of Tennessee<br>Knoxville, Tennessee |
| Organometallics as Reagents for the<br>Generation of Reactive Intermediates<br>M2 (1069) 40/68-1350A | Dietmar Seyferth<br>Department of Chemistry<br>Massachusetts Institute of Tech.<br>Cambridge, Massachusetts |
| Inelastic Collisions between<br>Molecular Systems, Neutral and/or Ionized<br>B4 (871) 39/68-1354A | Hyung Kyu Shin<br>Department of Chemistry<br>University of Nevada<br>Reno, Nevada |
| Ion-Radicals of Organic Sulfur<br>Selenium, Tellurium and Phosphorus<br>Compounds<br>M4 (969) 40/69-1635 | Henry J. Shine<br>Department of Chemistry<br>Texas Technological College<br>Lubbock, Texas |
| Ion Radical Chemistry<br>M1 (970) 40/70-1855 | |
| Quantum Chemistry Program Exchange<br>W6 (870) 39/67-0767A | Harrison Shull<br>Department of Chemistry<br>Indiana University<br>Bloomington, Indiana |

| | |
|---|---|
| Electronic Computer Calculations on Simple Diatomic and Polyatomic Molecules<br>E5 (870) 39/67-1242D | Harrison Shull and<br>Stanley A. Hagstrom<br>Department of Chemistry<br>Indiana University<br>Bloomington, Indiana |
| Atomic Chemistry<br>M3 (1169) 40/69-1702 | P. S. Skell<br>Department of Chemistry<br>Pennsylvania State University<br>University Park, Pennsylvania |
| Applications of Preferential Solvation Studies to Inorganic Reaction Mechanisms<br>M4 (971) 40/68-1384A | Thomas R. Stengle<br>Department of Chemistry<br>University of Massachusetts<br>Amherst, Massachusetts |
| Organometallic Chemistry<br>E5 (970) 40/0011 | F. G. A. Stone<br>Department of Chemistry<br>University of Bristol<br>Bristol, England |
| Quantum Organic Chemistry<br>M4 (370) 39/68-1364B | Andrew Streitwieser, Jr.<br>Department of Chemistry<br>University of California<br>Berkeley, California |
| Synchrotron Photoionization with Mass Spectrometric Detection<br>M2 (1070) 36/69-1725B | James W. Taylor<br>Department of Chemistry<br>University of Wisconsin<br>Madison, Wisconsin |
| Metallocene and Oxy Radical Chemistry<br>M2 (870) 40/69-1639A | T. G. Traylor<br>Department of Chemistry<br>University of California<br>La Jolla, California |
| Chemistry of Strained Ring Compounds<br>M4 (1269) 40/68-1381A | Nicholas J. Turro<br>Department of Chemistry<br>Columbia University<br>New York, New York |
| Kinetic Energy of Ionic Products from Electron and Ion-Molecule Reactions<br>W4 (370) 60/68-1380 | Eugene R. Weiner<br>Department of Chemistry<br>University of Denver<br>Denver, Colorado |
| Electron Paramagnetic Resonance of Matrix-Isolated Molecules<br>R2 (1070) 37/68-1588B | William Weltner, Jr.<br>Department of Chemistry<br>University of Florida<br>Gainesville, Florida |
| Transition Metal Ammine Complexes at High Pressures and Temperatures<br>E5 (870) 36/69-1620 | Wesley W. Wendlandt<br>Department of Chemistry<br>University of Houston<br>Houston, Texas |

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|---|---|
| Novel Organometallic Compounds<br>M4 (270) 40/69-1772 | Robert C. West<br>Department of Chemistry<br>University of Wisconsin<br>Madison, Wisconsin |
| Development of a Molecular Beam Accelerator<br>B5.5 (770) 36/70-1838 | Lennard Wharton<br>Department of Chemistry<br>University of Chicago<br>Chicago, Illinois |
| Electronic Structures of Molecules by Variational Methods and Correlation Corrections<br>B4 (1069) 39/68-1438A | Donald R. Whitman and<br>Douglas Carlson<br>Department of Chemistry<br>Case Western Reserve University<br>Cleveland, Ohio |
| Laser Photolysis and Spectroscopy in the Nanosecond Time Range<br>B2 (1070)38/0029 | Maurice W. Windsor<br>Chemical Sciences<br>TRW Systems<br>Redondo Beach, California |
| Flame Spectrometry and Gas Chromatographic Detectors<br>R6 (1069) 36/69-1685 | James D. Winefordner<br>Department of Chemistry<br>University of Florida<br>Gainesville, Florida |

# SRC INSTITUTION LISTING

July 1969

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J. J. Podesta

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Tufts University
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Utah, University
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Victoria University
J. F. Duncan

Virginia Polytechnic Inst.
Raymond E. Dessy

Washington University
B. S. Rabinovitch

Washington State U.
Glenn A. Crosby

Weizmann Inst. of Science
Zeev Luz

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Bruce G. Hyde

Western Ontario, U.
D. R. Bidinosti

Westinghouse Rsch.
H. C. Scala

Wisconsin, U.
Jerome A. Berson
Harlan L. Goering
James W. Taylor
Robert C. West

Yeshiva University
Irving J. Borowitz

# COMPLETED PROJECTS

## DIRECTORATE OF CHEMICAL SCIENCES

AFOSR ARLINGTON, VA.

## RESEARCH PROJECTS COMPLETED IN FY 1969

(Alphabetical by Principal Investigator)

| | |
|---|---|
| Multicharge Aromatic Ions<br>M4 (1068) 62/738-67 | Merle A. Battiste<br>Department of Chemistry<br>University of Florida<br>Gainesville, Florida |
| Study of The Light Emitted by Atomic Flames<br>B6 (968) 60/687-64 | Kyle D. Bayes<br>Department of Chemistry<br>University of California<br>Los Angeles, California |
| Photolytic and Pyrolytic Free Radicals<br>R4 (270) 10/1085-66 | A. S. Buchanan<br>Department of Chemistry<br>University of Melbourne<br>Parkville, N. 2, Melbourne<br>Australia |
| Sixth International Symposium on the Reactivity of Solids<br>B, H 1.5 (1068) 60/67-C-0078 | A. M. Bueche<br>Department of Chemistry<br>General Electric Company<br>Schenectady, New York |
| Heterogeneous Catalysis in Liquid Systems<br>E6 (968) 60/97-63 | Robert L. Burwell, Jr.<br>Department of Chemistry<br>Northwestern University<br>Evanston, Illinois |
| Synthesis of Triple Strand Polymers<br>M4 (669) 62/817-67 | George B. Butler<br>Department of Chemistry<br>University of Florida<br>Gainesville, Florida |
| The Gordon Research Conference on High Temperature Chemistry<br>B1 (469) 60/68-1522 | D. Cubicciotti<br>Gordon Research Conferences<br>University of Rhode Island<br>Kingston, Rhode Island |
| Reactions and Structures of Metal-Olefin Complexes and Related Substances<br>W4 (1268) 10/763-67 | John R. Doyle and<br>Norman C. Baenziger<br>Department of Chemistry<br>State University of Iowa<br>Iowa City, Iowa |
| Excited States of Uranium and Heavy Metals<br>E4 (169) 60/865-67 | Thomas Dunn<br>Department of Chemistry<br>University of Michigan<br>Ann Arbor, Michigan |
| Quantitative Conformational Analysis<br>M4 (669) 62/772-67 | Ernest L. Eliel<br>Department of Chemistry<br>University of Notre Dame<br>Notre Dame, Indiana |

| | |
|---|---|
| Laser-Temperature Jump Studies of Fast Reactions<br>R5 (1268) 10/68-1383 | Edward M. Eyring<br>Department of Chemistry<br>University of Utah<br>Salt Lake City, Utah |
| Molecular Structure of Carbanions and Kinetics of their Exchange Processes in Solution<br>W4.5 (968) 62/68-1441 | Gideon Fraenkel<br>Department of Chemistry<br>Ohio State University<br>Columbus, Ohio |
| Phosphorus Coordination Compounds<br>R4 (1068) 10/782-67 | Samuel O. Grim<br>Department of Chemistry<br>University of Maryland<br>College Park, Maryland |
| Chemical Characterization of Molecules Adsorbed on a Foreign Solid<br>B4 (1068) 60/734-67 | Melvin C. Hobson, Jr.<br>Department of Chemistry<br>Virginia Institute of Scientific Research<br>Richmond, Virginia |
| Coordination, Ligand Reactivity, and Catalysis<br>W4.5 (1268) 60/630-66 | Mark M. Jones<br>Department of Chemistry<br>Vanderbilt University<br>Nashville, Tennessee |
| Upper Atmosphere Ion-Molecule Reactions<br>E5 (868) 60/1301 | Walter S. Koski<br>Department of Chemistry<br>Johns Hopkins University<br>Baltimore, Maryland |
| Viscous Flow and Compressibility of Molten Borates at High Pressure<br>R4 (968) 10/1460 | John D. Mackenzie<br>Department of Chemistry<br>Rensselaer Polytechnic Institute<br>Troy, New York |
| Chemistry of Organolithium Compounds and Acetylenes<br>M4 (169) 62/720-65 | James Mulvaney<br>Department of Chemistry<br>University of Arizona<br>Tucson, Arizona |
| Reactions of Molecules in Excited States with Paramagnetic Gases<br>W4 (1268) 60/778-67 | W. Albert Noyes, Jr.<br>Department of Chemistry<br>University of Texas<br>Austin, Texas |
| Electrochemistry of Transition Metal Ions in Acetonitrile<br>W4 (1168) 10/777-67 | John W. Olver<br>Department of Chemistry<br>University of Massachusetts<br>Amherst, Massachusetts |
| Theoretical and Experimental Studies in Chemical Physics<br>B4 (1068) 60/781-67 | Stuart A. Rice<br>Department of Chemistry<br>University of Chicago<br>Chicago, Illinois |

| | |
|---|---|
| Fifth International Congress of Photobiology<br>R1 (369) 62/68-1546 | Russell B. Stevens<br>National Academy of Sciences<br>Washington, D.C. |
| Polynuclear Hydroxo Complexes<br>R4 (968) 10/691-67 | R. Stuart Tobias<br>Department of Chemistry<br>University of Minnesota<br>Minneapolis, Minnesota |
| Sigma Pi Rearrangement<br>M4 (569) 62/824-67 | Minoru Tsutsui<br>Department of Chemistry<br>New York University<br>New York, New York |
| Surface States in Pure Palladium<br>B6 (768) 60/65-0114 | Richard W. Zuehlke<br>Department of Chemistry<br>Lawrence College<br>Appleton, Wisconsin |

COMPLETED PROJECT SUMMARY

1. TITLE: Multicharge Aromatic Ions

2. PRINCIPAL INVESTIGATOR: Dr. Merle A. Battiste,
Department of Chemistry
University of Florida
Gainesville, Florida

3. INCLUSIVE DATES: 1 November 1964 - 31 October 1968

4. GRANT NOS.: AF-AFOSR 738-65; AF-AFOSR 738-67

5. COSTS AND FY SOURCE: $27,160 FY65; $56,932 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. Brian Halton
Dr. Rolf Rehberg
Dr. John Haywood-Farmer
Dr. K. C. Srivastava

7. JUNIOR RESEARCH PERSONNEL: Thomas J. Barton
Michael E. Brennan
Michael E. Burns
Margaret W. Couch
Cynthia L. Deyrup
Henry J. Gisler, Jr.
Paul Mushak
John W. Nebzydoski
Joseph B. Williams

8. PUBLICATIONS:

"The Synthesis and Valence Isomerization of 1,2-Diphenylcyclobutene," M. A. Battiste and M. E. Burns, Tetrahedron Letters, 523 (1966).

"Synthesis and Solvolytic Reactivity of endo, anti-and endo, syn-8-Tricyclo 3.2.1.0$^{2,4}$ octane Derivatives. Extensive Homoconjugative Participation by a Cyclopropane Ring," M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, J. Am. Chem. Soc., <u>89</u>, 1954 (1967).

"Decarbonylation Studies in the endo- and exo-Tricyclo [3.2.1.0$^{2,4}$] - octen-8-one Series," B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, J. Am. Chem. Soc., <u>89</u>, 5964 (1967).

"The Copper-Catalyzed Reaction of Benznorbornadiene with Benzoyl Peroxide and <u>t</u>-Butyl Perbenzoate. Nuclear Magnetic Resonance Spectra of anti-7-Benznorbornadiene Derivatives," M. E. Brennan and M. A. Battiste, J. Org. Chem., <u>33</u>, 324 (1968).

"Synthesis and Relative Stabilities of the 1,2,3,4-Tetraphenyltropylium and Hexaphenyltropylium Cations," M. A. Battiste and T. J. Barton, Tetrahedron Letters, 2951 (1968).

"Mass Spectrometry of Carbonium Ion Salts: 3-Halogeno-1,2,3-triphenylcyclopropenes," M. A. Battiste and B. Halton, Chem. Comm. (London), 1368 (1968).

"The Reaction of 1,2,3-Triphenylcyclopropene with Palladium (II) Chloride. A Novel Ring-Opening Reaction in the Cyclopropene Series," Paul Mushak and M. A. Battiste, J. Organometal. Chem., in press.

"The Thermal and Base-Promoted Rearrangement of Heptaphenylcycloheptatrien-7-ol," M. A. Battiste and H. J. Gisler, Jr., to be submitted to Tetrahedron Letters.

"Ionogenic Hexaphenyltropylium Halides," M. A. Battiste and T. J. Barton, in preparation.

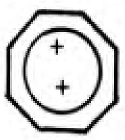
"Restricted Ring Inversion in Some Phenyl Substituted Tropilidenes," M. A. Battiste, H. J. Gisler, Jr., and T. J. Barton, in preparation.

"Multicharge Aromatic Ions," M. A. Battiste, Final Report.

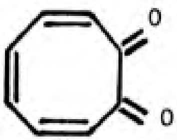
## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The original objectives of this research program were the synthesis and study of multicharged, fully conjugated carbocyclic ions possessing closed-shell ground states but they were later extended to include aromatic and homoaromatic monovalent ions of current interest. Of particular interest were the monovalent and divalent ions and related derivatives in the cyclobutenyl, cyclooctatrienyl and cycloheptatrienyl systems.

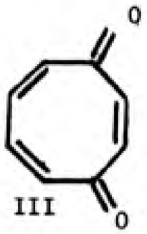
Synthetic routes to the cyclooctatrienyl dication (I) and the related 1,2- and 1,4-quinones II and III were explored, but without much success. The dienophilic properties of 1,2-dialkylcyclobutenes were examined in this work and found to be vastly inferior in reactivity to their cyclopropene counterparts. A convenient synthetic route to 1,2-diphenylcyclobutene was developed and a thorough kinetic investigation of its valence isomerization to 2,3-diphenyl-1,3-butadiene carried out in several solvents.



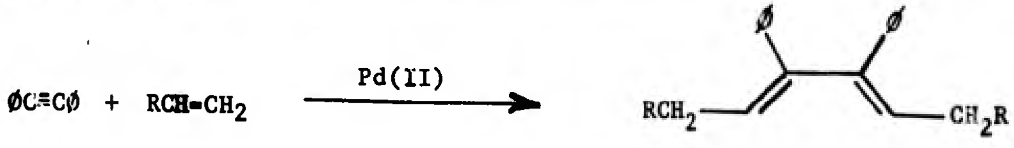
I



II



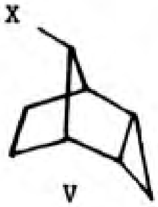
In an attempt to develop a more convenient synthetic entry into the cyclooctatriene series a study of transition metal-catalyzed cycloaddition reactions of olefins with acetylenes was initiated. The palladium (II) promoted reactions of olefins with diphenylacetylene follows the reaction course shown below. The scope and mechanism of this reaction is still under investigation. In the course of these studies a novel metal-promoted ring-opening reaction of triphenylcyclopropene was uncovered.



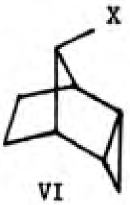
R=H, $CH_3$, $CH_3CH_2$, Ph

Paralleling these efforts with the multivalent ions, investigations into the chemistry and properties of monovalent cations in the arylcycloheptatriene series have continued. The question of intramolecular charge-transfer between an acceptor tropylium ring and an attached aryl group donor has been partially answered by examination of the solvent sensitivity of the long-wavelength maxima of a series of substituted phenyltropylium ions. A PPP-SCF-LCAO-MO calculation supports the conclusion that the lower lying excited states of the phenyltropylium ion should have appreciable charge-transfer character. Utilizing this novel feature of aryltropylium ions we have examined the extent of transannular interaction between the formally non-conjugated benzene rings in 2-triptycyltropylium perchlorate (IV). Comparison of the electronic spectra of IV with that of appropriate model compounds indicate that triptycene is a better electron donor than would be anticipated on the basis of non-interacting benzene rings. Several new polyphenylcycloheptatrienes and their corresponding cations have been prepared and their properties investigated.

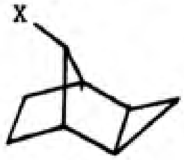
The availability of endo-8-tricyclo$[3.2.1.0^{2,4}]$ octenones from the Diels-Alder reaction of appropriate cyclopropene and cyclopentadienone derivatives afforded the opportunity to study the stereoelectronic requirements of cyclopropyl participation in the thermal decarbonylation of bridged ketones as well as in the solvolyses of syn and anti derivatives V and VI. Among the saturated or olefinic derivatives of the 7-norbornyl skeleton the endo-anti isomer V exhibited an extreme of solvolytic reactivity whereas VI, and the exo-anti isomer VII were



V

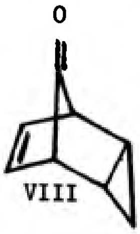


VI

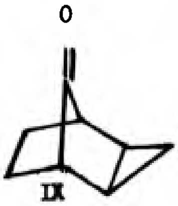


VII

only slightly more or less reactive than 7-norbornyl itself. Similarly endo ketone VIII undergoes decarbonylation some $10^6$ times faster than the corresponding exo ketone IX.



VIII



IX

These data vividly confirm that cyclopropane interacts with developing $\pi$ -or carbonium ion centers only via its "edge" but not with its "face." Preliminary evidence for weaker "edge" participation by cyclobutane was also obtained.

Dr. A. J. Matuszko

## COMPLETED PROJECT SUMMARY

1. TITLE: Light Emitted by Atomic Flames
   (Flames: Kinetics and Spectroscopy)

2. PRINCIPAL INVESTIGATOR: Dr. Kyle D. Bayes
   Department of Chemistry
   University of California, Los Angeles
   Los Angeles, California

3. INCLUSIVE DATES: 1 October 1961 - 31 September 1968

4 GRANT NOS.: AF-AFOSR-0062-62; AF-AFOSR-0687-64

5. COST AND FY SOURCE: $43,765 FY62; $44,721 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. Karl Heinz Becker
   Dr. Robert E. W. Jansson
   Dr. Kenneth A. Mantei
   Dr. David G. Williamson

7. JUNIOR RESEARCH PERSONNEL: Tom G. Slanger

8. PUBLICATIONS:

"The Origin of the Light Emission in the Atomic Hydrogen-Acetylene Flame," K. D. Bayes and R. E. W. Jansson, Proc. Royal Society A282, 275 (1964).

"The CO Emission from Acetylene-Oxygen Flames," K. H. Becker and K. D. Bayes, J. Chem. Phys. 45, 396 (1966).

"A Study of the Chemiluminescence from Oxygen Atom-Hydrazine Flames," K. H. Becker and K. D. Bayes, J. Phys. Chem. 71, 371 (1967).

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

"Reactions of Oxygen Atoms with Acetylene," D. G. Williamson and K. D. Bayes, J. Phys. Chem., to be published.

"Predissociation in $HBr^+$," M. Haugh and K. D. Bayes, in preparation.

"Rotational and Vibrational Excitation During Charge Exchange," M. Haugh and K. D. Bayes, in preparation.

"Flames: Kinetics and Spectroscopy," Final Technical Report, AFOSR 68-2199.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Several chemiluminescent reactions have been established by the previous seven years work. By far the most important of these is $O + C_2O$. This reaction is responsible for emission by the CO molecule which is observed in most organic-oxygen flames. It is one of the most exothermic reactions known, giving up to 9 eV (200 kcal/mole) concentrated in one molecule. Subsequent work in our laboratory and elsewhere has supported this proposed reaction. The reaction is of theoretical interest because although it is mechanically very simple, at least five and possibly all eight of the energetically allowed electronic states of CO are formed. This is an extreme example of the scrambling of electronic surfaces during a chemical reaction. Additional spectroscopic work is being done on this reaction to learn as much as possible about the quantum states of the excited CO molecules and about the potential energy surfaces which connect the reactants with products.

The mechanism of energy transfer has been established as the source of chemiluminescence in at least one flame; we suspect that it is important for most flames. The formation of metastable CO in hydrocarbon flames has been demonstrated, and this has sufficient energy to excite the other radicals which are observed (OH, CH, and $C_2$). Transfer of this energy between metastable CO and NO has been demonstrated. A curious difference was observed in the energy transfer to NO by metastable $N_2$, which forms $NO(A^2\Sigma)$, and by metastable CO, which forms predominately $NO(B^2\Pi)$. This difference is not due to differences in energy or Franck-Condon factors, but seems to be the operation of a new selection rule. Future work will explore the possibility of explaining the remaining chemiluminescence from hydrocarbon flames in terms of energy transfer.

A technique has been developed to study the transition state involved in charge exchange between atomic ions and molecules. By studying reactions which form electronically excited molecule ions, and observing the light emitted before collisions take place, we have determined the quantum numbers for rotation and vibration which are induced by the single collision. Large changes in quantum numbers indicate that a strong chemical bond is formed during the collision. These reactions have an advantage over molecular beam studies of neutral particals in that both vibrational and rotational excitation can be studied at the same time. Very efficient rotational relaxation has been observed due to the long range ion-dipole interaction. The formation in a single collision of a molecular ion that is rotationally very hot, but still maintaining a Boltzmann distribution, is a process that requires a theoretical analysis.

Dr. Donald L. Ball

# COMPLETED PROJECT SUMMARY

1. TITLE: Photolytic and Pyrolytic Free Radicals

2. PRINCIPAL INVESTIGATOR: Dr. A. S. Buchanan
Department of Chemistry
University of Melbourne
Melbourne, Australia

3. INCLUSIVE DATES: 1 March 1966 - 31 August 1968

4. GRANT NO.: AF-AFOSR-1085-66

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

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: P. J. Thistlethwaite

8. PUBLICATIONS:

"Photolytic and Pyrolytic Free Radicals," Final Technical Report, AFOSR-69-0925 PR.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective has been to devise means of observing reaction mechanisms in gases and vapours at elevated temperatures, particularly with systems involving metals and metal halides. A flash photolysis system was constructed to permit observation of species with life-times in the microsecond range and in very low concentration (using multiple traversal techniques for the light beam). Spectrographic equipment covers the range from about 1200 Å to the red end of the visible region.

As a supplement to the spectrographic system, a mass spectrometric procedure was brought into use particularly to assist in identifying species in the elevated temperature metal halide systems. This consisted of a Knudsen - type cell operating up to about 800°C connected directly to a quadrupole mass-spectrometer. This equipment was used to identify the vapour phase species in hot $PbCl_2$ vapor both alone and in the presence of HCl gas and $O_2$.

Studies have shown that boron trichloride will react with oxygen as a photolytically induced process in which the boron trichloride is decomposed to yield the BCl or $BCl_2$ radicals which then react with oxygen. The ultimate product is $B_3O_3Cl_3$ (trichloroboroxole), which decays to a polymer of boron and oxygen with loss of molecular chlorine. On any reasonable mechanistic basis it seems likely that the monomeric species BOCl is an intermediate in the synthesis reaction and evidence was found for this molecule as a gas phase entity in the reaction. Efforts are being directed towards obtaining the electronic absorption spectrum of BOCl and of observing the formation of the trimer $B_3O_3Cl_3$. (Ref. Knowles and Buchanan, Inorg. Chem. 4, 1799 (1965).)

D. W. Elliott

## COMPLETED PROJECT SUMMARY

1. TITLE: Heterogeneous Catalysis in Liquid Systems

2. PRINCIPAL INVESTIGATOR: Dr. Robert L. Burwell
Department of Chemistry
Northwestern University
Evanston, Illinois

3. INCLUSIVE DATES: 1 October 1962 - 30 September 1968

4. GRANT NOS.: AF-AFOSR 97-63; AF-49(638)-935; AF-18(603)-132

5. COSTS AND FY SOURCE: $27,372 FY63; $28,000 FY61; $28,000 FY57

6. SENIOR RESEARCH PERSONNEL: Dr. Andrew Schaefer

7. JUNIOR RESEARCH PERSONNEL: John F. Read
Kathleen C. Taylor
Gary L. Juller

8. PUBLICATIONS:

"Chemisorptive and Catalytic Behavior of Chromina," R. L. Burwell, Jr., G. L. Haller, K. C. Taylor and J. F. Read, Advances in Catalysis, 20, in press.

"Adsorptive and Catalytic Properties of Chromina," R. L. Burwell, Jr., J. F. Read, K. C. Taylor and G. L. Haller, Z. Physik. Chem., N.F. 64, 18 (1969).

"The Texture of Chromium Oxide Catalysts," R. L. Burwell, Jr., K. C. Taylor, and G. L. Haller, J. Phys. Chem., 71, 4580 (1967).

"Reactions between Deuterium and Benzene on Chromium Oxide Gel," R. L. Burwell, Jr., and C. J. Loner. Proceedings Third International Congress on Catalysis, Vol. II, p 804, North-Holland Publishing Company, (1965).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Most of the work in this project was concerned with the nature of active sites on chromia catalysts, the nature of their formation during activation, and the nature of the interaction of the sites with gases in processes leading either to chemisorption or to reaction (isotopic exchange between deuterium and benzene toluene, hydrogenation and isomerization of olefins.) When chromia hydrous gel is heated in a vacuum or flowing helium loss of water occurs and several percent of this leads to the formation of coordinatively unsaturated surface ions (cus) of chromium III and oxygen-2 minus. The concentration of chromium III (cus) as a function of temperature has been measured by measurement of the chemisorption of carbon monoxide, irreversible at minus 78 degrees. Adsorption of oxygen under the same conditions gives nearly the same result.

Activity for the hydrogenation of olefins rises much more steeply with temperature than does chemisorptive capacity. Clearly, chromium III (cus) generated at higher temperatures is in configurations which give higher catalytic activity. Catalytic activity for exchange between benzene and deuterium activates with a different dependence upon temperature than does that for olefin hydrogenation. That the two processes proceed on different sites is supported by results of competitive experiments, neither olefin nor benzene interferes with the reactions of the other.

We conclude that hydrogen is absorbed at the pair sites by heterolytic dissociative adsorption. Alkanes similarly undergo heterolytic dissociative adsorption although much less readily. Benzene undergoes this process more readily than alkanes.

D. W. Elliott

# COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis of Triple Strand Polymers

2. PRINCIPAL INVESTIGATOR: Dr. George Butler
Department of Chemistry
University of Florida
Gainesville, Florida

3. INCLUSIVE DATES: 1 January 1965 - 30 June 1969

4. GRANT NOS.: AFOSR-817-65; AFOSR-817-67

5. COSTS AND FY SOURCE: $57,504 FY65; $67,080 FY67

6. SENIOR RESEARCH PERSONNEL:
Dr. Jon Bacon
Dr. George C. Corfield
Dr. Raphael M. Ottenbrite
Dr. Tom McCall
Dr. Richard L. Dunn

7. JUNIOR RESEARCH PERSONNEL:
George H. Fisher
S. Richard Turner
James H. Riggsbee
Ken P. Keller

8. PUBLICATIONS:

"Cis-4a,5,8, 8a-Tetrahydro-6,7-di-(bromomethyl)-naphthoquinone From 2,3-Di-(bromomethyl)-1,3-butadiene," G. B. Butler and R. M. Ottenbrite, Tetrahedron Letters, <u>48</u>, 4873 (1967).

"Cis and Trans-4a-Chlorodecalin-1,5-dione and $\Delta^{9,10}$-Octalin-1,5-dione, G. B. Butler and R. L. Dunn, submitted to Tetrahedron Letters.

"Synthesis of 11-Cyanotricyclo $[4.4.2.0^{1,6}]$dodeca-3,8-diene and Tricyclo-$[4.4.3.0^{1,6}]$trideca-s,8-diene-12-one," G. B. Butler and R. L. Dunn, submitted to Tetrahedron Letters.

"Synthesis of 3,4-Dimethyltricyclo$[4.4.4.0^{1,6}]$ tetradeca-3,8,12-triene-7,10,11,14-tetraone and 6,11-Dihydroxy-1,4,4a,7,10,12a-hexahydronaphthacene-5,12-quinone," G. B. Butler and R. L. Dunn, submitted to J. of Organic Chem.

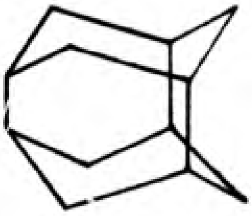
"The Preparation and Cyclopolymerization of Cis and Trans-1,3,5-tri-isocyanato-cyclohexane," G. B. Butler and G. C. Corfield, to be submitted to J. of Macromolecular Chemistry.

"Synthesis of Triple Strand Polymers," Final Technical Report.

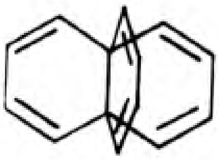
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of the research program were:

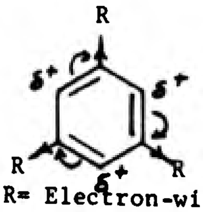
1. To synthesize the following model compound, the structure of which represents the dimeric unit that would result from a hypothetical triply-initiated polymerization of benzene:



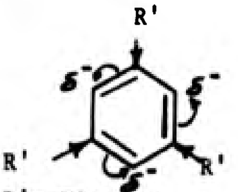
2. To synthesize the following compound which represents the simplest monomer which could conceivably be triply-initiated to produce a triple stand polymer by a 1,4-addition polymerization:



3. To investigate methods of polymerizing or copolymerizing aromatic compounds of the following type to triple strand polymers:



R= Electron-withdrawing group



R'= Electron - releasing group

Even though the original objectives of synthesizing triple strand polymers were not accomplished, a wide variety of new and unusual compounds were synthesized and characterized. A significant contribution was made to the theory of decarboxylation of carboxylic acids in that the reaction is subject to steric control. Both <u>cis</u>- and <u>trans</u>- 1,3,5-tri-isocyanatocyclohexane were synthesized; these compounds are functionally capable of cyclopolymerizing to linear polymers containing bicyclic and tricyclic units. Structural studies on the polymers obtained indicate that predominantly bicyclic structures were obtained. Before publication of many of the intermediate compounds synthesized by this group, three groups of workers at other locations published papers which include essentially all of these structures.

Although no compounds functionally capable of undergoing polymerization to triple strand polymers were obtained, one compound which is functionally capable of undergoing polymerization to yield a double strand polymer was obtained. All attempts to convert this compound to a polymer were unsuccessful. During the course of this work, contributions were made to the theory of intramolecular cyclizations and to use of charge-transfer complexes as intermediates in chemical reactions.

Dr. A. J. Matuszko

## COMPLETED PROJECT SUMMARY

1. TITLE: Reactions and Structures of Metal-Olefin Complexes and Related Substances

2. PRINCIPAL INVESTIGATORS: Dr. J. R. Doyle and
Dr. N. C. Baenziger
Department of Chemistry
State University of Iowa
Iowa City, Iowa

3. INCLUSIVE DATES: 1 January 1965 - 30 June 1969

4. GRANT NOS.: AF-AFOSR-763-65; AF-AFOSR-763-67

5. COSTS AND FY SOURCE: \$35,255 FY65; \$42,044 FY67

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: W. Partenheimer
C. V. Goebel
W. Duax
C. Hunt
T. D. Simpson
B. Storhoff
F. Schulz
E. Rowlee
E. Braulin
H. Streiter
H. Lewis
F. Swift
D. Drew
M. M. Howell
P. O'Donnell

8. PUBLICATIONS:

"Synthesis of Cyclopentadienide Derivatives," C. C. Hunt and J. R. Doyle, Inor. Nucl. Chem. Letters, 2, 283 (1966).

"Metal-Olefin Compounds. VIII. The Crystal Structure of a Norbornadiene-Silver Nitrate Complex, $C_7H_8 \cdot 2AgNO_3$," N. C. Baenziger, H. L. Haight, R. Alexander and J. R. Doyle, Inorg. Chem., 5, 1399 (1966).

"The Crystal Structure and Molecular Motion of Solid Carbon Disulfide," N. C. Baenziger and W. Duax, accepted for publication in J. Chem. Phys.

"Metal-Olefin Compounds. IX. The Reaction of Cyclooctatetraene with Dichlorobis (benzonitrile) - palladium (II)," J. R. Doyle, N. C. Baenziger, W. Partenheimer and Carol Valley Goebel, in preparation.

"Metal-Olefin Compounds. X. Crystal Structures of Two Complexes of Cyclooctatetraene and Palladous Chloride," N. C. Baenziger, J. R. Doyle and Carol Valley Goebel, accepted for publication in Inorg. Chem.

"Metal-Olefin Compounds. XI. Preparation and Proton Magnetic Resonance Spectra of Some Palladium and Platinum Diolefin Compounds," W. Partenheimer and J. R. Doyle, accepted for publication in Inorg. Chem.

"Metal-Olefin Compounds. XII. Solvent Effects on Proton Magnetic Resonance Spectra of Some Diolefin Compounds of Palladium and Platinum. Solvolysis in Dimethylsulfoxide," W. Partenheimer and J. R. Doyle, accepted for publication in Inorg. Chem.

"The Refinement of the Structure of Bis(benzonitrile)palladium Chloride," N. C. Baenziger and W. Duax, submitted to Inorg. Chem.

"Metal-Olefin Compounds. XIII. Organonitrile Complexes of Rhenium and Manganese," J. R. Doyle and B. N. Storhoff, accepted for publication in Inorg. Chem.

"Metal-Olefin Compounds. XIV. The Preparation and Investigation of Some Triphenylphosphine-Gold Compounds," C. C. Hunt, C. Fields and J. R. Doyle, accepted for publication in Inorg. Chem.

"The Crystal Structure of 1, 2 Diferrocenylethane," N. C. Baenziger, C. L. Carpenter and J. R. Doyle, in preparation.

"The Preparation of Copper(I)tetrafluoroborate Complexes of Cyclic Diolefins," H. Hagnauer, B. Bravlin and J. R. Doyle, in preparation.

"The Preparation of Platinum and Palladium Olefin Compounds," D. Drew and J. R. Doyle, in preparation.

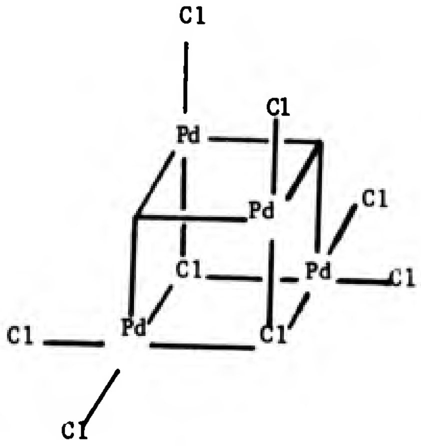
"Preparation, Reactions and Structures of Transition Metal Olefin Compounds and Related Substances," N. C. Baenziger and J. R. Doyle. Final Technical Report.

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

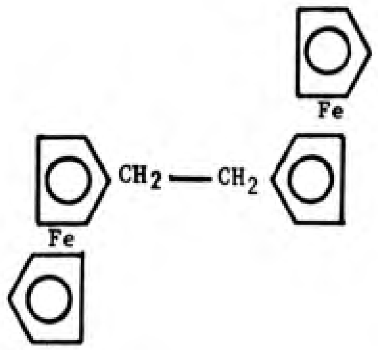
The objective of the research program was the preparation and characterization of metal-olefin compounds and related substances. The preparative work involved the synthesis of a series of new complexes containing olefinic or related substances and such metals as manganese, rhenium, platinum, palladium, copper, silver, thallium and gold. The physical characterization involved x-ray diffraction studies on selected metal-olefin compounds and related substances; a nuclear magnetic resonance study on a series of cyclic-poly-olefin compounds containing platinum or palladium; a kinetic-mechanistic study of the solvolysis of platinum and palladium compounds in dimethyl sulfoxide; an infrared study of manganese-olefin complex precursors such as the $(\text{nitrile})_2Mn(CO)_3Br$ system.

In the preparative studies several new preparations of thallium cyclopentadienide were developed and the utility of this compound was examined by preparing a series of representative cyclopentadiene derivatives. Another preparative study included development of two methods for the synthesis of copper(I)tetrafluoroborate-olefin complexes and a number of stable diolefin compounds were isolated. Gold compounds prepared included $(\phi_3P)_3Au_3Cl$, $[(C_6H_5)_3P]_2Au^+TCNE$, $[(C_6H_5)_3P]_3AuTCNE$, and $(\phi_3P)_2AuS_2C{=}O$. These were characterized by e.s.r. and infrared spectra. A systematic study of n.m.r. spectra of a series of ( diolefin ) platinum$(R)_2$ complexes and diolefin palladium compounds was completed. The most notable difference between the platinum and palladium was the larger chemical shifts of the coordinated olefinic protons of the palladium derivatives and the increased rates of solvolysis of the palladium compounds over analogous platinum derivatives. The reactions of manganese and rhenium pentacarbonyl bromide with organonitriles were examined as a possible route to olefin derivatives of these elements. A series of silver tetrafluoroborate complexes of diolefin complexes were prepared.

Structural studies were performed on COT-$PdCl_2$(COT=cyclooctatetraene), $AgBF_4$·COD(COD=cyclooctadiene), $CuBF_4$·COD, $AgBF_4$·NBD(NBD=norbornadiene) and bis(benzonitrile)palladium chloride. Two other compounds were prepared and data to date indicate the following interesting structures:



Butene-$PdCl_2$ complex



Bis(benzonitrile)palladium Chloride

In addition to the above preparative and structural studies computer programs for adsorption corrections, phase determination, and complete bond length-angle-error were developed.

Lt. Col. L. D. Whipple

# COMPLETED PROJECT SUMMARY

1. TITLE: Double Optical Resonance Spectra of Organic and Inorganic Molecules

2. PRINCIPAL INVESTIGATOR: Dr. Thomas M. Dunn
Department of Chemistry
University of Michigan
Ann Arbor, Michigan

3. INCLUSIVE DATES: 1 February 1965 - 31 January 1969

4. GRANT NOS.: AF-AFOSR-0865-65; AF-AFOSR-0865-67

5. COSTS AND FY SOURCE: $40,716 FY65; $39,252 FY67

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: L. A. Cross

8. PUBLICATIONS:

"The Excited States of Uranium and Heavy Metals," Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The original object of this project was to study the spectra and hence the energy levels of the heaviest elements in absorption fluorescence and phosphorescence. Attention was focused on the uranyl ion $UO_2^{+2}$, the lowest metastable state of which remained unidentified. It was known that this ion acts as a Q-switching medium in conjunction with the ruby laser, and as such implied the existence of excited state type transitions.

This work was carried out under the title of "The Excited States of Uranium and the Heavy Metals." The results obtained are predominantly contained in the doctoral thesis of Lee A. Cross. It gives a detailed discussion of spectra of uranyl compounds and of uranyl glass, their fluorescence spectra, together with the time-resolved induced absorption spectra of both the glass and uranyl sulfate and phosphate solutions. The transition giving rise to the Q-switching action of uranyl ion was positively identified in both uranyl glass and in uranyl solutions and has been demonstrated to be a broad structureless absorption system having an intensity maximum at about 5600 Å.

Following the successful detection and characterization of the induced absorption spectrum of the uranyl ion some preliminary work was performed on the existence of high lying metastable states in other inorganic compounds.

Since the emphasis seemed to lean toward the induced absorption spectra the title of the project was changed to "Double Optical Resonance Spectra of Organic and Inorganic Molecules" to correspond to the "double optical resonance" phenomena that appeared to be occurring.

Since nearly all molecules are in their lowest electronic state at room temperature their colour depends upon how "high" the excited state lies. However, some molecules possess excited electronic states which have very long lifetimes, comparatively, so that if one can get a large number of molecules into these states then a beam of light passed through might excite them to even higher excited states and a different "colour" may be seen.

Such a molecule is the uranyl ion $UO_2^{++}$, since it possesses an excited state which has a "half life" of about half a milli-second. This may not seem long until one compares it with the usual lifetime of one millionth of a millisecond. This "metastable" state is obtained when light of blue-green colour is absorbed and if a large amount of this is present, as is the case when a powerful flash-lamp is set off close to the uranyl compound, then a large number of uranyl ions go to the excited state. The "absorption" spectrum of the ions in this state is then taken and is found to have a maximum at ~5800 Å.

From such experiments it is possible to find out more about the highly excited states of molecules and so to learn more about those states which are likely to be important when the molecules react with other molecules.

D. W. Elliott

## COMPLETED PROJECT SUMMARY

1. TITLE: Quantitative Conformational Analysis

2. PRINCIPAL INVESTIGATOR: Dr. Ernest L. Eliel
Department of Chemistry
University of Notre Dame
Notre Dame, Indiana

3. INCLUSIVE DATES: 1 November 1964 - 30 June 1969

4. GRANT NOS.: AF-AFOSR-772-65; AF-AFOSR-772-67

5. COSTS AND FY SOURCE: $41,632 FY65; $63,946 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. R. O. Hutchins
Dr. R. J. L. Martin
Dr. J. M. McKenna
Dr. F. W. Nader
Dr. D. G. Neilson
Dr. B. C. Newman

7. JUNIOR RESEARCH PERSONNEL: R. M. Enanoza
E. C. Gilbert
A. A. Hartmann
M. K. Kaloustian
Sister M. C. Knoeber
L. D. Kopp
C. W. Maloney
M. C. Reese

8. PUBLICATIONS:

"A Facile Synthesis of $\beta$-Alkoxy Mercaptans and $\beta$-Thioalkoxy Mercaptans," E. L. Eliel, T. W. Doyle, R. A. Daignault, and B. C. Newman, J. Amer. Chem. Soc., 88, 1828 (1966).

"The 'Size' of a Lone Pair of Electrons. Evidence for an Axial *t*-Butyl Group," E. L. Eliel and Sr. M. C. Knoeber, J. Amer. Chem. Soc., 88, 5347 (1966).

"Conformational Analysis. XIII. The Validity of the Nuclear Magnetic Resonance Method of Establishing Conformational Equilibria," E. L. Eliel and R. J. L. Martin, J. Amer. Chem. Soc., 90, 682 (1968).

"Conformational Analysis. XIV. Conformational Equilibria of Cyclohexyl Halides," E. L. Eliel and R. J. L. Martin, J. Amer. Chem. Soc., 90, 689 (1968).

"Conformational Analysis. XV. The Conformational Enthalpy, Entropy, and Free Energy of the Carboxyl, Carboxylate, Carbomethoxy, Carbonyl Chloride, and Methyl Ketone Groups," E. L. Eliel and M. C. Reese, J. Amer. Chem. Soc., 90, 1560 (1968).

"Konformationsanalyse in Beweglichen Systemen - Methodik und Resultate," E. L. Eliel, Chimia, 22, 201 (1968).

"Conformational Free Energies of the Formyl, Hydroxymethyl, Acetal, and Hydroxyl Groups as Determined by the Equilibration Method," E. L. Eliel, D. G. Neilson, and E. C. Gilbert, Chem. Commun., 360 (1968).

"Conformational Analysis. XVI. 1,3-Dioxanes," E. L. Eliel and Sr. M. C. Knoeber, J. Amer. Chem. Soc., 90, 3444 (1968).

"Repulsion of *syn*-Axial Electron Pairs. The 'Rabbit-Ear Effect'," R. O. Hutchins, L. D. Kopp and E. L. Eliel, J. Amer. Chem. Soc., 90, 7174 (1968).

"Stereochemistry of the Reaction of Grignard Reagents with Ortho Esters. A Case of Orbital Overlap Control. Synthesis of Unstable Polyalkyl-1,3-dioxanes," E. L. Eliel and F. Nader, J. Amer. Chem. Soc., 91, 536 (1969).

"Conformational Analysis. XVIII. 1, 3-Dithianes. Conformational Preferences of Alkyl Substituents and the Chair-Boat Energy Difference," E. L. Eliel and R. O. Hutchins, J. Amer. Chem. Soc., 91, 2703 (1969).

"The 'Rabbit Ear' Effect. Polar Interactions of Hetero Atoms," E. L. Eliel, Kemisk Tidskrift, 81, 22 (1969).

"Conformational Analysis in Saturated Heterocyclic Compounds," E. L. Eliel, Accounts of Chemical Research, in press .

"Conformational Analysis. XIX. The Conformational Enthalpy and Entropy of the Hydroxyl Group in Various Solvents. Conformational Energy of Methoxyl," E. L. Eliel and E. C. Gilbert, J. Amer. Chem. Soc., in press.

"Conformational Analysis. XX. The Stereochemistry of Reaction of Grignard Reagents with Orthoesters. Synthesis of 1,3-Dioxanes with Axial Substituents at C-2," E. L. Eliel and F. W. Nader, submitted to J. Amer. Chem. Soc.

"Reduction of Dithioacetals and Dithioketals with Sodium in Liquid Ammonia," E. L. Eliel and B. C. Newman, in preparation.

"Conformational Equilibria in 1,3-Dioxanes with Polar Substituents in the 5-Position," E. L. Eliel and M. K. Kaloustian, in preparation.

"Conformational Analysis in 1,3-Dithianes with Hetero Substituents," E. L. Eliel and A. A. Hartmann, in preparation.

"Conformational Equilibria in 2-Substituted 1,3-Dioxanes," E. L. Eliel and F. W. Nader, in preparation.

"Stereochemistry of Reduction of 2-Alkoxy-1,3-dioxanes with Lithium Aluminum Hydride and 'Mixed Hydrides'," E. L. Eliel and F. W. Nader, in preparation.

"Insights Gained from Conformational Analysis in Heterocyclic Systems," E. L. Eliel, to be published in Pure and Applied Chemistry.

"Quantitative Conformational Analysis," Final Technical Report.

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research performed under this grant has, above all, led to a major advance of our understanding of the conformation of heterocyclic systems, especially six-membered rings. At the beginning of the investigation, very little was known in a quantitative way regarding the conformational features of heterocycles; in fact, it was common practice to assume that they were very similar to those of the corresponding carbocycles. The work done on this project has clearly shown that, in a quantitative sense, this is an unwarranted oversimplification.

Three major features distinguish saturated heterocycles from carbocycles. One is the difference in intramolecular dimensions, as evidenced, for example in the differenee of the C-C distance (1.53 Å), C-O(1.42 Å ) and C-S(1.81 Å) or the C-C-C angle (111.5°) from C-S-C (99°). There result such anticipated findings as a much greater conformational energy of axial substituents at C-2 in oxygen containing heterocycles (e.g. 4.0 kcal/mol for 2-methyl-1,3-dioxane as compared to 1.7 kcal/mol for methylcyclohexane) and such unanticipated ones as a much more accessible twist-boat form in the case of 1,3-dithiane than in the case of cyclohexane or 1,3-dioxane.

A second distinguishing feature between heterocycles and carbocycles lies in the fact that the former may have unshared electron pairs (on oxygen, nitrogen or sulfur) where the latter have hydrogen atoms. It thus became possible to attack the controversial problem of the "space requirement" of an unshared electron pair. The remarkable finding that the conformational energy of a 5-t-butyl group in 5-t-butyl-1-3-dioxane is only 1.4 kcal/mol as compared to a value of over 5.5 kcal/mol for axial t-butyl in t-butylcyclohexane, and that cis-2-methyl-5-t-butyl-1,3-dioxane exists virtually exclusively in the conformation with axial t-butyl and equatorial methyl shows conclusively that the space requirement of an unshared electron pair is small or negligible compared to that of a hydrogen atom; in fact, it may be that the unshared pair can be altogether neglected in computing non-bonded interactions, the interaction of axial t-butyl at C-5 in 1,3-dioxane possibly being entirely due to interaction with the ring oxygens themselves.

A third distinguishing feature of heterocycles, especially those with polar substituent groups, lies in the fact that important dipole interactions may come into play in such molecules. Such interactions had previously been seen in the "anomeric effect," i.e. the preference of the axial for the equatorial position for the aglycone group in glycosides. Dr. Eliel and his coworkers have seen similar effects in 2-alkoxy-1,3-dioxanes (axial alkoxyl preferred) and N,N-dimethyl-1,3-diazanes (axial methyl on nitrogen preferred) and have rationalized the findings in what they have called the "rabbit ear" effect, i.e. the tendency of unshared electron pairs on atoms located 1,3 with respect to each other to avoid a parallel orientation. Once recognized, the effect may be found in many instances already documented in the literature.

The 1,3-dioxane and (to a lesser extent) 1,3-dithiane rings have been found very convenient systems for conformational analysis from the synthetic point of view, from the point of view of facile equilibration and from the point of view of NMR study of configuration and conformation. Also, the 1,3-dioxane system has supplied a framework for other stereochemical studies, e.g. of the stereochemistry of the orthoester - Grignard and orthoester - metal hydride reactions.

The work is continuing under other auspices. Present research deals with a more extensive study of dipolar effects (especially in 5-hetero-substituted 1,3-dioxanes) including solvent effects, a study of five-membered rings, a study of geminally disubstituted dioxanes and an attempt to use four-component equilibria in conformational study. Dr. Eliel and his research group are collaborating with Dr. E. L. Beeson (Louisiana State, New Orleans) on microwave spectral analysis of 1,3-dioxane, with Dr. Gerhard Schmidt (Weizmann Institute) on X-ray analysis of substituted 1,3-dioxanes and with Dr. Shneior Lifson (Weizmann Institute) on a priori calculations of conformation and energetics in heterocycles.

When this work was initiated in 1964, there was hardly any activity in the area of heterocyclic conformational study. Now there are approximately a dozen laboratories, all over the world, active in this field. A high interest in the area is documented by the request for reviews (see List of Publications) and by the large number of invitations to lecture which the Senior Investigator has received, including, in 1969, an invited lecture at the American Chemical Society Meeting in Minneapolis, Minnesota, in April, a plenary lecture at the Symposium on Conformational Analysis in Brussels, Belgium in September and an invited lecture at the Thirteenth Annual Organic Chemistry Conference at Natick, Massachusetts in October.

Dr. A. J. Matuszko

# COMPLETED PROJECT SUMMARY

1. TITLE: Laser Temperature-Jump Studies of Fast Reactions

2. PRINCIPAL INVESTIGATOR: Dr. Edward M. Eyring
Department of Chemistry
University of Utah
Salt Lake City, Utah

3. INCLUSIVE DATES: 1 October 1963 - 31 December 1968

4. GRANT NOS.: AF-AFOSR-476-64; AF-AFOSR-476-66; AF-AFOSR 68-1383

5. COSTS AND FY SOURCE: $27,056 FY64; $27,248 FY66; $10,160 FY68

6. SENIOR RESEARCH PERSONNEL: Dr. W. T. Silfvast

7. JUNIOR RESEARCH PERSONNEL:
B. C. Bennion
G. A. Christiansen
D. L. Cole
J. L. Haslam
W. H. Inskeep
R. P. Jensen
D. L. Jones
M. H. Miles
J. D. Owen
L. D. Rich

8. PUBLICATIONS:

"Intramolecular Hydrogen Bonding in cis-Cyclopropanepolycarboxylic Acids," J. L. Haslam, E. M. Eyring, W. W. Epstein, G. A. Christiansen, and M. H. Miles, J. Am. Chem. Soc., 87, 1 (1965).

"Equilibrium and Kinetic Studies of the Deprotonation of the Monoanion of Several Dicarboxylic Acids in Water and in Deuterium Oxide," J. L. Haslam, E. M. Eyring, W. W. Epstein, R. P. Jensen, and C. W. Jaget, J. Am. Chem. Soc., 87, 4247 (1965).

"Solvent Deuterium Isotope Effects on Intramolecularly Hydrogen-Bonded Dicarboxylic Acid Monoanions," E. M. Eyring and J. L. Haslam, J. Phys. Chem., 70, 293 (1966).

"Deuterium Oxide Solvent Isotope Effects on N-H...O, O-H...N, and N-H...N Intramolecular Hydrogen Bonds," J. L. Haslam and E. M. Eyring, J. Phys. Chem., 71, 4470 (1967).

"Intramolecular Hydrogen Bonding of Azo Dyes in Aqueous Solution," W. H. Inskeep, D. L. Jones, W. T. Silfvast, and E. M. Eyring, Proc. Natl. Acad. Sci. U. S., 59, 1027 (1968).

"Fast Reactions in Solution," E. M. Eyring and B. C. Bennion, Ann. Rev. Phys. Chem., 19, 129 (1968).

"Kinetics of Aqueous Scandium (III) Perchlorate Hydrolysis and Dimerization," D. L. Cole, L. D. Rich, J. D. Owen, and E. M. Eyring, Inorg. Chem., 8, 682 (1969).

"Hydrolysis Kinetics of Dilute Aqueous Chromium (III) Perchlorate," L. D. Rich, D. L. Cole, and E. M. Eyring, J. Phys. Chem., 73, 713 (1969).

"Hydrolysis Kinetics of Dilute Aqueous Gallium (III), Indium (III), and Erbium (III) Perchlorates," L. D. Rich, D. L. Cole, and E. M. Eyring, in preparation.

"Kinetics of Hydrolysis of Aqueous Ferric Ion," D. L. Cole, L. D. Rich, and E. M. Eyring, in preparation.

"Laser Temperature-Jump Studies of Fast Reactions," Final Technical Report, AFOSR 69-0260.

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research provided answers to three major questions: Is it feasible to measure microsecond and submicrosecond chemical relaxation times following a small, rapid jump in sample solution temperature caused by a pulsed laser? Is there a systematic correlation between the nature of the atoms involved in an intramolecular hydrogen bond and the rate at which the bond is broken by hydroxide ion in aqueous solution? Does the specific rate of hydrolysis of trivalent metal ions in aqueous solution increase dramatically by several powers of ten as the charge density of the ion decreases? An abbreviated summary of the answers obtained to these questions is given below.

A Q-switched pulsed neodymium-in-glass laser capable of delivering a one Joule ~ 30 nanosecond duration pulse of energy at a wavelength of 1.06 microns was assembled from commercial components. This laser was fired into a glass cuvette that in the early experiments contained acidic aqueous solutions of sodium molybdate and bromocresol purple. Laser light at this wavelength is weakly absorbed by a vibrational band of water thus heating the solvent directly. A millisecond time scale relaxation of the temperature dependent polymerization equilibrium $8\ H^+ + 7\ MoO_4^{2-} \rightleftharpoons H_8(MoO_4)_7^{6-}$ coupled to the bromocresol purple indicator equilibrium gave rise to large changes in absorbance at 579 nm that were measured spectrophotometrically. Subsequent laser temperature jump experiments with alkaline aqueous solutions of 2,4-dihydroxy-4'-sulfonateazobenzene yielded chemical relaxations as short as 20 microseconds. In this instance the chemical reaction observed was the breaking of a strong intramolecular hydrogen bond in the azo dye by an external hydroxide ion to form an azo anion and another water molecule. In both cases the relaxation obtained duplicated those measured previously for the same sample systems using the conventional Joule heating temperature jump relaxation technique. The principal impediment to wide applications of this laser technique was the weakness of the laser beam. Its weakness necessitated a focusing of the laser beam to heat a ~1 $mm^3$ volume in the sample solution. It was also necessary to focus the monochromatic sample beam (at a right angle to the laser beam) into the same tiny volume. In spite of the focusing of the laser beam the actual jump in temperature was so small that only those chemical equilibria the perturbation of which gave large light absorbance changes were susceptible to kinetic investigation. Thus the conclusion was reached that a Q-switched neodymium laser delivering at least 10 Joules per pulse would be required to carry out aqueous solution rate studies in the submicrosecond time range, if sample equilibria were to be picked for their intrinsic chemical interest rather than for large values of $\Delta H$ associated with large light absorbance changes.

Equilibrium and kinetic solvent deuterium oxide isotope effects were measured for tropaeolin D, 2,4-dihydroxy-4'-nitroazobenzene, N,N-dimethylanthranilic acid, N-methyl-N-ethylanthranilic acid, N, N-diethylanthranilic acid, 3,7-diaza-3, 7-dimethyl-1, 5-diphenyl-9-hydroxybicyclo [3.3.1] nonane, and a variety of dicarboxylic acids. The conventional Joule heating temperature jump technique was used in these rate studies. The solvent kinetic isotope effects for the reaction $HA + OH^- \longrightarrow A^- + H_2O$ lie between 316 and ~ 1.2 for these compounds. The rate constants for the various intramolecular hydrogen bond types overlap to some extent but roughly confirm an earlier generalization based on spectroscopic data that intramolecular hydrogen bonds have strengths that decrease in the following order from left to right: O-H···N > O-H···O ≅ N-H···N >N-H···O. The kinetic data emphasize that structural variations in a molecule near its intramolecular hydrogen bond have a greater impact on the reactivity of the bond than the fact, say, that it is an O-H···N rather than an O-H···O bond.

The conductimetric dissociation field effect or electric field jump relaxation method was used in kinetic studies of the reaction

$$M^{3+}\ (aq) \underset{}{\overset{k_1}{\rightleftharpoons}} MOH^{2+}\ (aq) + H^{+}\ (aq)$$

in dilute aqueous solutions of low ionic strength where $M^{3+}$ was any one of several trivalent metal ions. Some of the results can be summarized thus:

| $M^{3+}$ | Ionic radius A | $k_{-1}$ $10^9 M^{-1} sec^{-1}$ | $k_{-1}$ $10^5$ $sec^{-1}$ |
|---|---|---|---|
| $Al^{3+}$ | 0.57 | 4.4 | 1.1 |
| $Cr^{3+}$ | 0.65 | 0.78 | 1.4 |
| $Ga^{3+}$ | 0.62 | 4.4 | 2.7 |
| $In^{3+}$ | 0.81 | 9.1 | 1.1 |
| $Sc^{3+}$ | 0.83 | 10 | 1.7 |
| $Er^{3+}$ | 1.04 | 32 | 2.8 |

Two conclusions follow at once from these results: (1) Quite unlike the much studied specific rate of inner coordination sphere water loss, the specific rate of hydrogen ion loss $k_1$ is essentially independent of the radii (i.e. charge density) of the metal ions. (2) The specific rate of ion recombination $k_{-1}$ is essentially diffusion controlled and roughly proportional to metal ion radii except for $Cr^{3+}$, the only one of the above ions with an incomplete shell of d-orbital electrons.

Dr. W. L. Ruigh

## COMPLETED PROJECT SUMMARY

1. TITLE: Structure of Carbanions and the Kinetics of their Exchange Processes in Solution

2. PRINCIPAL INVESTIGATOR: Dr. Gideon Fraenkel
Department of Chemistry
Ohio State University
Columbus, Ohio

3. INCLUSIVE DATES: 1 July 1965 - 31 March 1969

4. GRANT NOS.: AF-AFOSR-251-65; AF-AFOSR-68-1441

5. COSTS AND FY SOURCE: $54,048 FY65; $7,044 FY68

6. SENIOR RESEARCH PERSONNEL: Dr. S. Dayagi
Dr. K. Dhami
Dr. N. Wilson
Dr. R. Dean
Dr. T. Tokuhiro

7. JUNIOR RESEARCH PERSONNEL: D. Adams
R. Carlson
W. Breitigam
K. Christenson
C. Cottrell
E. Pecchold
P. Tuazon

8. PUBLICATIONS:

"Hexamethyl Phosphoramide: A New Solvent For Electrons," G. Fraenkel, S. M. Ellis and D. T. Dix, J. Am. Chem. Soc., 87, 1406 (1965).

"Inversion in a Primary Grignard Reagent," G. Fraenkel, D. T. Dix and D. G. Adams, Tetrahedron Letters, 3155 (1964).

"Kinetics of Inversion of Lithium and Aluminum Organometallic Reagents," G. Fraenkel, D. T. Dix and M. Carlson, Tetrahedron Letters, 579 (1968).

"Nuclear Magnetic Resonance and Ultraviolet Spectroscopy of Substituted Aromatic Organometallic Compounds of Lithium, Magnesium and Calcium," G. Fraenkel, S. Dayagi and S. Kobayashi, J. Phys. Chem., 72, 953 (1968).

"Nuclear Magnetic Resonance and Ultraviolet Spectroscopy of Phenylmagnesium Bromide, Phenyllithium and Pyridine," G. Fraenkel, D. G. Adams and R. R. Dean, J. Phys. Chem., 72, 944 (1968).

"Kinetics of Inversion of 2-methylbutyl-magnesium bromide and Related Compounds," G. Fraenkel and D. T. Dix, J. Am. Chem. Soc., 88, 979 (1966).

"Structure of Butyllithium-pyridine Adduct" G. Fraenkel and J. W. Cooper, ibid., 1825, (1968).

"Kinetics of Carbon-metal Bond Exchange in Dimethylcadmium," G. Fraenkel and N. Wilson, J. Am. Chem. Soc., submitted.

"Carbon-13 Resonance of Phenyllithium," G. Fraenkel, J. Russell, A. Jones and D. Grant, J. Phys. Chem., in press.

"Generation and Capture of t-Butylpotassium from an Azo Compound in a Homogeneous Medium," G. Fraenkel and E. Pecchold, J. Am. Chem. Soc., submitted.

"Alcoxide Cleavage of Benzoyl-t-butyldiimide: Ionic and Radical Mechanism," G. Fraenkel and E. Pecchold, ibid., submitted.

"The Reaction of t-Butyllithium with Methyl Benzoate, A Route to Complex Compounds," G. Fraenkel and E. Pecchold, ibid., submitted.

"Electrocyclic Reaction of a Cyclohexadienyl Anion with a Diene," G. Fraenkel, E. Pecchold, C. Cottrell and R. Dougherty, ibid., submitted.

"Calculations of Carbon Shifts in Azines," G. Fraenkel and T. Tokuhiro, J. Chem. Soc., in press.

"Carbanion Bridging in the Inversion Process for Organomagnesium Compounds," G. Fraenkel and D. T. Dix, in preparation.

"Nmr Studies of Carbanions Stabilized by Sulfur," G. Fraenkel and P. Tuazon, in preparation.

"Photolysis of Organomagnesium Compounds," G. Fraenkel and W. Breitigam, in preparation.

"Molecular Structure of Carbanions and the Kinetics of Their Exchange Processes in Solution,"Final Report AFOSR 251-65 and AFOSR 68-1441.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The first aim of this research was to develop a technique for measuring rates of inversion, carbon-metal bond exchange and metal base exchange for organometallic compounds in solution and to learn something about the electronic structure of carbanions.

These measurements were accomplished with the nmr line-shape method which enables one to study the rate of an exchange process which is already at equilibrium. From these kinetic data there developed some conclusions about mechanisms for bond exchange and inversion. In almost every case the results indicate that these processes involve aggregates of organometallics, never monomers. Hence, it is concluded that the transition states for these processes involve carbanion bridging, $M. . . .R^{\delta -}. . . .M$. Although the details vary among the different systems studied, (Mg, Li, Be, Al, Cd, Tl) bridging is a common feature.

Since many organometallic compounds behave like carbanions chemically, it was felt that they would reflect useful information about carbanions in their physical properties. For instance, nmr and uv spectroscopy of aryl organometallics shows that the magnitudes of the $\alpha$ proton and $\alpha$-carbon-13 shift are a measure of the ionic character of the carbon metal bonds. Since these shifts are large and negative, very similar to the corresponding amines, experimental bond ionicities can be assigned. Furthermore, using these shifts in conjunction with uv data, it proved the existence of $n \rightarrow \pi^*$ type excitations where the n electrons are associated with the carbon metal bond.

Nmr spectroscopy in conjugated organometallics gives information on the charge distribution from the shifts. In the case of triphenylmethyl, diphenylmethyl, phenyldimethyl-potassium there are very large shifts due to charge. These are mostly independent of solvent. Similarly, nmr studies of anions stabilized by sulfur have given insight into the electronic origin of the stabilization. The study of ground state carbanions has led to work on excited states of organometallics and here it is found that the excited states act as if they were much more polar than the ground states.

Work on exchange processes and electronic structure has inevitably lead to studies on their chemistry. Recently, research was started on generating carbon atoms in solution from carbanions, on generating carbanions by new methods, and doing this in solution. There is evidence of the presence of the t-butyl anion in solution. Finally, the first example of an electrocyclic reaction of a $\pi$-conjugated anion with a diene has been uncovered.

Although such a process is allowed by the rules governing orbital symmetry and the aromaticity of transition states, so far no other examples have been published.

These studies demonstrate that the chemical behavior of carbanionic species can be predicted from the physical, i.e., spectral properties.

Lt. Col. L. D. Whipple

## COMPLETED PROJECT SUMMARY

1. TITLE: Phosphorus Coordination Compounds

2. PRINCIPAL INVESTIGATOR: Dr. Samuel O. Grim
Department of Chemistry
University of Maryland
College Park, Maryland

3. INCLUSIVE DATES: 1 November 1964 - 31 October 1968

4. GRANT NOS.: AF-AFOSR-782-65; AF-AFOSR-782-67

5. COST AND FY SOURCE: $9,552 FY64; $20,052 FY65; $43,356 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. Helen R. H. Patil

7. JUNIOR RESEARCH PERSONNEL: R. A. Ference
R. L. Keiter
P. J. Lui
P. R. McAllister
L. C. Satek
R. M. Singer
D. A. Wheatland

8. PUBLICATIONS:

"$^{183}W-^{31}P$ Spin-Spin Coupling Constants in Octahedral Complexes," S. O. Grim, W. McFarlane and D. A. Wheatland, Inorg. Nuc. Chem. Letters, 2, 49 (1966).

"Phosphorus-31 NMR Spectra of Some Tertiary Phosphine Rhodium Compounds," S. O. Grim and R. A. Ference, Inorg. Nuc. Chem. Letters, 2, 205 (1966).

"A Phosphorus-31 NMR Study of Tertiary Phosphine Complexes of Platinum(II), S. O. Grim, R. L. Keiter and W. McFarlane, Inorg. Chem., 6, 1133 (1967).

"A Phosphorus-31 NMR Study of Tertiary Phosphine Derivatives of Group VI Metal Carbonyls," S. O. Grim, D. A. Wheatland and W. McFarlane, J. Am. Chem. Soc., 89, 5573 (1967).

"A Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine Derivatives of Group VI Metal Carbonyls. II. Mixed Ligand Complexes," S. O. Grim, D. A. Wheatland and P. R. McAllister, Inorg. Chem., 7, 161 (1968).

"Tungsten-Phosphorus Spin-Spin Coupling in Tungsten Carbonyl Derivatives," S. O. Grim and D. A. Wheatland, Inorg. Nucl. Chem. Letters, 187 (1968).

"Mercury-199-Phosphorus-31 Nuclear Spin-Spin Coupling in Tertiary Phosphine Complexes of Mercury(II) Bromide," R. L. Keiter and S. O. Grim, Chem. Commun., 521 (1968).

"Correlation between Phosphorus-Tungsten Coupling Constants and Carbonyl Stretching Frequencies in Phosphorus-ligand Derivatives of Tungsten Hexacarbonyl," S. O. Grim, P. R. McAllister, and R. M. Singer, Chem. Commun., 38 (1969).

"A Phosphorus-31 NMR Study of Tertiary Phosphine Derivaties of Group VI Metal Carbonyls. III. Disubstituted Compounds," S. O. Grim, and D. A. Wheatland, in preparation.

"$^{31}$P Studies of Rhodium(III) and Rhodium(I) Compounds," S. O. Grim and R. A. Ference, Inorg. Chim. Acta., in preparation.

"$^{31}$P Studies of Iridium(III) Compounds," S. O. Grim and R. A. Ference, Inorg. Chim. Acta., in preparation.

"$^{31}$P Studies of Palladium Compounds," S. O. Grim and R. L. Keiter, Inorg. Chim. Acta., in preparation.

"$^{31}$P Studies of Mercury(II) Halides," S. O. Grim, R. L. Keiter, and P. J. Lui, in preparation.

"Phosphorus Coordination Compounds," Final Technical Report

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to investigate the utility of phosphorus-31 magnetic resonance in the study of coordination compounds. For this purpose the phosphorus nmr spectra were recorded for more than two hundred compounds of which about one hundred were specifically prepared for this purpose.

The utility of phosphorus-31 magnetic resonance techniques has been shown by this research group under the sole sponsorship of AFOSR to be of great significance in the study of coordination compounds of phosphorus, with particular importance to theoretical bonding studies and stereochemical problems. At the beginning of this research in the Autumn, 1964, there were only two publications in this field in all the chemical literature. The publications resulting from this work currently represent about 20% of all publications in this area.

The tabulation of chemical shift data for the phosphorus compounds has led to some practical applications, such as the qualitative and rough quantitative (peak areas) determinations of different isomers in reaction mixtures, and for equilibrium studies between isomers, e.g., cis and trans isomers of square planar $(R_3P)_2PdCl_2$. More important from the point of view of bonding studies in coordination compounds has been the study of phosphorus heavy metal nuclear spin-spin coupling.

It has been shown that the platinum-195-phosphorus-31 coupling constants measured from $^{31}$P nmr spectra of cis and trans platinum compounds of the type $(R_3P)_2PtCl_2$ can be used to assign stereochemistries for these compounds. They also found that the magnitude of $J_{Pt-P}$ is related to the $\pi$-acceptor ability of the ligand. In addition, conductimetric, nmr, and analytical evidence has been obtained to establish the first reported existence of a trisubstituted phosphine derivative of platinum of the type $[(R_3P)_3PtCl]^+$.

They reported the first rhodium-103-phosphorus-31 couplings in the $^{31}$P nmr spectra of rhodium complexes of the type $(R_3P)_3RhCl_3$ and found these spectra useful in assigning unequivocally the stereochemistries of these compounds. The first phosphorus-phosphorus coupling in coordination compounds is also reported for the rhodium series.

They reported the first tungsten-183-phosphorus-31 coupling constants in compounds of the type $R_3PW(CO)_5$, and have found the infrared stretching frequencies of the carboxyl groups to be linearly related to $_{W-P}$ values. This adds further confirmation to the platinum results that $J_{M-P}$ is related to the $\pi$-acceptor ability of the ligand. These results add a new type of evidence to the growing current controversy over the $\sigma$ versus $\pi$-effects of the ligands (phosphines, amines, etc.) in derivatives of metal carbonyls and their resulting influence on carbonyl stretching frequencies. Their data measure a property intrinsic to the bond under scrutiny, viz. the metal-donor atom, whereas previous infrared data for carbonyl stretches, which are properties of bonds somewhat removed from the bond in question, were previously used to infer bonding characteristics.

They observed the first mercury-199-phosphorus-31 couplings in the $^{31}P$ nmr spectra of compounds of the type $(R_3P)_2HgX_2$ and $(R_3P)_2Hg_2H_4$ and have related these couplings to the σ-bonding strength of the ligands. These data are complementary to $J_{W-P}$ and $J_{Pt-P}$ values since in the case of tetrahadral Hg(II), the d-orbitals are not as conveniently arranged for π-bonding as in octahedral (W) and square planar (Pt) stereochemistries. As a result σ-effects are more important than π-effects.

They prepared the first mixed monodentate ligand complexes of the metal carbonyls (specifically, Group VI) and have observed phosphorus-phosphorus couplings directly in the $^{31}P$ nmr spectra. Chemical shift data are important for identification of products in these syntheses since these compounds, i.e., $LL'M(CO)_4$, are not always formed in clean reactions. The magnitute of P-P coupling observed has generally confirmed the order of magnitude calculated from proton and fluorine nmr spectra by other workers.

Dr. W. L. Ruigh

# COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Characterization of Molecules on a Foreign Solid

2. PRINCIPAL INVESTIGATOR: Dr. Melvin C. Hobson, Jr.
Virginia Institute for Scientific Research
Richmond, Virginia

3. INCLUSIVE DATES: 1 November 1964 - 31 October 1968

4. GRANT NOS.: AF-AFOSR-734-65; AF-AFOSR-734-67

5. COSTS AND FY SOURCE: $28,128 FY65; $44,663 FY67

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: Helen M. Gager

8. PUBLICATIONS:

"Adsorption of Polar Compounds on Amorphous Boron," J. S. Gillespie, Jr., M. C. Hobson, Jr., and H. M. Gager, Nature, 212, 137 (1966).

"Mössbauer Effect Spectra of Ammonia Adsorption on a Supported Iron Catalyst," M. C. Hobson, Jr., Nature, 214, 79 (1967).

"Mössbauer Effect Spectra of a Supported Iron Catalyst," M. C. Hobson, Jr. and A. D. Compbell, J. Catalysis, 8, 294 (1967).

"The Study of Surface Chemistry by the Mössbauer Effect," M. C. Hobson, Jr., J. Electrochem. Soc., 115, 175C (1968).

"Mössbauer Effect Studies of Butene-1 Hydrogenation on Supported Iron Catalysts," M. C. Hobson, Jr. and H. M. Gager, Proc. 4th Intern. Congr. Catalysis, Moscow, June 23-29, (1968), to be published.

"The Determination of Microcrystallite Size from Mössbauer Spectra," H. M. Gager and M. C. Hobson, Jr., to be published.

"Mössbauer Effect Studies of Chemisorption on Supported Iron Catalysts," M. C. Hobson, Jr. and H. M. Gager, to be published.

"Chemical Characterization of Molecules Adsorbed on a Foreign Solid," Final Technical Report, AFOSR 68-2774.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to apply spectroscopic techniques to the study of surface structures of catalysts of supported transition metals. Infrared, visible, ultraviolet and Mössbauer spectroscopy were used, but Mössbauer spectroscopy was found to be the more powerful and productive one for investigation of the adsorbent when using iron and its compounds supported on silica gel and alumina as model catalyst systems. The latter technique yielded information on crystallite size, oxidation state and surface complex formation of the iron catalysts.

Early in this investigation an infrared study of the adsorption and reaction of some simple gases on boron surfaces led to some practical applications. The conditions for the formation of acidic species on the surface explained

strain failures of boron composites undergoing humidity tests. It also suggested an area of research for the improvement of coupling agents between boron fibers and the organic matrix for a research and development program being conducted by the Air Force Systems Command, Dayton, Ohio. However, the main effort was directed toward the Mössbauer spectroscopy studies.

Microcrystallite size of ferric oxide on silica gel and alumina was calculated by Kündig's method from Mössbauer spectra of the catalysts. It was found that reproducible results could be obtained with the silica gel samples, but that the method was severely limited for the alumina samples because of compound formation between the ferric oxide and the alumina.

Several species have been observed in the Mössbauer spectra of these catalysts which have neither been observed by any other method nor positively identified from their Mössbauer parameters. In addition to the compound formed with the alumina support a ferrous oxide species was observed on reduction of both silica gel and alumina samples. This species did not have the Mössbauer parameters of wustite and could not be observed by x-ray diffraction analysis. For catalyst samples having the smallest crystallite size, 30 to 50 Å, two distinct species could be resolved in the spectra of the reduced state. One was a ferrous species, but the identification of the other remains uncertain. The latter proved to be the one affected most by chemisorption. The effect on the intensity of the Mössbauer spectrum of this species varied with the compound that was chemisorbed. The compounds could be classified in an order of decreasing ability to affect the intensity of the spectrum as follows; ammonia $\sim$ trimethylamine $\sim$ methanol $>$ acetonitrile $>$ carbon monoxide $\sim$ hydrogen.

These results have shown the scope of the application of Mössbauer spectroscopy to the study of heterogeneous catalysts. Although limited in the number of elements that can be studied, the technique yields detailed information on the structure and composition of model catalysts that would be difficult, if not impossible, to obtain by any other method.

Dr. D. L. Ball

# COMPLETED PROJECT SUMMARY

1. TITLE: Coordination, Ligand Reactivity and Catalysis

2. PRINCIPAL INVESTIGATOR: Dr. Mark M. Jones
Department of Chemistry
Vanderbilt University
Nashville, Tennessee

3. INCLUSIVE DATES: 1 March 1964 - 31 December 1968

4. GRANT NOS.: AF-AFOSR-630-64; AF-AFOSR-630-66

5. COSTS AND FY SOURCE: $27,480 FY64; $27,480 FY66

6. SENIOR RESEARCH PERSONNEL: Dr. D. G. Lambert
Dr. J. W. Hosking
Dr. D. O. Johnston
Dr. W. Mac Allister

7. JUNIOR RESEARCH PERSONNEL: C. J. Barnett
H. Clark

8. PUBLICATIONS:

"Kinetic Patterns of Ligand Reactivity," M. M. Jones, Advances in Chemistry 49, Am. Chem. Soc., 153 (1965).

"The Retardation of Ligand Oxidations by Coordination," D. O. Johnston, Charles J. Barnett and M. M. Jones, J. of Inorg. and Nuclear Chem. 29, 1927 (1966).

"Oxidation of Some Chelating Agents with Alkaline Ferricyanide," D. G. Lambert and M. M. Jones, J. Am. Chem. Soc., 88, 4615, (1966).

"The Iodination of Coordinated Imidazole," D. G. Lambert and M. M. Jones, J. Am. Chem. Soc., 88, 5537 (1966).

"The Oxidation of Borate Sugar Complexes by Alkaline Ferricyanide," D. G. Lambert and M. M. Jones, J. Inorg. and Nuclear Chem., 29, 579 (1967).

"The Masking of Ligand Reactivity by Coordination," M. M. Jones, Advances in Chemistry 62, Am. Chem. Soc., 229, (1967).

"The Suppression of Bromodecarboxylation of Salicylic Acid by Coordination," John W. Hosking and M. M. Jones, J. Inorg. and Nuclear Chem. 29, 2295 (1967).

"The Nickel Ion Catalyzed Iodination of 2-Amino-2-Hydroxymethyl-1,3-Propanediol," John W. Hosking and M. M. Jones, J. Inorg. and Nuclear Chem. 29, 2321 (1967).

"Coordination, Ligand Reactivity and Catalysis," Final Report AFOSR-630-64 and AFOSR-630-66.

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this work was to examine some of the ways in which coordination can alter the reactivity of typical ligands. This is necessary if a firm understanding of the role played by metal ions in altering ligand reactivity patterns is to be achieved. The principal accomplishments of this work can be summed up in the statement that "coordination affects ligand reactivity by altering the accessibility and type of transition state available for a reaction." In some cases where the coordination site is far removed from the metal ion the change is minimal. In other cases (where masking is found) coordination of a ligand to a metal ion prevents the ligand from achieving a transition state. In the oxidation of some ligands by ferricyanide it was found that the rate was profoundly affected by the presence of cationic bridging ions which facilitate electron transfer. In many cases, the metal ion polarizes a complexed ligand strongly enough to facilitate its transformation into a more reactive anion. In such cases, catalysis of the characteristic anion reactions is a consequence of coordination.

Many ligand reactions are determined by the same features which lead to coordination: one or more pairs of electrons which can form coordinate bonds to other species. In these one generally finds that coordination pre-empts the reaction site needed by the attacking reagent and leads to a suppression of the reaction. This has been demonstrated on the oxidation of chelating agents by species containing a metal ion in a high oxidation state such as the vanadate ion.

Lt. Col. L. D. Whipple

# COMPLETED PROJECT SUMMARY

1. TITLE: Upper Atmosphere Ion-Molecule Reactions

2. PRINCIPAL INVESTIGATOR: Dr. Walter S. Koski
Department of Chemistry
The Johns Hopkins University
Baltimore, Maryland

3. INCLUSIVE DATES: 1 September 1963 - 31 August 1968

4. CONTRACT NO.: AF-AFOSR-49(638)-1301

5. COSTS AND FY SOURCE: $71,320 FY64; $45,030 FY66; $47,341 FY67; $35,000 FY68

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: E. R. Weiner
G. R. Hertel
M. A. Berta
R. W. Rozett
B. Y. Ellis
D. F. Munro
C. R. Iden

8. PUBLICATIONS:

"Cross Sections for Some Gas-Phase Single-Charge-Transfer Reactions of $N_2^{++}$ and $Ar^{++}$," E. R. Weiner, G. R. Hertel, and W. S. Koski, J. Chem. Phys. 39 3538 (1963).

"Cross Sections for the Single Charge Transfer of Doubly-Charged Rare-Gas Ions in Their Own Gases," G. R. Hertel and W. S. Koski, J. Chem. Phys. 40 3452 (1964).

"Rare Gas Ion Reactions with Ammonia," G. R. Hertel and W. S. Koski, J. Am. Chem. Soc. 86 1683 (1964).

"The Argon-Deuterium Hydride Ion Reaction," M. A. Berta and W. S. Koski, J. Am. Chem. Soc. 86 5098 (1964).

"Reaction of $HD^+$ with Rare Gases," M. A. Berta, B. Y. Ellis and W. S. Koski, J. Chem. Phys. 44 4612 (1966).

"Isotope Effect in the Reaction of $HD^+$ with Rare Gases," M. A. Berta, B. Y. Ellis, and W. S. Koski, Advances in Chemistry Series, 58 80 (1966).

"Spectator Mechanism for Ion-Molecule Reactions," R. W. Rozett and W. S. Koski, J. Chem. Phys. 49 3737 (1968).

"Helium Ion-Hydrogen Reactions," R. W. Rozett and W. S. Koski, J. Chem. Phys. 48 533 (1968).

"Collision-Induced Dissociation on $HD^+$ by Rare Gases," R. W. Rozett and W. S. Koski, J. Chem. Phys. 49 2691 (1968).

"Ion-Molecule Reactions of $C^+$ with $N_2$ and $O_2$," R. C. C. Lao, R. W. Rozett, J. Chem. Phys. 49 4202 (1968).

"Simplified Mounting for Quadrupole Mass Filter Rods," D. F. Munro, The Review of Scientific Instruments, 38 1532 (1967).

"Theoretical Justification of the Apparently Anomalous Low Energy Behavior of Some Ion-Molecule Reactions," J. J. Kaufman and W. S. Koski, J. Chem. Phys. in press (1969).

"Upper Atmosphere Ion Molecule Reactions," Final Technical Report

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Using a two-stage mass spectrometer, which was developed in the investigator's laboratory, a number of ion-molecule reactions of significance in various upper atmosphere phenomena have been studied. The reactions of hydrogen deuterium ion with Argon were studied. An energy dependent isotope effect was found. At the time, this was an unexpected effect. The large isotope effect can now be explained as arising mainly from the restriction that the energy and total angular momentum must be conserved in the reaction.

In some of the ion-molecule studies it was noted that, if the bombarding ion is of the same mass as the target molecule, anomalously low cross-sections are obtained. This study was extended to the rare gas ion reactions with methane, and the lowest cross section was found for neon ion plus methane.

The hydrogen-helium ion reaction to give protons and deuterons was investigated as a function of bombarding ion energy. This reaction was of special interest since attempts to study it in other laboratories were unsuccessful. The variation of the isotope effect was interpreted in terms of the stripping theory.

The reaction of carbon plus one ions with various atmospheric constituents is being carried out in the 5 - 200 electrons-volt bombarding ion energy region. Charge transfer, mass transfer, and charge transfer dissociation reactions were observed. These measurements afford useful leads on the mechanism of fixation of carbon fourteen in the earth's atmosphere.

It is generally observed that cross sections for exothermic ion-molecule reactions decrease with increasing ion kinetic energies indicating a negligible activation energy. An important exception to this behavior is exhibited by the exothermic reaction $O^+ + N_2 \rightarrow NO^+ + N$, the cross section of which goes through a maximum as a function of ion energies. A study of the pertinent potential energy curves, taking into account the proper symmetry- and spin-allowed combinations of the reactants and products, shows the origin of the apparently anomalous behavior of this reaction.

D. W. Elliott

## COMPLETED PROJECT SUMMARY

1. TITLE: Viscous Flow and Compressibility of Molten Borates at High Pressure.

2. PRINCIPAL INVESTIGATOR: Dr. J. D. Mackenzie
Materials Division
Rensselaer Polytechnic Institute
Troy, New York

3. INCLUSIVE DATES: 1 October 1964 - 30 September 1968

4. CONTRACT NO.: AF 49(638) - 1460

5. COSTS AND FY SOURCE: $35,000 FY65; $37,500 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. L. L. Sperry

7. JUNIOR RESEARCH PERSONNEL: K. Fujiwara

8. PUBLICATIONS:

"High Pressure Effects on Glass," S. Sakka and J. D. Mackenzie, J. Non-Crystalline Solids, 1, 107 (1969).

"Electrical Properties of Glass and Glass-Ceramics," J. D. Mackenzie, International Commission on Glass Publication, (1969).

"Ceramics in Ocean Engineering," J. D. Mackenzie, Ocean Engineering, 2, 100 (1969).

"Pressure Dependence of Viscosity of $B_2O_3$," L. L. Sperry and J. D. Mackenzie, Phys. Chem. Glasses, 9, 91 (1968).

"Glass in Electronics," J. D. Mackenzie, Magazines for Industry, Inc., New York (1968).

"Journal of Non-Crystalline Solids," a new International Journal on Glass, edited by J. D. Mackenzie, (1968).

"High Pressure, High Temperature Viscometer," L. L. Sperry and J. D. Mackenzie, Rev. Scie. Instr., 38, 1646 (1967).

"Modern Aspects of the Vitreous State," J. D. Mackenzie, Butterworths, Washington (1964).

"Viscosity of Molten Borates under Pressure," K. Fujiwara, J. D. Mackenzie and L. L. Sperry, in preparation.

"P-V-T Relation of Liquid Boron Oxide," K. Fujiwara, J. D. Mackenzie and L. L. Sperry, in preparation.

"Physical Properties of Molten Oxides at Elevated Pressures," J. D. Mackenzie, in preparation.

"Relationship between the Glass Transition Temperature and Liquidus Temperature," S. Sakka and J. D. Mackenzie, in preparation.

"Viscous Flow and Compressibility of Molten Borates at High Pressure," Final Technical Report.

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Molten oxides constitute a special family of high temperature liquids. On cooling, their viscosity would increase and, if crystallization is suppressed, glasses would be formed. The study of variation of viscosity with temperature is of obvious importance because of the intimate relation between viscous flow and structure. Theoretical considerations suggest that if viscosity is measured as a function of temperature at constant volume, rather than at constant atmospheric pressure, the results should be simpler for interpretation. This would involve the application of pressure to the liquid while its temperature is varied. Because of experimental difficulties, no such constant volume measurements have been attempted for molten oxides. The objective of this project is to develop a technique for measuring viscosity of simple glass-forming oxide melts at constant volume so that a better understanding of the structures of liquid oxides as well as those of glasses will result.

An apparatus was successfully developed for measuring viscosity of molten oxides up to 600°C and 400 bars. Results were obtained for molten boric oxide and molten binary alkali borates. The P-V-T relationships of these systems were separately obtained in a separate apparatus. From these measurements, viscosity at constant volume, viscosity at elevated pressures, activation energy for flow at constant volume and expansion as well as compressibility data at elevated pressures were obtained for the first time for molten oxides.

The most important results are: (a) Activation energy at constant volume is almost as large as that at constant pressures for all systems studied. (b) The structures of the melts vary with temperature. (c) The so-called two-state model is inadequate to describe this structural variation. A many-state model is more compatible with the experimental findings. (d) The activation volume for flow increases drastically when the temperature is decreased. The significant achievement of this research was recognized by the award of the Lebeau Medal for 1969 to Dr. J. D. Mackenzie by the French Societé des Hautes Temperatures et des Refractoires in Paris on March 18, 1969.

Dr. W. L. Ruigh

# COMPLETED PROJECT SUMMARY

1. TITLE: Studies in Stereochemistry

2. PRINCIPAL INVESTIGATOR: Dr. Kurt Mislow
Department of Chemistry
Princeton University
Princeton, New Jersey

3. INCLUSIVE DATES: 1 July 1966 - 31 July 1968

4. GRANT NOS.: AF-AFOSR-1188-66 and AF-AFOSR-1188-67

5. COSTS AND FY SOURCE: $122,777 FY66; $77,392 FY67

6. SENIOR RESEARCH PERSONNEL:
Dr. F. W. Carson
Dr. J. S. Chickos
Dr. K. De Bruin
Dr. A. W. Herriott
Dr. J. Jacobus
Dr. K. Kondo
Dr. O. Korpiun
Dr. E. G. Miller
Dr. K. Naumann
Dr. R. Scartazzini
Dr. F. D. Saeva

7. JUNIOR RESEARCH PERSONNEL:
M. Axelrod
P. Bickart
D. L. Doerfler
W. M. Egan
R. Gans
M. L. Goldstein
J. D. Gust
E. Halpern
R. A. Lewis
M. Raban
D. R. Rayner
D. J. Sandman
R. T. H. Tang
H. Thomas
G. Zon

8. PUBLICATIONS:

"The Absolute Configuration of Methyl Allyl Sulfoxide. Stereochemistry of the Grignard Synthesis of Optically Active Sulfoxides," P. Bickart, M. Axelrod, J. Jacobus, and K. Mislow, J. Am. Chem. Soc., 89, 697 (1967).

"Chemical Shift Nonequivalence of Diastereotopic Groups in Sulfonium Salts," K. Kondo and K. Mislow, Tet. Letters, No. 14, 1325 (1967).

"Pyramidal Inversion of Sulfonium Ions. The Racemization of 1-Adamantylethylmethylsulfonium Perchlorate," R. Scartazzini and K. Mislow, Tet. Letters, No. 28, 2719 (1967).

"A New Route to the Preparation and Configurational Correlation of Optically Active Phosphine Oxides," O. Korpiun and K. Mislow, J. Am. Chem. Soc., 89, 4784 (1967).

"Configurational Correlation of Phosphinates by Nuclear Magnetic Resonance and Optical Rotatory Dispersion," R. A. Lewis, O. Korpiun, and K. Mislow, J. Am. Chem. Soc., 89, 4786 (1967).

"Conformational Flexibility of Thianthrene and Its Oxides," J. Chickos and K. Mislow, J. Am. Chem. Soc., 89, 4815 (1967).

"Chemical Shift Nonequivalence of Diastereotopic Protons Due to Restricted Rotation around Aryl-Nitrogen Bonds in Substituted Amides," Y. Shvo, E. C. Taylor, K. Mislow and M. Raban, J. Am. Chem. Soc., 89, 4910 (1967)

"Conformational Analysis of Tritolylphosphines," E. Halpern and K. Mislow, J. Am. Chem. Soc., 89, 5224 (1967).

"Racemization and Cleavage of Sulfoxides by Methyllithium," J. Jacobus and K. Mislow, J. Am. Chem. Soc., 89, 5228 (1967).

"On the Stereomutation of Sulfoxides," K. Mislow, Rec. Chem. Progr., 28, 217 (1967).

"The Preparation of (+)-N-Methyl-1-(1-naphthyl) ethylamine and the Determination of Its Optical Purity by Nuclear Magnetic Resonance,"J.Jacobus, M. Raban and K. Mislow, J. Org. Chem., 33, 1142 (1968).

"The Synthesis of Optically Active Sulphoxides from Sulphinamides," J. Jacobus and K. Mislow, Chem. Commun., 253 (1968).

"Rearrangement of Allyl Phosphinites and Optical Stability of Allyl Phosphine Oxides," A. W. Herriott and K. Mislow, Tet. Letters, 3013 (1968).

"Absolute Configuration and Optical Rotatory Dispersion of Methyl Alkyl Sulfoxides," M. Axelrod, P. Bickart, M. L. Goldstein, M. M. Green, A.Kjaer and K. Mislow, Tet. Letters, 3249 (1968).

"Stereoisomerism in Biergostatrienol," P. Crabbe and K. Mislow, Chem. Commun., 657 (1968).

"Optical Purity and Optical Rotatory Power of Dekydronorcamphor," D. J. Sandman and K. Mislow, J. Org. Chem., 33, 2924 (1968).

"A Novel Synthesis of 2,3-Seco-A-nor-$5\alpha$-cholestane-2-diol," D. Gust, J. Jacobus and K. Mislow, J. Org. Chem., 33, 2996 (1968).

"Direct Configurational Correlation of Sulfoxides and Phosphine Oxides by Intersystem Matching of Cotton Effects," F. D. Saeva, D. R. Rayner, K. Mislow, J. Am. Chem. Soc., 90, 4176 (1968).

"The Absolute Configuration of Sulfoxides and Sulfinates," M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, J. Am. Chem. Soc., 90, 4835 (1968).

"Synthesis and Absolute Configuration of Optically Active Phosphine Oxides and Phosphinates," O. Korpiun, R. A. Lewis, J. Chickos and K. Mislow, J. Am. Chem. Soc., 90, 4842 (1968).

"Proton Magnetic Resonance Spectra of Menthyl Phosphinates," R. A. Lewis, O. Korpiun, K. Mislow, J. Am. Chem. Soc., 90, 4847 (1968)

"Thermal Racemization of Diaryl, Alkyl Aryl, and Diaklyl Sulfoxides by Pyramidal Inversion," D. R. Rayner, A. J. Gordon, K. Mislow, J. Am. Chem. Soc., 90, 4854 (1968).

"Thermal Racemization of Benzyl p-Tolyl Sulfoxide and Thermal Rearrangement of Benzyl p-Toluenesulfenate," E. G. Miller, D. R. Rayner, H. T. Thomas, K. Mislow, J. Am. Chem. Soc., 90, 4861 (1968).

"The Thermal Racemization of Allylic Sulfoxides and the Interconversion of Allylic Sulfoxides and Sulfenates. Mechanism and Stereochemistry," P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, J. Am. Chem. Soc., 90 4869 (1968).

"Stereochemistry of 2-Benznorbornenone," D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam, and G. C. Hanson, J. Am. Chem. Soc., 90, 4877 (1968).

"Stereochemistry of 9-Dimethylamino-9, 10-dihydro-4, 5-dimethylphenanthrene," H. Joshua, R. Gans, K. Mislow, J. Am. Chem. Soc., 90, 4884 (1968).

"Studies in Stereochemistry," Final Technical Report, AFOSR-1188-67.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of the research supported by this grant are broad and deal with problems in structure and reaction mechanism of organic compounds, with special emphasis on stereochemistry. Development and organization of stereochemical principles constitute an integral part of these studies.

Major accomplishments have been scored in the still relatively unexplored stereochemistry of sulfur and phosphorus. The first synthesis of optically active sulfoxides from diastereomerically enriched sulfinamides by reaction with alkyllithium reagents has been reported. It has been shown unequivocally that this synthesis, as well as the Grignard synthesis of optically active sulfoxides from sulfinates, proceeds with inversion of configuration. It has been shown for the first time that optically active phosphine oxides may be conveniently prepared by reaction of Grignard reagents with diastereomerically enriched phosphinates, and that this method permits the configurational correlation of optically active phosphine oxides. An extensive investigation into the mechanisms of racemization of sulfoxides has resulted in the recognition that thermal racemizations of sulfoxides may proceed by at least three distinct pathways: a pyramidal inversion mechanism, corresponding to a conformational change, a homolytic scission-recombination mechanism, involving the intermediacy of a radical pair, an allylic rearrangement mechanism, involving the intermediacy of allyl sulfenates. The above studies have led to ancillary investigations: the thermal racemization of certain sulfonium ions has been shown to proceed with pyramidal inversion at sulfur; racemization of sulfoxides may be accomplished by use of methyllithium (this is the first example of such a racemization under basic conditions; it has been possible to show that this racemization proceeds by a cleavage-recombination mechanism); the rearrangement of allyl phosphinites to phosphine oxides has been shown to be a completely concerted intramolecular $\alpha,\gamma$-shift.

Considerable effort has been expended in the structural analysis of molecules by optical methods. As part of a study of chemical shift nonequivalence in compounds which contain "diastereotopic protons," it has been found that optical purities of alcohols and amines may be determined quite conveniently by use of O-methylmandelyl chloride, a derivatizing agent which converts a mixture of enantiomers into a mixture of diastereomers the ratio of intensities of the signals of the O-methyl resonances equals the ratio of diastereomers. The ratio of precursor enantiomers, and from this ratio, the optical purity is immediately derived. This method for the determination of optical purities is a general one and is now being widely used in other laboratories. In connection with our continuing investigation of the relationship between structure and optical activity, we have completed a study in which 2-benznorbornenone has been shown to be a typically dissymmetric chromophore of the $\beta,\gamma$-unsaturated ketone type. Along different lines, it has been possible to relate directly the configurations of sulfoxides and of phosphine oxides by a matching of Cotton effects of anisyl derivatives. This represents the first instance where intersystem matching of Cotton effects has led to a configurational correlation.

Other completed studies: An approach to the critical evaluation of kinetic and thermodynamic restrictions on ring flipping, torsional, and inversional modes of conformational interchange has been developed. Evidence has been adduced that thianthrene and its oxides are conformationally mobile, i.e., that these are molecules which are folded in solution, but which undergo a rapidly flapping butterfly-like motion. It has been shown that changes of the dipole moment of differently substituted triaryl phosphines are satisfactorily accounted for by twisting of the phenyl groups around the P-C bond axis, while the C-P-C angle remains constant. The method of conformational analysis originally employed by Wood, Fickett and Kirkwood, in which a study of temperature dependent physical properties leads to a conformational analysis of systems at equilibrium, has been extended to a number of mobile systems and the method itself has been critically evaluated through an extensive computer-aided study.

Dr. Anthony J. Matuszko

## COMPLETED PROJECT SUMMARY

1. TITLE: Chemistry of Organolithium Compounds and Acetylenes

2. PRINCIPAL INVESTIGATOR: Dr. James E. Mulvaney
Associate Professor
Department of Chemistry
University of Arizona
Tucson, Arizona

3. INCLUSIVE DATES: 1 November 1964 - 31 January 1969

4. GRANT NOS.: AFOSR-720-65; AFOSR-720-67

5. COSTS AND FY SOURCE: $27,270 FY65; $29,656 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. S. Groen

7. JUNIOR RESEARCH PERSONNEL: L. J. Carr
T. L. Folk
J. G. Dillon
J. L. Laverty
D. Savage

8. PUBLICATIONS:

"Addition and Metalation Reactions of Organolithium Compounds. I. Products," J. E. Mulvaney, Z. G. Gardlund, Sharon L. Gardlund and D. J. Newton, J. Am. Chem. Soc., 88, 476 (1966).

"Poly-Lithiated Species from 1-Phenylpropyne and Organolithium Reagents," J. E. Mulvaney, T. L. Folk and D. J. Newton, J. Org. Chem., 32, 1674 (1967).

"Anionic Polymerization and Copolymerization of Acrylophenone," J. E. Mulvaney and J. G. Dillon, J. Polymer Sci., A-1, 6, 1849 (1968).

"Polymerization and Copolymerization of Acrylophenone," J. E. Mulvaney, J. G. Dillon and J. L. Laverty, J. Polymer Sci., A-1, 6, 1841 (1968).

"Sequence in Addition-Metalation of Diphenylacetylene," J. E. Mulvaney and L. J. Carr, J. Org. Chem., 33, 3286 (1968).

"Organolithium Compounds and Acetylenes. V. Electron Transfer Plus Addition-Metalation in the Case of a Tertiary Organolithium Compound," J. E. Mulvaney, S. L. Groen, L. J. Carr, Z. G. Gardlund, S. L. Gardlund, J. Amer. Chem. Soc., 91, 388 (1969).

"Organolithium Compounds and Acetylenes. VI. p-Chloro diphenylacetylene," J. E. Mulvaney and D. J. Newton, J. Org. Chem. 134, 1177 (1969).

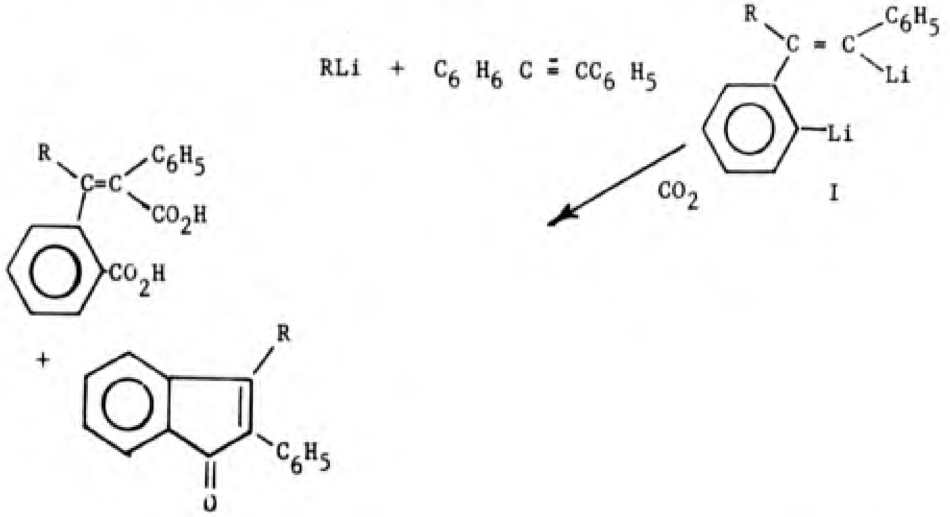
"Organolithium Compounds and Acetylenes. VII. Effect of N,N,N,N - Tetramethylethylenediamine on Reactivity and Products," J. E. Mulvaney and D. J. Newton, J. Org. Chem., 34, 1936 (1969).

"Chemistry of Organolithium Compounds and Acetylenes," Final Technical Report.

9. ABSTRACTS OF OBJECTIVES AND ACCOMPLISHMENTS:

During the past five years reactions of organolithium compounds and acetylenes have been studied in these laboratories. New reactions involving addition metalation to produce polylithiated species and electron-transfer reactions have been observed. Because of the newness of this chemistry very little is known of the scope, synthetic utility or mechanism of such reactions. It was Dr. Mulvaney's objective to exploit these new observations in terms of synthetic possibilities and understanding of these reactions with respect to both small molecules and polymers.

Dr. Mulvaney and his research group found that primary organolithium compounds react in ether with diphenylacetylene to produce a dilithiated species (I) with the indicated trans-stereochemistry



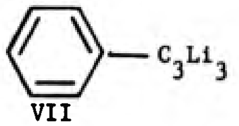
It has been shown that addition to the triple bond precedes metalation.

Using t-butyllithium and diphenylacetylene in hydrocarbon solvent at 90° two of the products (after hydrolysis) are cis-cis-1,2,3,4-tetraphenylbutadiend (II) and trans-stilbene.

Reaction of either primary or tertiary organolithium compounds with 1-phenylpropyne followed by treatment with deuterium oxide leads to the following:

$$RLi + C_6H_5C \equiv CCH_3 \xrightarrow{D_2O} \underset{3.2D\ /molecule}{C_6H_5CD_2C \equiv CD}$$

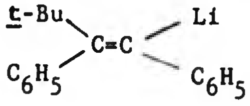
In this case no addition occurs but the highly unusual polylithiated species VII must arise as an intermediate. This result is very similar to West's observation

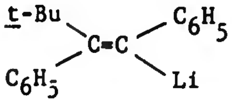


VII

that propyne plus excess n-butyllithium leads to $C_3Li_4$.

The activating effect of N,N,N,N-tetramethylethylenediamine (TMEDA) on organolithium reagents has recently been described. Mulvaney found this compound to be a very efficient promoter in our organolithium work. Diphenylacetylene reacts with primary organolithium compounds to give much higher yields of I more rapidly. With *t*-butyl-lithium, diphenylacetylene reacts at least 100 times more rapidly in the presence of TMEDA, and does not result in the formation of a polylithiated species - or electron transfer products but simply a 7:1 *cis*:*trans* mixture of VIII and IX.


VIII


IX

An investigation of lithium metal as an initiator for vinyl copolymerization was also carried out. Lithium metal produced highly unusual copolymer compositions with acrylophenone and styrene and the significance of these findings was discussed in the third publication listed.

Dr. A. J. Matuszko

## COMPLETED PROJECT SUMMARY

1. TITLE: The Reactions of Molecules in Excited Electronic States with Paramagnetic Gases

2. PRINCIPAL INVESTIGATOR: Dr. W. Albert Noyes, Jr.
Department of Chemistry
University of Texas
Austin, Texas

3. INCLUSIVE DATES: 1 November 1965 - 31 December 1968

4. GRANT NOS.: AF-AFOSR-778-65; AF-AFOSR-778-67

5. COSTS AND FY SOURCE: $34,850 FY65; $38,424 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. T. H. McGee
Dr. D. Phillips
Dr. D. Roscher
Dr. H. D. Mettee
Dr. D. Anderson
Dr. C. Y. Mok
Dr. C. Burton

7. JUNIOR RESEARCH PERSONNEL: C. Burton

8. PUBLICATIONS:

"The Photochemistry of Ketene. The Methylene Radical," Shih-Yeng Ho, I. Unger, and W. A. Noyes, Jr., J. Am. Chem. Soc., <u>87</u>, 2297 (1965).

"Some Aspects of Energy Degradation of Excited Molecules," W. Albert Noyes, Jr., IIlnd Werner Kuhn Memorial Lecture, 12th General Assembly, IUPAC, Basle, Switzerland, 1966.

"Photolytic Processes in Perfluorocyclobutanone Vapor," David Phillips, J. Phys Chem., <u>70</u>, 1235 (1966).

"Possible Mechanisms of Energy Dissipation," D. Phillips and W. A. Noyes, Jr., Zh. Vseo. Khim. Obshchestva im D. I. Mendeleeva, <u>11</u>, 2 (1966).

"Triplet State Yield of Fluorobenzene by the Sensitization of the Isomerization of Cis-butene-2," David Phillips, J. Phys. Chem., <u>71</u>, 1839 (1967).

"The Photolysis of Cyclobutanone," T. Howard McGee, J. Phys. Chem., <u>72</u>, 1621 (1968).

"Primary Photochemical Processes in Some Simple Aromatic Molecules," W. Albert Noyes, Jr. and Charles S. Burton, Ber. Bunsenges, Physik. Chem. <u>72</u>,146 (1968).

"Isomerization as a Route for Radiationless Transitions," W. Albert Noyes, Jr., David Phillips, J. Lemaire, and Charles S. Burton, Advances in Photochemistry, <u>5</u>, 329 (1968).

"Electronic Energy Relaxation in Toluene Vapor," W. Albert Noyes, Jr. and Charles S. Burton, J. Chem. Phys. Soc., <u>49</u>, 1705 (1968).

"Effects of Low Energy Radiation," W. A. Noyes, Jr., and C. S. Burton, chapter to appear in Vol. III of Comprehensive Chemical Kinetics, Elsevier Publishing Company, Amsterdam, The Netherlands.

"Isomerization as a Route for Radiationless Transitions," D. Phillips, J. Lemaire, and C. S. Burton. Submitted to Advances in Photochemistry series for 5, (1968).

"Fluorescence and Triplet State of Hexafluorobenzene," David Phillips. Submitted to the J. Chem. Phys.

"The Reaction of Molecules in Excited Electronic States with Paramagnetic Gases," Final Reports, AFOSR 778-65 and AFOSR 778-67.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This work is concerned with the dissociation of complex molecules by photochemical irradiation. Emphasis is on the mechanisms, the necessary conditions, and the quantitative results. The products are determined by gas chromotography and mass spectroscopy. The information obtained in this study should result in a better understanding of the light degrading processes in polymers and of the photochemical reactions in the atmosphere.

The following molecules have been studied photochemically: perfluorocyclobutanone, perfluorobenzene, fluorobenzene, benzene, toluene, substituted cycloheptatrienes. Light emission from perfluorobenzene is very weak but is wave length dependent. Both singlet and triplet states play important parts in these reactions, the former being more important at short wave lengths. All molecules of fluorobenzene which do not fluoresce become triplet molecules. Thus fluorobenzene is a good example for investigation. Perfluorobenzene emits very little radiation and triplet state formation does not permit an energy balance to be achieved.

The photochemical reactions of cyclobutanone were studied. The yield of cyclopropane from cyclobutanone proved to be independent of all variables while the yield of propylene increased at low pressures and at short wave lengths. The isomerization of xylenes in the liquid phase was studied. These isomerizations proceed through isomers such as dimethyl benzvalene and dimethyl prismane. M-xylene isomerizes to either o-xylene or p-xylene and the ratio of the isomers is different in the liquid phase than in the gas phase. Quantum yields were independent of wave length in the liquid phase but not in the gas phase. The photochemistry of toluene was studied. The ratio of triplet state yield to fluorescent yield is independent of exciting wave length. Preliminary results have been obtained in studies of the photochemistry of cyclopentanone.

Lt. Col. L. D. Whipple

# COMPLETED PROJECT SUMMARY

1. TITLE: Electrochemistry of Transition Metal Ions in Acetonitrile

2. PRINCIPAL INVESTIGATOR: Dr. John W. Olver
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts

3. INCLUSIVE DATES: 1 November 1964 - 31 January 1969

4. GRANT NO.: AF-AFOSR 777-65; AF-AFOSR 777-67

5. COSTS AND FY SOURCE: $36,090 FY65; $34,320 FY67

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: R. R. Bessette
G. A. Forcier
E. W. Zink
T. E. Crumm

8. PUBLICATIONS:

"Simplified Purification of Acetonitrile for Electroanalytical Applications," G. A. Forcier and J. W. Olver, Anal. Chem. 37, 1447 (1965).

"High Sensitivity Coulometric Analysis in Acetonitrile," R. R. Bessette and J. W. Olver, J. Electroanal. Chem. 17, 327 (1968).

"Voltammetric and Spectral Studies on Zirconium in Chloride Media in Acetonitrile," J. W. Olver and R. R. Bessette, J. Inorg. Nucl. Chem. 30, 1791 (1968).

"Association of Common Polarographic Supporting Electrolytes in Acetonitrile," G. A. Forcier and J. W. Olver, Electrochemica Acta 14, 135 (1969).

"Measurement of Diffusion Coefficients for the Reduction of Copper(I) and (II) in Acetonitrile," R. R. Bessette and J. W. Olver, J. Electroanal. Chem. 21, 525 (1969).

"Dissociation of 1:1 Electrolytes Containing Trifluoroacetate Anion," G. A. Forcier and J. W. Olver, Electrochemica Acta, in press.

"Electrical Double Layer Studies in Acetonitrile," T. E. Crumm and J. W. Olver, in preparation.

"Electrochemistry of Transition Metal Ions in Acetonitrile," J. W. Olver, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The original objectives of this research were to achieve an electrolytic separation of hafnium from zirconium in acetonitrile as suggested by previous work, to electrochemically produce lower oxidation states of these and similar elements in acetonitrile which cannot be produced in aqueous solution and to study the association properties of these elements with common electrolytes to understand the first two occurrences.

The accomplishments are very varied. A new method for purification of acetonitrile was required using reduction of impurities with sodium and calcium hydride prior to distillation. Controlled potential electrolysis of zirconium halide solutions produced neither stable solutions of Zr(III) as anticipated nor Zr(0) in an identifiable form. Infra-red spectral studies of zirconium chloride solutions revealed $ZrCl_3^+$, $ZrCl_4$, $ZrCl_5^-$, and $ZrCl_6^{=}$ species. On electrolytic reduction the products formed react with solvent, electrolyte and residual water which is so difficult to remove.

At this point it was clear we did not know enough about electrolytic dissociation in acetonitrile and that we did not have adequate non oxidizing and unreactive electrolytes for use in acetonitrile. We therefore determined the dissociation properties of a series of useable polarographic electrolytes such as alkali and tetraalkylammonium halides, perchlorates, tetrafluoroborates, and trifluoracetates. Partial electrolyte association and in trifluoracetate cases triple ion formation (determined by conductance measurements) make precise interpretation of polarographic data very uncertain, and make quantitative correlation of spectral and polarographic data uncertain.

We undertook a study of the properties of the electrical double layer in acetonitrile at a mercury interface which shows extensive adsorption of both anions and cations on the electrode again complicating electrolytic data.

We then studied the electrolytic properties in acetonitrile of copper(II) and copper(I) as a model case for reduction through lower oxidation states to the metal. These ions could be precisely coulometrically reduced to the lower states as in water and the precision was great enough to determine diffusion coefficients for the respective species by the Cottrell method.

So we have been thwarted in the objective of reducing Zr(IV) cleanly through the gross states Zr(III) and Zr(II) to separable Zr[0]for unknown reasons. While this work was in progress Zr(III) was reported to be stable in acetonitrile by other workers and we are continuing in this laboratory to try to determine why the electrolytic route to production of gross quantities of lower oxidation states of zirconium and hafnium does not succeed.

LtCol L. D. Whipple

## COMPLETED PROJECT SUMMARY

1. TITLE: Theoretical and Experimental Studies in Chemical Physics

2. PRINCIPAL INVESTIGATOR: Dr. Stuart A. Rice
The James Franck Institute
The University of Chicago
Chicago, Illinois

3. INCLUSIVE DATES: 1 November 1966 - 31 October 1968

4. GRANT NO.: AF-AFOSR-0781-67

5. COST AND FY SOURCE: $165,373 FY67; $163,732 FY68

6. SENIOR RESEARCH PERSONNEL:
Dr. B. J. Berne
Dr. M. Bixon
Dr. J. P. Boon
Dr. R. Brout
Dr. M. H. Cohen
Dr. K. Freed
Dr. S. Fischer
Dr. R. Gomer
Dr. R. Gordon
Dr. I. H. Hillier
Dr. N. Hurt
Dr. P. M. Johnson
Dr. J. Jortner
Dr. B. Katz
Dr. J. J. Kozak
Dr. D. H. Levy
Dr. I. L. McLaughlin
Dr. G. C. Morris
Dr. G. Nicolis
Dr. J. Popielawski
Dr. R. J. Silbey
Dr. M. Vala, Jr.
Dr. I. Webman

7. JUNIOR RESEARCH PERSONNEL:
A. S. Abramson
A. N. Bloch
J. A. Boiani
D. P. Chock
B. L. Clarke
D. K. Evans
W. M. Gelbart
L. M. Glass
W. L. Greer
B. L. Halpern
A. U. Hazi
A. R. Hinds
I. Katz
J. Lekner
A. E. Martin
M. R. Martin
R. I. Milstein
S. A. Newman
J. L. Richards
B. Siskind
K. G. Spears
B. Springett
J. D. Weeks
H. R. Wilson
D. A. Young

8. PUBLICATIONS:

"Drift Velocity and Energy of Electrons in Liquid Argon." Phys. Rev. 156, 351 (1967). With Bret Halpern, John Lekner, and Robert Gomer.

"On the Interpretation of the Factor Group Splitting in Naphthalene Crystal." Mol. Crystals 2, 385 (1967). With R. Silbey, J. Jortner, and M. Vala.

"Functional Integral Representation of Nonequilibrium Statistical Mechanics." J. Chem. Phys. 46, 3707 (1967). With Jan Popielawski and Norman Hurt.

Erratum: "Functional Integral Representation of Nonequilibrium Statistical Mechanics." J. Chem. Phys. 46, 3707 (1967), J. Chem. Phys. 48, 2834 (1968).

"On the Equation of State of a Monoatomic Fluid with 6-12 Potential." With David A. Young. Discussion of the Faraday Society, 43, 16 (1967).

"On the Theory of Excitons in Liquids. II. A Classical Model of Polarization Waves in a Simple Liquid." With Gregoire Nicolis. J. Chem. Phys. 46, 4445 (1967).

"Intermediate Excitons in Molecular Crystals: A Study of the Excited States of Crystalline Iodine." With Ian H. Hillier. J. Chem. Phys. 47, 498 (1967).

"On the Theory of Excitons in Liquids III. Nonresonant Broadening of Impurity Spectra in Simple Liquids." With Jan Popielawski. J. Chem. Phys. 47, 2292 (1967).

"Study of the Rydberg States of $H_2$." With Andrew U. Hazi. J. Chem. Phys. 47, 1125 (1967).

"Memory Effects and the Autocorrelation Function of a Dynamical Variable." With Jean-Pierre Boon. J. Chem. Phys. 47, 2480 (1967).

"Reformulation of the Representation of Transport Coefficients Using the Autocorrelation Function Formalism and the Linear-Trajectory Approximation." With Bruce J. Berne and Jean-Pierre Boon. J. Chem. Phys. 47, 2283 (1967).

Erratum: "Reformulation of the Representation of Transport Coefficients Using the Autocorrelation Function Formalism and the Linear-Trajectory Approximation," J. Chem. Phys. 47, 2283 (1967), J. Chem. Phys. 48, 2833 (1968).

"Comments on the Equation of State of the Square-Well Fluid." With David A. Young. J. Chem. Phys. 47, 4228 (1967).

"Theory of Excitons in Liquids. IV. A Simplified Treatment of the Shift and Damping of Polarization Waves." With Gregoire Nicolis and Joshua Jortner. J. Chem. Phys. 48,2482 (1968).

"Studies of the Electronic States of Simple Liquids." Accounts of Chemical Research 1, 81 (1968).

"New Approximation for the Calculation of Neutron Scattering from a Simple Liquid." With Leon Glass. Phys. Rev. 165, 186 (1968).

"Elementary Description of the Equation of State of a Simple Fluid." With John J. Kozak. J. Chem. Phys. 48, 1226 (1968).

"Use of Model Potentials in the Study of Molecular Rydberg States." With Andrew U. Hazi. J. Chem. Phys. 48, 495 (1968).

"Optical Model Calculation of the Electronic States of Mixed Disordered Systems." With Gregoire Nicolis and Joshua Jortner. J. Chem. Phys. 48, 3544 (1968).

"Theory of Radiationless Transitions in an Isolated Molecule." With David P. Chock and Joshua Jortner. J. Chem. Phys. 49, 610 (1968).

"Re-examination of the Theoretical Interpretations of the Spectra of Crystalline Benzene and Naphthalene." With William L. Greer, Joshua Jortner, and Robert Silbey. J. Chem. Phys. 48, 5667 (1968).

"On the Use of Pseudopotentials in the Quantum Theory of Atoms and Molecules," in Advances in Chemical Physics. With John D. Weeks and Andrew Hazi. In Press.

"Intramolecular Formation of p-Methylbenzyl Radical from p-Xylene." With Philip M. Johnson. Chem. Phys. Letters 1, 709 (1968).

"Conjecture Concerning an Asymptotic Modification of the Yvon-Born-Green Equation for Fluids of Rigid Spheres and Disks." With David A. Young. J. Chem. Phys. 47, 5061 (1967).

"Secular Behavior and Frieman's Multiple-Time-Scale Theory of Irreversible Processes." With Hugh Wilson. J. Chem. Phys. 49, 1697 (1968).

"On the Use of Pseudopotentials in Atomic Structure Calculations." With John D. Weeks. J. Chem. Phys. 49, 2741 (1968).

"Cooperative Excitons in a Crystal with Two Molecules per Unit Cell." With David P. Chock. J. Chem. Phys. 49, 4345 (1968).

"A Theoretical Study of the Low Energy Photoionization of Large Molecules: Benzene." With Philip M. Johnson. J. Chem. Phys. 49, 2734 (1968).

"Some Comments on a Formal Theory of Photochemical Dissociation Reactions." With Ian McLaughlin and Joshua Jortner. J. Chem. Phys. 49, 2756 (1968).

"A Unified Approximation for the Velocity Autocorrelation Function and the Structure Function of a Simple Liquid." With Leon Glass. Phys. Rev. In Press.

"Properties of Simple Liquids." The Science Teacher 35, No. 5, p. 17, May 1968.

"A Study of Exciton Dynamics in a Simple Liquid." With Sighart Fischer. Phys. Rev. 176, 409 (1968).

"Radiationless Transitions in Photochemistry." With Joshua Jortner. Submitted to Advances in Photochemistry.

"Long Radiative Lifetimes of Small Molecules." Mordechai Bixon and Joshua Jortner. Submitted to J. Chem. Phys.

"On the Radiative Decay of Polyatomic Molecules." Karl F. Freed and Joshua Jortner. Submitted to J. Chem. Phys.

"Vibrational Relaxation of Diatomic Molecules in Gases and Liquids." Bruce J. Berne, Joshua Jortner, and Roy Gordon. J. Chem. Phys. 47, 1600 (1967).

"Motion of Electrons in Liquid Argon." J. Lekner. Phys. Rev. 158, 130 (1967).

"Theory of Hot Electrons in Gases, Liquids, and Solids." Morrel H. Cohen and J. Lekner. Phys. Rev. 158, 305 (1967).

"Properties of an Excess Electron in Liquid Helium: The Effect of Pressure on the Properties of the Negative Ion." B. E. Springett, Morrel H. Cohen, and Joshua Jortner. Phys. Rev. 159, 183 (1967).

"Energy Dependence of Two Photon Absorption Cross Sections in Anthracene." Itzchak Webman and Joshua Jortner. Submitted to J. Chem. Phys.

"Observation of Molecular Rydberg States in Rare Gas Solids." Benjamin Katz and Joshua Jortner. Submitted to Chem. Phys. Letters.

"Rydberg States of Benzene in Rare Gas Matrices." Benjamin Katz and Joshua Jortner. To be submitted to J. Chem. Phys., in preparation.

"Electron Cavity Formation in Solid Helium." Morrel H. Cohen and Joshua Jortner. To be submitted to Phys. Rev.

"Antiresonances in the Optical Spectrum of Polyatomic Molecules." G. C. Morris and Joshua Jortner, in preparation .

"Quadratic Zeeman Effect in Asymmetric Rotors." Donald H. Levy. J. Chem. Phys. 48, 5026, (1968)

"Some Comments of the Usefulness of the Concept of Coherence Time in the Statistical Theory of Liquids," in Statistical Mechanics--Foundations and Application, Proceedings of the I.U.P.A.P Meeting, Copenhagen, ed. Thor A. Bak, W. A. Benjamin, Inc., New York and Amsterdam (1966), pp. 475-510.

"Some Properties of the Liquid State," in Journeys in Science, Proceedings of Twelfth AFOSR Science Seminar, Albuquerque, New Mexico, 1967, ed. David L. Arm, The University of New Mexico Press, Albuquerque (1967) pp. 242-303.

"Theoretical and Experimental Studies in Chemical Physics," Final Technical Report, AFOSR 69-0045TR, AD 681168.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of the research supported under this grant are very broad, but all are related to the attempt to establish a relationship between the microscopic structure of matter and the macroscopic manifestations of that structure.

The major accomplishments during the support period include the following:

(a) The development of a theory of radiationless processes and the beginnings of a theory of photochemical reactions.

(b) The development of a theory of electronic states of dielectric liquids including the effects of scattering of electrons or excitons by translational motion of the atoms of the fluid.

(c) Continuation of our studies of the stationary states of molecular solids including a reinterpretation of the nature of the excited states of benzene and naphthalene and other topics.

(d) Completion of a set of studies of the equation of state of a simple liquid using a modified form of the YBG integral equation and development of a simplified interpretation of neutron scattering from a simple liquid.

(e) Development of a new approach to nonequilibrium statistical mechanics based on the use of functional integrals and its application to a number of problems in kinetic theory.

(f) Development of a pseudopotential theory of the Rydberg states of simple molecules and development of a pseudopotential algorithm for calculation of the correlation energy of simple atoms.

Wherever possible the theoretical study has been tested against observations with the intent, not only of explaining the observations, but also of using the discrepancies between theory and experiment to further refine our understanding of the properties of matter.

Dr. D. L. Ball

# COMPLETED PROJECT SUMMARY

1. TITLE: Medium Effects on Acid-Catalyzed Reactions

2. PRINCIPAL INVESTIGATOR: Dr. W. M. Schubert
Department of Chemistry
University of Washington
Seattle, Washington

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

4. GRANT NOS.: AF-AFOSR-590-64; AF-AFOSR-590-66

5. COSTS AND FY SOURCE $51,600 FY64; $52,800 FY66

6. SENIOR RESEARCH PERSONNEL: Dr. J. Wardell
Dr. R. Kintne

7. JUNIOR RESEARCH PERONNEL:
Y. Motoyama
J. R. Keeffe
D. C. Ross
A. L. Schy
D. F. Gurka
J. A. Orvik
L. Milakofsky
P. LeFevre
U. Varanasi
J. L. Jensen
W. A. Baker
W. Gill
P. Nutkowitz

9. PUBLICATIONS:

"The Effect of Mineral Acid Medium upon $\underline{f}_{SH}{}^{+}/\underline{f}_{tr}{}^{+}$," W. M. Schubert, Howard Burkett and Alfred L. Schy, J. Am. Chem. Soc., 86, 2520 (1964).

"The Hydration of Styrenes," W. M. Schubert, Bo Lamm and James R. Keeffe, J. Am. Chem. Soc., 86, 4727 (1964).

"An Example of $S_N1$ Cleavage of a Sulfide," W. M. Schubert and Yoshiaki Motoyama, J. Am. Chem. Soc., 87, 5507 (1965).

"Mechanism of Hydration of Styrenes," W. M. Schubert and James R. Keeffe, J. Am. Chem. Soc., submitted.

"Medium Effects on Protonated Transition States. Hydration of Aminostyrenes," W. M. Schubert and James L. Jensen, J. Am. Chem. Soc., submitted.

"Solvent Isotope Effects in the Hydration of Styrenes," W. M. Schubert and James L. Jensen, J. Am. Chem. Soc., submitted.

"The Hydrolysis of N,N-Dimethyl Iminium Ions," W. M. Schubert and Louis Milakofsky, J. Am. Chem. Soc., submitted.

"$S_N1$ Carbon-Sulfur Cleavage in the Hydrolysis of 1-N,N-Dimethylaminosulfides," W. M. Schubert and Yoshiaki Motoyama, J. Am. Chem. Soc., submitted.

"Medium Effects on Protonated Transition States in Mineral Acids. Hydrolysis of 2-Dimethoxymethylquinolines," W. M. Schubert and Alfred L. Schy, in preparation.

"Medium Effects on Protonated Transition States in Trifluoroacetic Acid-Water and Dioxane-Water Solutions," in preparation.

"The Hydrolysis of 1-Aminoethers," W. M. Schubert, Michael Minch and David Ross, in preparation.

"Hydrolysis of Cyclic Acetals," W. M. Schubert and Jon A. Orvik, in preparation.

"Medium Effects on Acid-Catalyzed Reaction," Final Technical Report.

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

### I. Medium Effects on Protonated Activated Complexes

The probing devices were reactions in which both ground state and activated complex contain a single proton. For such reactions, $\underline{k}_{obsd}$ changes with medium are independent of the acidity per se, and measure directly changes in free energies of solvation of the protonated activated complex ($tr^+$) relative to the protonated substrate ($SH^+$). Two systems fulfilling the necessary requirements were investigated: (1) the hydrolysis of basic acetals (acetals of pyridine- and quinoline-2-aldehydes), in which the activated complex has the exact same net composition as the ground state in acidic media; and (2) hydration of basic alkenes (m- and p-amino-styrenes) in which activated complex, formed by rate-controlling proton transfer from $H_3O^+$ to the double-bond of the free amino-styrene, contains the additional elements of a molecule of water.

The results obtained constitute the first unequivocal proof that the medium dependence of the free energy of $tr^+$ relative to $SH^+$ can be appreciable, and is a function of the specific structures of the two states. This invalidates the extensively applied Zucker-Hammett hypotheses, and negates the use of the dependence of $\underline{k}_{obsd}$ on acidity functions as a sole criterion of mechanism.

The behavior of the relative free energy of solvation of $tr^+$ and $SH^+$ is related to the ability of the medium to specifically solvate these states, through hydrogen-bonding of water to electron-deficient hydrogens. The evaluation of such effects provides a valuable means of probing the intimate nature of an activated complex of an acid-catalyzed reaction, once the net composition and gross structure of the activated complex have been established.

### II. Other Mechanistic Investigations

In the search for suitable systems to evaluate medium effects on protonated activated complexes, a number of other reactions were studied in considerable detail.

Hydration of Styrenes. - It was established that the transition state of the rate-controlling step has the composition $S + H^+ + H_2O$, equation 1 representing the most likely rate-controlling step. The widely accepted mechanistic assignment for alkene hydration, i.e., rate-controlling rearrangement of a $\pi$-complex between alkene and a proton, was clearly ruled out.

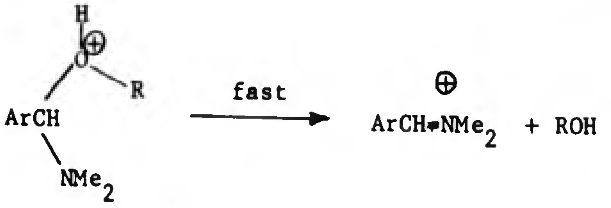
$$ArCH{=}CH_2 + H_3O^+ \longrightarrow tr^+ \longrightarrow Ar\underset{+}{C}H{-}CH_3 + H_2O \qquad (1)$$

Hydrolysis of 1-Aminosulfides. - In pH solutions through moderately concentrated mineral acid, the rate-controlling step is C-S heterolysis of the free aminosulfide. This is the first instance of an $S_N1$-like cleavage of a C-S bond. In more concentrated mineral acid solution, the concentration of free amine is too low, and the cleavage is proton assisted ($ArCHSRN\overset{\oplus}{H}Me_2 \rightleftharpoons ArCH\overset{\oplus}{S}HRNMe_2 \longrightarrow ArCH{=}\overset{\oplus}{N}Me_2 + RSH$).

Hydrolysis of 1-Aminoethers. - In contrast to the C-S cleavage, proton assistance is required for C-O cleavage. Over the pH range 1 to 6 proton-transfer step of equation 3 is rate-controlling:

$$\underset{SH^+}{ArCH(OR)NHMe_2^{\oplus}} + H_2O \rightleftharpoons \underset{S}{ArCH(OR)NMe_2} + H_3O^{\oplus} \qquad (2)$$

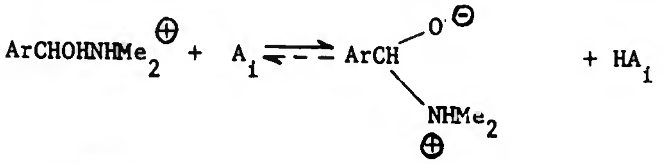
$$ArCH(OR)NMe_2 + HA_i \longrightarrow ArCH(O\overset{\oplus}{H}R)NMe_2 + A_i \qquad (3)$$



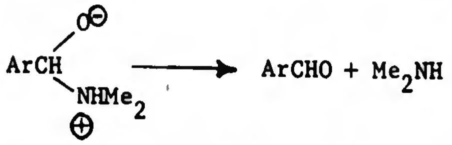
(4)

Hydrolysis of Iminium Ions. - Zwitterion formation, equation 6, is rate-controlling above pH 1 to 2 (dependent on structure of Ar), with $H_2O$ as the participating solvent base over a wide pH range, and $OH^-$ as the participating solvent base at high pH (> pH 7). In acidic media, < pH 1, zwitterion formation is reversible, hence zwitterion collapse (equation 7) becomes rate-controlling.

$$ArCH{=}\overset{\oplus}{N}Me_2 + H_2O \rightleftharpoons ArCHOHNHMe_2^{\oplus} \quad \text{(three steps)} \qquad (5)$$



(6)



(7)

Findings of general interest are (1) proton-transfer from oxygen is rate-controlling in a reaction involving C to nucleophile bond cleavage; (2) carbon-nucleophile bond cleavage is not synchronous with proton transfer; (3) the transition state in acid solution contains one less proton than the transition state in neutral solutions.

Hydrolysis of Cyclic Acetals. - Carbon-oxygen heterolysis of the oxygen conjugate acid (equation 8) is reversible. In the hydrolysis of corresponding acyclic acetals this step is rate-controlling, i.e., irreversible.

(8)

$$ArCH{=}\overset{\oplus}{O}CH_2CH_2OH + H_2O \longrightarrow Prods \qquad (9)$$

Dr. A. J. Matuszko

## COMPLETED PROJECT SUMMARY

1. TITLE: Electronic Computer Calculations On Simple Polyatomic Molecules

2. PRINCIPAL INVESTIGATOR: Dr. Harrison Shull
Department of Chemisty
Indiana University
Bloomington, Indiana

3. INCLUSIVE DATES: 1 March 1963 - 31 December 1966

4. GRANT NOS.: AFOSR-62-183;AFOSR-63-362; AFOSR-362-64

5. COST AND FY SOURCE: $87,787 FY62; $84,840 FY63; $171,334 FY64

6. SENIOR RESEARCH PERSONNEL:

Dr. Stanley Hagstrom
Dr. David Winkel
Dr. Kenneth Banyard
Dr. George Hall
Dr. Peter Politzer
Dr. Tsuyoshi Ando
Dr. Spangler
Dr. Darrell Ebbing
Dr. Ricardo Ferreira
Dr. T. Tietz
Dr. David Lin
Dr. Brian Pedley
Dr. Franklin Prosser
Dr. Keith Howell

7. JUNIOR RESEARCH PERSONNEL:

R. Fern
D. Munch
M. Levy
A. Macias
G. Barnett
H. Cox
R. Christoffersen
R. Brown
J. Sims
H. Kiang
R. Hosteny
J. Allen
G. Scarzafava
C. Causey
R. Harris
R. Moll
O. Hofer
A. Hosch
W. Yang

8. PUBLICATIONS:

"Statistical Theory of the Error in Approximate Wavefunctions," George G. Hall. J. Chem. Phys. 38, No. 5, 1104 (1963).

"Ground State of the HeH$^+$ Molecule Ion," Basil G. Anex, J. Chem. Phys. 38, No. 7, 1651 (1963).

"Properties of Fermion Density Matrices," Tsuyoshi Ando, Revs. Mod. Phys. 35, No. 3, 690 (1963).

"The Nature of the Two-Electron Chemical Bond. IV. Natural Orbitals for He$_2^{++}$," Harrison Shull and Franklin Prosser, J. Chem. Phys. 40, 233 (1964).

"The Nature of the Two-Electron Chemical Bond. V. Electron Pairing and H$_3^+$," Harrison Shull, J. Am. Chem. Soc. 86, 1469 (1964).

"The Nature of the Two-Electron Chemical Bond. VI. Natural Orbital Analysis for HeH$^+$," Basil G. Anex and Harrison Shull, Molec. Orbitals in Chem., Phys., and Biol., Acad. Press, New York-London, 227 (1964).

"$H_3^+$ Molecule Ion. Its Structure and Energy," Ralph E. Christoffersen, Stanley Hagstrom and Franklin Prosser, J. Chem. Phys. 40, No. 1, 236 (1964).

"A Zeroth-Order Approximation for Bond Energies, Hybridization States, and Bond Ionicities. I. Diatomic Molecules and $A^{I}$ -$B^{I}$ Crystals," Ricardo Ferreira, J. Phys. Chem. 68, 2240 (1964).

"Configuration-Interaction Study of the Ground State of the $H_3^+$ Molecule," Ralph E. Christoffersen, J. Chem. Phys. 41, No. 4, 960 (1964).

"The Relative Stabilities of Noble Gas Compounds," Ricardo Ferreira, Inorganic Chemistry 3, 1803 (1964).

"Approximate Natural Orbitals for Four-Electron Systems," Gene P. Barnett, Jan Linderberg, and Harrison Shull, J. Chem. Phys. 43, No. 10, 580 (1965).

"A Generalization of the Rasetti and Slater Methods for Determining the Eigenvalues and Eigenfunctions for a Given Atomic Field," T. Tietz, Can. J. Phys. 43, 250 (1965).

"Analytical Expressions for the Total Elastic Cross Section of Electron Scattering , by Thomas-Fermi-Dirac and Hartree-Fock Atom," T. Tietz, J. Chem. Phys. 42, No. 4, 1462 (1965)

"Simple Analytical Formula for the Phase Shifts of Electron Scattering by Given Atomic Fields," T. Tietz, J. Chem. Phys. 42, No. 6, 2251 (1965).

"Semi-Empirical Approximations for the Coulomb and Bond Integrals in Simple LCAO-MO Methods. I. Alternant and Non-Alternant Hydrocarbons," Ricardo Ferreira, Theoret. Chim. Acta (Berl.) 3, 147 (1965).

"Formula for the Asymmetry in Double Scattering of Fast Electrons, Thomas-Fermi-Dirac Field," T. Tietz, Phys. Rev. 138, No. 4A, A998 (1965).

"Approximate Formulas for the Intensity and Asymmetry of the High-Energy Electron Beam after Two Scatterings in the Hartree-Fock Field," T. Tietz and L. S. Su, Can. J. Phys. 43, 1518 (1965).

"Quantum-Mechanical Study of Some Three-Center Two-Electron Systems. I. Energy Calculation," K. E. Banyard and Harrison Shull, J. Chem. Phys. 44, No. 1, 384 (1966).

"Do the New Machines Really Think?" Harrison Shull, The Review VIII, No. 4, 1 (1966).

"Quantum Chemistry," Franklin Prosser and Harrison Shull, Annual Rev. Phys. Chem. 17, 37 (1966).

"Covalent and Ionic Bond Orders: Applications to the Alkali Halide Molecules," Owen C. Hofer and Ricardo Ferreira, J. Phys. Chem. 70, 85 (1966).

"A Study of the Bonding in the Hydrogen Molecule," Peter Politzer, J. Phys. Chem. 70, 1174 (1966).

"Accurate Analytical Hartree-Fock Potentials for Neutral Atoms as a Sum of Yukawa Terms," T. G. Strand and T. Tietz, Il Nuovo Cimento XLI, 89 (1966).

"Energy Calculation for the Hydride Ion," K. E. Banyard, J. Chem. Phys. 44, No. 12, 4645 (1966).

"Electronic Density Distribution in Lithium Hydride," Peter Politzer and Richard E. Brown, J. Chem. Phys. 45, No. 2, 451 (1966).

"Low Energy Scattering of Electrons by Hartree-Fock Neutral Atoms," H. Kiang and T. Tietz, Acta Phys. Hung. 21, 199 (1966).

"Bond Lengths and Atomic Orbital Radii in the Diatomic Hydrides," Peter Politzer, J. Phys. Chem. 70, No. 12, 4041 (1966).

"Polarization and Exchange Effects in Some Simple Molecular Ions," Peter Politzer, J. Chem. Phys. 45, No. 5, 1856 (1966).

"Electronic Computer Calculations on Simple Polyatomic Molecules," H. Shull, Final Technical Report AFOSR 69-0820TR, AD685133.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research centered upon a concerted effort to apply large-scale digital computers to the problem of accurate computation of polyatomic molecules. Specific objectives of the program included:

(a) Development of better computing algorithms for the three- and four-center integrals necessary in the rather conventional SCF and configuration interaction techniques as applied to polyatomic molecules.

(b) Application of configuration interaction techniques based upon orbital-product wave functions to the ground states of polyatomic molecules.

(c) Application of configuration interaction techniques based upon geminal-product wave functions to polyatomic molecules. The objective in this case was to secure basic calculated wave functions that were applicable for study of the question: "What is a chemical bond?"

Three- and Four- center integral algorithms have largely been worked on by Professor Stanley Hagstrom and by a series of students who have used portions of his programs in a number of computations carried on by the group. These algorithms have been made part of a large quantum chemistry program package which has been under development by Dr. Hagstrom.

Probably the unique feature of this more recent work is the transferability of these programs from computer to computer.

$H_3^+$ was treated thoroughly with a landmark computation by Christoffersen demonstrating clearly the triangular shape, the electron density distribution, and providing an analysis in terms of natural orbitals, which is a useful tool for qualitative understanding of the bonding. This molecule is of especial interest since it is the simplest example of an electron-deficient bonding situation, and the pair of electrons is not associated mainly with any single nuclear pair, but is rather equally associated with all three nuclei.

The fine work of Ebbing on LiH, done in this laboratory, was extended by Richard Brown to excited states, including quite accurate computations of the first two of these, and somewhat less accurate ones on higher states. These computations make possible a fascinating study of the differences between ground and excited states.

The molecule LiH is a particularly interesting example because of the wide variations in the dipole moment.

A study was made of the molecule $BeH^+$, isoelectronic with LiH. This molecule is interesting because it has a stronger bond, a shorter equilibrium internuclear distance, than LiH, and one can expect it to have somewhat less $H^-$ character.

A survey and discussion of natural orbitals for four-electron systems has been pbulished. Additional such analyses for two-electron systems ($He_2^{++}$, $H_3^+$, $HeH^+$, and $H_2$) have been carried through. These demonstrate thoroughly the utility of such natural orbital analyses as a capstone to theoretical computational work.

D. W. Elliott

## COMPLETED PROJECT SUMMARY

1. TITLE: Polynuclear Hydroxo Complexes

2. PRINCIPAL INVESTIGATOR: Dr. R. Stuart Tobias
Department of Chemistry
University of Minnesota
Minneapolis, Minnesota

3. INCLUSIVE DATES: 1 October 1964 - 30 September 1968

4. GRANT NOS.: AF-AFOSR-691-65; AF-AFOSR-691-67

5. COSTS AND FY SOURCE: $29,851 FY65; $29,495 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. H. N. Farrer
Dr. M. G. Miles
Dr. S. J. Harris

7. JUNIOR RESEARCH PERSONNEL: Mary M. McGrady
R. C. Splinter
Gary E. Glass
Charles W. Hobbs
William M. Scovell

8. PUBLICATIONS:

"Electromotive Force, Raman, and Nuclear Magnetic Resonance Studies on the Interaction of Chloride and Bromide Ions with the Dimethyltin(IV) Ion, Inner and Outer Sphere Complexes," H. N. Farrer, M. M. McGrady, and R. S. Tobias, J. Am. Chem. Soc., 87, 5019 (1965).

"Sigma Bonded Organometallic Cations in Aqueous Solutions and Crystals," R. S. Tobias, Organometal. Chem. Revs., 1, 93 (1966).

"Structure of Dimethylgold(III) Coordination Compounds," M. G. Miles, G. E. Glass, and R. S. Tobias, J. Am. Chem. Soc., 88, 5738 (1966).

"The Hydration Number and the Rate of Water Exchange of the Trimethylplatinum(IV) Ion in Aqueous Solution Determined by Oxygen-17 n.m.r.," G. E. Glass and R. S. Tobias, J. Am. Chem. Soc., 89, 6371 (1967).

"The Crystal and Molecular Structure and the Solution Conformation of Dimethylgold(III) Hydroxide, and Inorganic Intermediate Ring Compound," G. E. Glass, J. H. Konnert, M. G. Miles, D. Britton, and R. S. Tobias, J. Am. Chem. Soc., 90, 1131 (1968).

"The Solvent Isotope Effect on the Dissociation of the Aquopentaaminecobalt(III) Ion," R. C. Splinter, S. J. Harris, and R. J. Tobias, Inorg. Chem., 7, 897 (1968).

"Oxygen-17 Nuclear Magnetic Resonance Studies on the Hydration of Organometallic Cations," G. E. Glass, W. B. Schwabacher, and R. S. Tobias, Inorg. Chem., 7, in press.

"Kinetics of the Ligand Exchange Between Organogold(III), -Gallium(III), Thallium(III), and Tin(IV) Acetylacetonates and Free Acetylacetone, G. E. Glass, and R. S. Tobias, J. Organometal. Chem., in press.

"Hydrolytic Condensation of Dimethylgold(III), S. J. Harris and R. S. Tobias, in preparation.

"Polynuclear Hydroxo-Complexes," Final Technical Report, AF-AFOSR 68-2881.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of this research program was to investigate the hydrolytic condensation and depolymerization reactions of organometallic compounds and the factors which affect the reaction rates. Hydrolysis of dimethyldichlorosilane yields a very stable and tractable inorganic polymer. Hydrolysis of dimethyldichlorostannane produces intractable materials which are depolymerized very rapidly by acids. Two related factors have been found to be responsible for this behavior which is typical for the heavy metal alkyls. In the presence of oxygen ligands, the metal coordination number increases, and marked changes in the metal-carbon bonds occur. Ligands other than the carbanions are bound by very polar and relatively weak bonds. Polymerization occurs in at least two dimensions instead of one. Secondly, the rates of substitution reactions of ligands bound in these organometallic complexes are very high.

The reaction $2[(CH_3)_2SnOH]^+ = [(CH_3)_2Sn(OH)_2Sn(CH_3)_2]^{+2}$ in aqueous solution was studied using a flow system and found to be complete within the time of mixing of the reagents, ca. 10 msec. Using $^{17}O$ n.m.r., an upper limit to the average lifetime of a water molecule bound to $(CH_3)\ Sn_2^{+2}$ was determined to be $1 \times 10^{-5}$ sec., but the true lifetime is probably much shorter. The expulsion of a water molecule from the first coordination sphere appears to govern the rate of such reactions, and consequently condensation processes are very fast. Since the equilibrium constant for the dimerization is $10^3$, the reverse reaction is also very fast.

The trimethylplatinum(IV) cation was examined by $^{17}O$ n.m.r., since platinum(IV) complexes are among the most inert known. Three water molecules were found to be bound in the first coordination sphere, and their average lifetime is ca. $9 \times 10^{-5}$ sec.at 25°C. The strictly inorganic Pt(IV)complexes undergo substitution processes at rates which would be immeasurably slow were it not for catalysis by Pt(II) impurities. This is the most striking example of the labilizing effect of organo groups bound in the first coordination sphere. Studies by n.m.r. of the exchange of acetylacetonate between organometallic chelates and the proton chelate, acetylacetone, showed all of these complexes, both transition and representative element, to be very labile.

The deuterium isotope effect on the "model" aquocation $[Co(NH_3)_5OH_2]^{+3}$ was examined by e.m.f. and spectrophotometric techniques. The value of log $K_H/K_D$ was 0.48 ± 0.01 and is typical for an acid of this strength. There do not appear to be any anomalies in the transfer of a proton from an aquoacid compared to other acids.

The new compound $[(CH_3)_2AuOH]_4$ was synthesized by hydrolysis of $(CH_3)_2 AuClO_4$ as a model of a polycondensed transition metal organometallic. The crystal structure was determined by X-ray diffraction and found to be closely related to $[(CH_3)_3PtOH]_4$ for which the structure has been reported recently. The molecule has a case-like structure with $S_4$ symmetry and a flattened tetrahedron of gold atoms together with an interpenetrating tetrahedron of hydroxo oxygens. Bond angles at oxygen are approximately tetrahedral. The structure appears to persist in solutions in organic solvents and is stereochemically rigid at temperatures as high as 100°C. The compound is only slightly soluble in water, and only dimer $[(CH_3)_2Au(OH)_2(CH_3)_2]$ is found in significant concentrations in solution. The structure of the parent aquo-cation $(CH_3)_2Au^+$, the mono-nuclear anion $(CH_3)_2Au(OH)_2{}^-$, and several related species were characterized by Raman and in some cases infrared spectroscopy. All were found to have exclusively the <u>cis</u> structure.

Dr. W. L. Ruigh

# COMPLETED PROJECT SUMMARY

1. TITLE: Sigma-Pi Rearrangement

2. PRINCIPAL INVESTIGATOR: Dr. Minoru Tsutsui
Department of Chemistry
New York University
New York, New York

3. INCLUSIVE DATES: 1 March 1965 - 31 May 1969

4. GRANT NOS.: AF-AFOSR-824-65; AF-AFOSR-824-67

5. COSTS AND FY SOURCE: $22,215 FY65; $27,394 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. Michael Hancock

7. JUNIOR RESEARCH PERSONNEL: Junji Ariyoshi, M. Haya, E. Manda, M. N. Levy

8. PUBLICATIONS:

"Sigma-Cyclopentadienyliron Derivatives as Intermediates in the Formation of Ferricenium Chloride and Ferrocene," J. Am. Chem. Soc., in press.

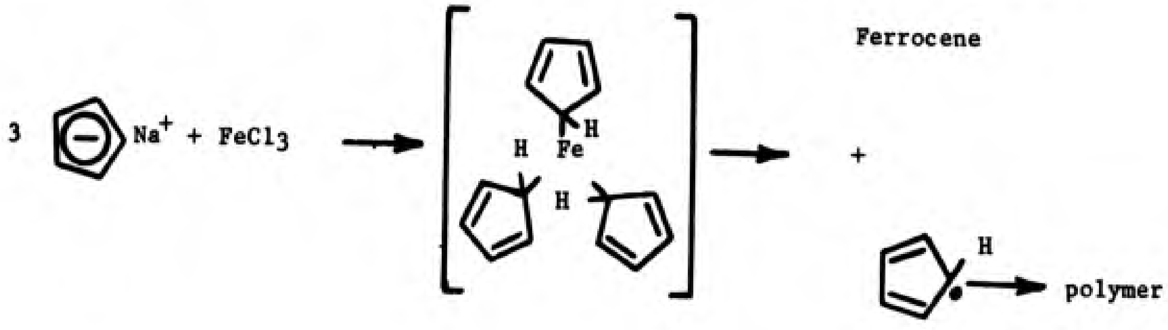
"Sigma-Pi Rearrangements of Organotransition Metals," Angew. Chem., in press.

"Sigma-Pi Rearrangement" Final Technical Report, AFOSR-824-67.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The object of this project was to establish a new intramolecular rearrangment of organotransition metals, and to elucidate a mechanism of the rearrangment. For those purposes, the formation of ferricenium chloride and ferrocene from reactions of sodium cyclopentadienide and ferric chloride in tetrahydrofuran (THF) was chosen.

Di-σ-cyclopentadienyliron chloride monotetrahydrofuranate was prepared from the reaction of sodium cyclopentadienide and iron(III) chloride in a 2:1 molar ratio at -80° in THF. This compound is stable either as a yellow solid at -80° or in THF solution at room temperature. Above -50° or upon the addition of organic solvents, such as ether or n-pentane, the compound rearranges to a blue solid, ferricenium chloride. Tris-σ-cyclopentadienyliron was not isolated from the reaction of sodium cyclopentadienide and iron(III) chloride in a 3:1 molar ratio in THF. However, studies on periodic hydrolysis of each reaction mixture (2:1 or 3:1) at -80° and room temperature establish that tris-σ-cyclopentadienyliron is an intermediate in the formation of ferrocene.



The establishment of $\sigma$-$\pi$ rearrangement, a new rearrangement, has elucidated insights of mechanisms of many known chemical reactions: polymerization reaction of olefin with Ziegler catalyst, oxidation of olefin with palladium catalysts (Wacker reaction), carbonylation of olefin with metal carboryls (Oxo reaction) and many other reactions using transition metal derivatives as catalysts.

During this investigation, many works on $\sigma$-$\pi$ or $\pi$-$\sigma$ rearrangements have been reported. A new area in chemistry, $\sigma$-$\pi$ rearrangements, is being rapidly developed. A review article on this topic was written by the principal investigator.

The rearrangement of tri-$\sigma$-perfluorophenylchromium to diperfluoroarenechromium and on $\pi$-$\sigma$ rearrangements of ferrocene, ferrocenium chloride, and other $\pi$-complexes is currently being investgated. The results obtained are still not conclusive.

Nature of cleavage of metal-carbon bond when $\sigma$-bond rearranges to $\pi$-complex bond was studied by esr. Evidence for homolytic cleavage for rearrangement of tri-$\sigma$-phenylchromium tris-tetrahydrofuranate was obtained. However, no esr signal was detected in the case of the rearrangement of di-$\sigma$-cyclopentadienyliron(III) chloride to ferricenium chloride.

Dr. A. J. Matuszko

## COMPLETED PROJECT SUMMARY

1. TITLE: Surface States in Pure Palladium

2. PRINCIPAL INVESTIGATOR: Dr. Richard W. Zuehlke
Department of Chemistry
Lawrence University
Appleton, Wisconsin 54910

3. INCLUSIVE DATES: 1 October 1962 - 1 July 1968

4. GRANT NOS.: AF-AFOSR-0114-63; AF-AFOSR-0114-65

5. COST AND FY SOURCE: $26,550 FY63; AF-AFOSR-0114-65

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: C. Manser
M. J. G. Skibba
F. Szitta

8. PUBLICATIONS:

"On the Possible Existence of Surface States in Metallic Palladium, R. W. Zuehlke, J. Chem. Phys., 45, 411 (1966).

"Sorption and Magnetic Susceptibility Studies on Metal-Free Radical Systems," R. W. Zuehlke, M. Skibba and C. Gottlieb, J. Phys. Chem. 72,

"Electronic Structure of Metal-NO Surface Complexes," R. W. Zuehlke, in preparation.

"Surface States in Pure Palladium," Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The study has concentrated on two fronts. In the first, careful magnetic susceptibility studies as a function of particle size in finely divided palladium has verified the existence of electronic surface states. These states apparently lie at the top of the palladium d-band, but are not significantly perturbed by any chemisorption process at the surface; this suggests that most of the states are found at interfaces between facing crystallites and are essentially independent of interactions at the observed, exposed faces.

The second part of the study has dealt with sorption characteristics of nitric oxide on finely divided palladium. Nitric oxide was found to physically adsorb with a magnetic susceptibility comparable to that of the gas phase, although this adsorption is anomalous in several respects. It occurs extensively at relatively high temperatures (i.e., above the critical point) and also at very low pressures.

This physically adsorbed state was shown to be the precursor of chemisorption which can take place in two states. The first, and low temperature form, is an immobile chemisorption which takes place with the net transfer of approximately 1.2. electrons to the palladium d-band. A transition temperature of 120° was observed for the immobile - mobile equilibrium, with the mobile form carrying the same electronic characteristics as the immobile form. Comparison of magnetic data and infra-red adsorption observations made by other investigators provided information on the apparent classical electronegativities of the palladium surface and the nitric oxide molecule.

The existence of an apparent negative activation energy for the chemisorption process suggests again the existence of physisorbed nitric oxide as the precursor for chemisorption. On palladium, this activation energy is found to be identical with that of nitric oxide on alumina, thus suggesting the possibility that patches of oxide formation of the palladium surface may be involved in the chemisorption process.

Comparison of this system with a number of others in the literature suggests the possibility that the adsorption of stable free radicals on metallic surfaces begins with a precursor physisorption state which has the usual characteristics resulting from the interaction of two chemical species, each with different spin multiplicities. If, in fact, the ultimate manifestation of an adsorptive interaction between these species is a corroded surface, it is suggested that control of corrosion may be possible through careful study and modification of the precursor physisorption state.

Dr. D. L. Ball

# 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. ACKNOWLEDGMENT

If you forget to include the acknowledgment, "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.

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# 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

*Science, p. 1523, March 26, 1965

Comments by

Mr. Daddario

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### RESEARCH PROJECTS

(Mr. DADDARIO asked and was given permission to address the House for 1 minute and to revise and extend his remarks.)

Mr. DADDARIO. Mr. Speaker, the act authorizing fiscal year 1970 military research and development has been recently signed into law by the President. That legislation contains language which may affect in a fundamental way our mechanisms for allocating Federal resources for the support of scientific research and development activities. I refer to section 203, which states:

> None of the funds authorized by this Act may be used to carry out any research project or study unless such project or study has a direct and apparent relationship to a specific military function.

This provision was adopted without discussion of its implications for the future of American science, which must have thoughtful and imaginative implementation if it is not to be severely injured. Section 203 has also triggered a crisis which our Subcommittee on Science, Research, and Development has been developing and with which it has been intimately concerned since the early 1960's.

That crisis stems to a considerable extent from undue dependence of the scientific community upon military support.

I fear that there exists today a very real danger that research in the universities and elsewhere, now funded from defense appropriations and which should be continued in the national interest, will be fatally disrupted by a mechanistic and legalistic application of the strictures of section 203.

We must not lose sight of the fact that basic research is good for the country, not just for the Department of Defense. We must further see to it that support for basic research is divorced from partisan and passionate argument such as that with which it is presently involved so that basic research activity remains sufficient to meet the needs of the precarious times we face.

Congress must give urgent and immediate thought to arrangements that will identify and provide for the orderly, uninterrupted transfer and continuation of any research adversely affected by section 203, which should still be carried on in the national interest.

We have long been concerned that the mission-oriented agencies, under financial pressure, would be forced to give up much of their research. Recognizing this problem, we restructured the National Science Foundation in 1968 so it would be able to fill the gap. Specifically, we made arrangements whereby the Secretary of Defense and the Secretary of State, for example, may request the Foundation to do certain basic but unclassified research.

It was our purpose in this restructuring to allow transfers to be effected gradually over a number of years. Section 203 has the purpose of accelerating that process dramatically. Without careful, well-planned, and immediate action, however, it can cause major disruption.

Whatever basic research the Department of Defense does, it must in some way decide for itself. Research it is doing beyond that, and which, because of its nature, the country needs, ought to be carefully reviewed and handled in a special way.

Most importantly, we must be very careful that, in making program transfers, our most talented young people are not adversely affected. It would be especially unfortunate if competition between the recognized high-quality transfer projects and the new projects of our younger investigators resulted in alienation of these new young talents. We can ill afford a lost generation of science skills.

#### SUBCOMMITTEE'S INVOLVEMENT

Long before the distinguished Senate majority leader spoke out against Defense Department research, our subcommittee had been examining the question of scientific research and its relationship to the goals, objectives and functions of Federal agencies. We have made numerous recommendations to this body. It has been the subject of the distinguished report done for the Committee on Science and Astronautics by the National Academy of Sciences in 1965, entitled "Basic Research and National Goals." It has been the topic of discussion at two of our formal annual meetings of the Committee's Panel on Science and Technology, in 1966 and 1967.

The conclusions drawn from all of these efforts have shown a basic consensus that mission-oriented agencies have a responsibility—an obligation—to conduct a certain amount of basic research so as to be able to innovate in the applied area and to insure the capability to meet future needs.

#### DEFINITIONS

By basic research I mean research which at present may only vaguely seem as presenting prospects for direct application. Nonetheless, such basic research is a vital investment in our national future. It is directed not at solving the problems of today but at providing the knowledge for meeting unforeseen problems of tomorrow. It is a means of insuring that we have what Churchill called the tools to do the job.

Let me elaborate. We have an obligation today to the future, particularly when we are in competition with an economic system and an ideology which emphasizes the benefits of long-range planning. I do not have to remind this body of the fact that three of the most significant scientific and technological developments of the century—nuclear fission, radar and jet propulsion—were all based upon fundamental work done mainly from abroad. It is true that since then, we have done well. Nonetheless, until the massive mobilization of American science during World War II, we routinely looked to Western Europe for the scientific ground breaking needed by our technologies. And since that time, much of the finest fundamental research—including Charles Townes' laser—has been supported with funds from mission-oriented agencies with no firm goals in mind.

It is axiomatic that no modern American corporation would dare to cut itself off from future-oriented research. It is this research, often not related to products and services of the day, that so often will determine the profit-and-loss statement and the industrial standing of the company 10 years later. Similarly, the future of this Nation cannot rest upon an accidental, ad hoc science policy. We have to plan and make provisions for the future. This is the raison d'etre for our faith in and support of basic research.

### OUR DECENTRALIZED SYSTEM

Since World War II we have successfully relied upon the principle that each department and agency which needs science and technology shall both carry on the short-term research and development to resolve immediate problems and also sponsor and conduct the exploratory research which can well shape its future. We have always thought it more healthy for our agencies and for the health of American science that each agency fund a certain amount of high-quality future-oriented research without regard for an immediate connection with present problems. Our own investigation shows that such involvement is necessary and vital. Our agency heads are responsible not only for meeting the issues of the day, but for preparing to meet the issues of tomorrow. For this, they have to look and work ahead.

Dr. Lee DuBridge, the President's Science Adviser, testified recently before my subcommittee:

> We encourage every agency which has major technological enterprises under way to spend a portion of its funds to support fundamental science. Such agencies select those areas of fundamental science which appear to be most relevant to their agency missions, although the term "relevance" needs to be interpreted broadly since the results of science are always in part unforseeable.

The pluralistic system of supporting science has served us well. That system has in many ways provided an open market place where ideas could compete for attention. We do not claim that it is free from fault. But it does have many years of success behind it. So far, no other system suggested to replace it has received tangible support.

It would be a national tragedy were other Federal agencies to adopt the theme of section 203 and find their research limited to short-term, well-defined, highly visible needs. This was the fate of the buggy whip makers and the wagon craftsmen who kept on working to improve their whips and wagons long after the internal combustion engine had arrived. Our departments must continue to sponsor and carry on future-oriented research that can and will respond to the new discoveries and progress in science.

### RESPONSIBILTIY FOR RELEVANCE

If "relevance" is to be emphasized, an appropriate question is: who should have the responsibility for determining the degree of relevance of research to the goals, objectives and functions of our Federal agencies?

I believe this the the first responsibility of the mission-oriented agencies themselves. It is they who must continue to assume the primary responsibility for demonstrating the functional relevance of the research they support. This point was emphasized by Mr. Elmer Staats, the Comptroller General, in his recent testimony before Congress—

> I believe that the determination on individual research projects, after these guidelines have been established, has to be made pretty much within the Defense Department. We may want to test some of these . . . but it is somewhat a subjective kind of judgment in many cases.

While I agree that outside advice may be needed for questioned projects, I doubt if it is a proper role of the National Academy of Sciences to place itself in an adjudicating position with regard to relevance—an idea that has been suggested by the distinguished Senate majority leader. Perhaps the Secretary of Defense should request, as an alternative, that the Academy make a review in collaboration with the already constituted Defense Science Board, which does have extensive knowledge of defense needs. Or, for that matter, the President could decide to convene a special study panel from among the members of his President's Science Advisory Committee to undertake such a review. And this Congress should most certainly be involved in the determination—having made the recommendation to which we have referred.

The point is, however, that as we go about apportioning our national resources for scientific research, we must continue to realize that "relevance" itself needs to be interpreted broadly. And I repeat again—it is the primary responsibility of the individual mission-oriented agency to make the judgment, according to its own view as to its future needs and potential problems. This does not mean improvement should not be fostered. The hearings of our subcommittee into the way in which our science resources are administered and organized is, in fact, aimed in this very direction.

### A TIME OF TRANSITION

Today, our mission-oriented agencies account for some 80 to 85 percent of the total Federal support for basic research. This is, in itself, largely the result of historical circumstance.

The National Science Foundation, when it was established in 1950, was conceived as the principal agent for the support of fundamental research in the Federal Government. However, from its earliest days, the Foundation never received funds to carry out this role adequately. Instead, while the NSF was being formed and, afterwards, as it grew, basic research being performed in mission-oriented agencies was jealously guarded. Much of this work would have been done in the NSF had it been formed earlier. But it was not, and thus our philosophy of decentralized science support took form, with the Defense agencies becoming a major source of funds.

Now we are in a period of transition. Many of the mission-oriented agencies are beginning to retrench in their support for basic research. This retrenchment is caused not so much out of belief that basic research is no longer relevant to their functions or missions, but is the result of severe budgetary stringency. In this process, much good has come, and, as anticipated, the National Science Foundation is playing a key role.

Already the National Science Foundation has been asked to take responsibility for $19 million in research projects, largely from the Department of Defense. In addition, and estimated $20 to $30 million in projects is also being considered for transfer to the Foundation because of mission agency budget cutbacks. It is apparent that the total could easily reach $200 to $300 million in the near future.

Section 203 not only compounds this problem, but presents two very serious potential dangers.

First, it is clear that American science is already in an unhealthy situation. It is rapidly being backed into a situation whereby no "new starts" will be possible. Because of the present decline in funding for research, Section 203 has the potential of encouraging not only the Department of Defense, but other mission-oriented agencies, to cut back their support for university research more heavily than they might otherwise under the same circumstances. As a result: improvements in the quality of our college and university science departments and curricula must be terminated or delayed indefinitely; scientifically excellent projects are continued at the expense of new and innovative projects; and our most promising and talented young students are discouraged from entering the scientific profession. These are things the Nation can ill afford to let happen.

Second, there is the dangerous effect of creating an even more intense polarization between the Defense Department and the university community. The Senate majority leader has pointed out that the intention of section 203 is not to "ban the Defense Department from sponsoring research in universities." Nonetheless, the seed has been sown. And such a polarization would work to the detriment of both the Defense Department and the universities.

We must recognize that much current criticism is against military participation in research. At the same time, many of these programs are necesary to the country, and our research effort should not suffer simply because a military label has been attached. There must be a gradual adjustment here in the best interests of the country—as we on the Science Committee have stressed time and time again.

The interaction between the Department of Defense and the university-based research community is of profound significance and importance to the Nation and its future defense position. The unique resources of scientific excellence in the university community are of critical importance if we are to meet effectively the increasing complexity of our national security problems.

It is obvious that if this relationship is not continued the Department of Defense will necessarily move elsewhere to fill the need. In turn, this will have the effect of removing the academic community from its critical role of informally monitoring such activities and through which it has provided balance and judgment in the past.

Similarly, the universities themselves have a unique opportunity through interaction with the Defense Department to make important inputs into the shaping of our future national security policies.

The level and degree of this interaction is a most delicate problem. Having had the opportunity of testifying before the Pounds Panel in its deliberations on the future of MIT's two off-campus research laboratories, I am keenly aware of the great sensitivities of this issue. There is no question in my mind about the pressing needs to begin to apply our great scientific and technological expertise to the many civilian problems that confront this Nation. However, we must be ever mindful of the need to balance these efforts with those necessary to maintain the national security.

### TRANSITION MECHANISMS

Mr. Speaker, there may be some areas of work which have been or are being supported by the Department of Defense that could be more properly supported by the National Science Foundation. Scientific research is a dynamic process subject to continual change. Similarly, agency mission requirements are also subject to change. Our guidelines and criteria for support of research in the mission agencies should, therefore, reflect the dynamic nature of these changing requirements.

Nonetheless, given the present fiscal stringency and the reductions in agency budgets, it is clear that some of the highest quality research will have to be either terminated or transferred. Of course, it is one thing to talk generally about arrangements to effect a smooth and orderly transfer, and another to see that such arrangements actually materialize. One thing required, beyond coordination between the agencies involved, is close collaboration between them and the committees of Congress. We all have an obligation to see that programs worthy of support are transferred and that such transfers are, indeed, planned and not just accidental. Such arrangements should also provide for transfer of projects as on-going entities, complete with funds, equipment and facilities.

For the Defense research affected by section 203 which should be continued in the national interest, and for which the National Science Foundation or other agencies do not have funds in their fiscal year 1970 budgets to take over, it becomes important that the Defense appropriations provide some funds for transfer. Then, adjustments can be made in the various fiscal year 1971 budgets which will be presented to the Congress next month in the President's budget message.

Such arrangements should be possible. Consider, for example, the National Science Foundation. The present statutory authority of the National Science Foundation provides for exactly this eventuality. Section 3(b) of this statutory authority states:

> The Foundation is authorized to initiate and support specific scientific activities in connection with matters relating to international cooperation or national security by making contracts or other arrangements (including grants, loans, and other forms of assistance) for the conduct of scientific activities. Such activities when initiated or supported pursuant to requests made by the Secretary of State or the Secretary of Defense shall be financed solely from funds transferred to the Foundation by the requesting Secretary as provided in section 15(g), and any such activities shall be unclassified and shall be identified by the Foundation as being undertaken at the request of the appropriate Secretary.

Should such a funding procedure be followed on a large scale by the mission—oriented agencies, new statutory authority would probably be desirable. But this does illustrate that there is a feasible procedure for funding mission-oriented research through the National Science Foundation, and that the Congress has favorably considered the issue in the past.

Nonetheless, we should not focus solely upon the question of transferring projects from the Department of Defense to the National Science Foundation. Other agencies, such as the Departments of Housing and Urban Development, Transportation, and Commerce need to expand their own research and development efforts.

### SUMMARY

No matter how much we may be concerned about the effects of section 203, it is now a matter of law. How it is administered by the Defense Department and how the Congress and the General Accounting Office will oversee its implementation are the matters now before us.

It is critical that any transfers be effected in an orderly, time-phased manner. When necessary, these should extend over a number of years.

Fiscal year 1970 is virtually half gone and the Defense appropriations are not yet made. Even were the bill signed into law this afternoon, the Bureau of the Budget and the departments would still need time to allocate the funds to the research administrators. By the time this is done, we will be well into the third quarter of the fiscal year.

I further propose as a matter of policy that the Congress relate section 203 to the fiscal year 1971 budget, which is even now being prepared, rather than to expect it be given full effect in the remaining quarter of this fiscal year.

The problem we are faced with is far too serious and far too long range to be dealt with summarily. This is especially so since budget cuts already made have caused intensive review of science programs, and further action should be carefully accomplished with long-range objectives in mind.

Mr. Mansfield discusses

Defense Department

Research Projects and

Studies

Mr. MANSFIELD. Mr. President, it will be noted from that memorandum that the Office of the Secretary of Defense passed the word throughout the Defense Department that any project which does not comply with section 203 must be terminated in an orderly way as soon as possible. In addition, the Department is reviewing all current studies and projects as well as the selection criteria used to evaluate proposed work to assure that the criterion will be applied explicitly in every case. Furthermore, in addition to the internal review now begun, the National Academy of Sciences has been asked by the Defense Department to carry out a complete examination of all projects and studies in the gray area—those projects and studies that do not have a readily apparent military application—and to adjudge independently which do not meet the criteria of section 203.

The gray area in my judgment would certainly be larger than those projects presently sponsored under the heading of basic research. In other words, some applied research certainly would fall within the possible challenge of section 203.

Dr. Packard's response is positive and constructive, and is to be commended. I am well aware of the magnitude of the change required by section 203, but I am encouraged by his attitude that its implementation can go forward in an orderly, thoughtful way. With such a positive attitude, precipitate, last-minute action that might seriously disrupt research projects can be averted. Our joint emphasis will be the orderly transfer to other agencies of projects that do not meet the criteria of section 203.

Several points bear repeating. Section 203 is not intended to cause needless disruption of high quality research; nor is Secretary Packard's attitude indicative of an intended overresponse.

Section 203 has the positive aim of reducing the dependence of basic, scientific research upon military appropriations. Let us be specific on this point. It affects military support of those scientists who pursue the uncovering of new knowledge in whatever direction and way they find most interesting. This is the basic research of which Dr. Vannevar Bush wrote so eloquently in his report to President Truman about scientific research after World War II. Section 203 contemplates that scientists whose interests and way of work focus upon solving problems may continue to receive military funds provided their research has a direct and visible relationship to military needs.

Section 203 does not ban the Defense Department from sponsoring research in universities, or in not-for-profit research institutions. The Defense Department retains ample authority to fund research by university scientists who wish to apply their talents to solving problems of national defense.

Section 203 is not intended to disrupt the work of any scientist simply because his work now funded by defense appropriations does not meet the new criteria. The cooperative attitude apparent in Secretary Packard's letter encourages me to expect that the Defense Department, the civil departments and agencies, the Bureau of the Budget and Congress can arrange for the orderly transfer of quality research projects that should be continued by other agencies, and for appropriate funding arrangements.

Section 203 makes it abundantly clear to students, to scientists, to officers of universities and not-for-profit institutions and to industrial contractors that money received from defense appropriations for research is needed to carry out a specific military need or function and is directly related to the defense needs of this country. No need is of higher importance. The work that will be sponsored by the Defense Department will be able to stand on its own feet and meet the true and open test of a valid need of the Department. The National Science Foundation and other civil agencies will be charged with the responsibility for continuing the investigations that expand our existing base of knowledge in the various scientific disciplines.

As I said on November 6, the performing of research to meet the needs of defense is honorable work. Scientists and universities who receive defense funds for a valid defense need should be proud, never ashamed. It is only when the sponsorship of a project is questionable or the subject matter of the mission is questionable does an element of doubt enter the relationship.

Section 203 reminds all of us that scientists who are interested in problem-solving are just as much a part of the scientific community as are those who pursue knowledge for its own sake. Both outlooks are necessary not only for defense, but also for resolving the many urgent civil problems of our Nation.

In carrying out section 203, we can now expect the Defense Department to identify its needs for research to further defense science and technology, and to publish these needs so that well-qualified, problem-oriented scientists can match their interests and abilities with the defense needs. Some of the requisite research in the future will be suitable for universities and nonprofit institutions. And I would expect it to be carried on in a close, collaborative relation with the Department's research administrator and its own laboratories.

Naturally, I expect that the total of defense-funded research will decrease as section 203 takes effect. I would point out, however, that section 203 is not intended to stimulate a transfer of funds to in-house defense laboratories. The thrust of section 203 is to confine the type of research sponsored by the Department of Defense—not simply to change the identity of the Defense contractors. The latter would be senseless subterfuge.

To expedite the working out of arrangements for orderly transfer of researce concerned to other agencies, I have written to the Director of the Budget Bureau and to the Comptroller General. Today I have written to the President of the National Academy of Sciences and to the heads of the National Science Foundation, the Department of Health, Education, and Welfare and other civil agencies to urge their cooperation with the Defense Department and with the Congress in working out final arrangements for the orderly transfer of projects and funds.

The working out of section 203 will be difficult. Nevertheless, whatever the temporary difficulties may be in the long term both the Defense Department and the Nation will benefit from the assertion of the principle in section 203.

And, in conclusion, I would again congratulate the Defense Department for its positive and cooperative response to section 203. I am confident that together the Congress and the Department of Defense will be able to implement the prescription of section 203 and accomplish what is truly in the best interests of the Department and contribute significantly to a healthier attitude in our society toward those who perform research and those who sponsor it.

EXHIBIT 1

NOVEMBER 20, 1969.

Hon. MELVIN R. LAIRD,
*Secretary of Defense, Department of Defense,*
*Washington, D.C.*

DEAR SECRETARY LAIRD: The consideration of the military procurement authorization bill—entailing many weeks of consideration by the entire Senate and the House—reflected a growing interest on the part of Congress in the specifics of the recommendations contained in military expenditure bills. One provision of this year's bill—which is now law—is Section 203 which, as you know, was added by the Senate and retained by the House. The intention of this section is rather clear. The language really needs no explanation since it specifies a restrictive policy with respect to the sponsorship of research by Defense. I was added by the Senate with the specific intent to reduce the sponsorship by the Department of Defense of non-mission oriented research—research that did not have a direct *and* apparent relationship to a specific mission of the Department of Defense.

Over the past two decades, the Department of Defense has sponsored far-reaching and significant research throughout the full spectrum of science. The contributions that have been made to the health and vitality of the Nation's scientific structure by the Defense Department is not disputed. However, the language of Section 203 expresses a clear policy of Congress to reduce this dependency by the scientific community on the Department of Defense. The National Science Foundation was established in 1950 to contribute the Government's share to maintain a proper level of scientific inquiry—investigations for the pursuit of knowledge per se.

I was greatly dismayed upon being informed of Dr. John Foster's attitude with respect to Section 203. In answering a letter from Senator Fulbright concerning the Defense Department sponsorship of a study of birds, he expressed the belief that Section 203 would have no effect on that study or on the operations of his office and the research that was being sponsored. The Congress of the United States does not attempt to enact futile gestures; it should be most resentful when an Executive agency decides to ignore its clear expression of intent.

I am writing today to Mr. Staats, the Comptroller General, and requesting him to establish appropriate guidelines and machinery to determine the effectiveness of Section 203 and to return a preliminary finding prior to the consideration of the appropriations bill this year.

I think an appropriate test of these guidelines would be to determine what impact they would have had on last year's expenditures if it had been enacted last year.

With warm regards, I am

Sincerely yours,

MIKE MANSFIELD.

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THE SECRETARY OF DEFENSE,
*Washington, D.C., December 2, 1969.*

Hon. MIKE MANSFIELD,
*U.S. Senate,*
*Washington, D.C.*

DEAR SENATOR MANSFIELD: I thank you for your letter of November 20 inquiring about the Department's views regarding Section 203 of the Military Procurement Authorization Act. We appreciate your concerns and would like to explain our position.

There is absolutely no question that the Department will comply fully with the law I have directed all components to review critically all current and proposed research and development projects and studies to ensure that they have a direct, apparent, and clearly documented relationship to one or more specifically identified military functions or operations. Any project or study which does not fulfill the criterion of Section 203 will be terminated. For your information, a copy of my memorandum on this matter is enclosed.

In addition to this comprehensive review within the Department, we have contacted the National Academy of Sciences and invited them to consider carrying out a complete examination of all projects and studies which might be regarded as marginal under the provisions of Section 203.

With respect to Dr. Foster's recent letter to Senator Fulbright concerning the impact of Section 203, I have discussed the issue in detail with Dr. Foster. He shares without reservation my firm intent to comply completely with the law.

I intend to follow this issue closely and personally in the future, and to cooperate fully with Comptroller General Staats in his review of this matter. Please be assured that in our FY 1971 budget requests and program plans, we will reflect detailed consideration of the intent of Section 203 in relation to Defense needs for research and development.

Sincerely,

DAVID PACKARD,
*Deputy.*

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THE SECRETARY OF DEFENSE,
*Washington, D.C., December 2, 1969.*

Memorandum for the Secretary of the Army, Secretary of the Navy, Secretary of the Air Force, Director of Defense Research and Engineering, Assistant Secretaries of Defense, Directors of Defense Agencies

Subject: Section 203 of Military Procurement Authorization Act.

Section 203 of the Military Procurement Authorization Act, P.L. 91-121, approved November 19, 1969, provides as follows:

"Sec. 203. None of the funds authorized to be appropriated by this Act may be used to carry out any research project or study unless such project or study has a direct and apparent relationship to a specific military function or operation."

This provision is, in effect, reiterative of the legal principles and longstanding RDT&E policies which have governed and will continue to govern the use of Defense appropriations for RDT&E. activities. However, insufficient attention has been given to making clear to the Congress the basis for deciding to support work in a particular field, and particularly the connections between relatively basic research and the long-range Defense problems and missions which require such research.

In order to assure full compliance with the intent of Congress as expressed in Section 203 addresses are requested to assure that prior to the approval of a new research project or study, or the continuation, modification or extension of an existing research project or study, the project manager furnishes a written statement which describes, as clearly and simply as possible, the project or study and its purpose, together with its direct and apparent relationship to one or more designated military functions or operations. Any project which does not have a direct and apparent relationship to a specific military function or operation must be terminated in an orderly way as soon as possible.

I have asked Dr. Foster to work with you in reviewing all current RDT&E efforts, as well as selection criteria used to evaluate proposed RDT&E studies and projects. The purpose of this review will be to assure that the long-standing Department policy, requiring that the criterion of relevance-to-military-missions be applied throughout the RDT&E program, has been and is being applied explicitly in every case. If necessary, please consider supplementing the appropriate directives to ensure that the provisions of Section 203, P. L. 91-121, are followed completely.

In summary, addressees are requested to take all necessary actions, beginning immediately, to comply fully and scrupulously with the law. Under no circumstances shall the Department support work which does not have a direct, apparent, and clearly documented relationship to one or more specifically identified military functions or operations.

DAVID PACKARD,
*Deputy.*

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13. ABSTRACT

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 presents highlights of chemical methods from the program and includes papers on kinetic methods, electrochemical methods, chemical lasers, trace element analysis, photoionization and photoelectron spectroscopy. The second section contains summaries of program statistics. The third section consists of factual summaries of each project completed during fiscal year 1969.

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