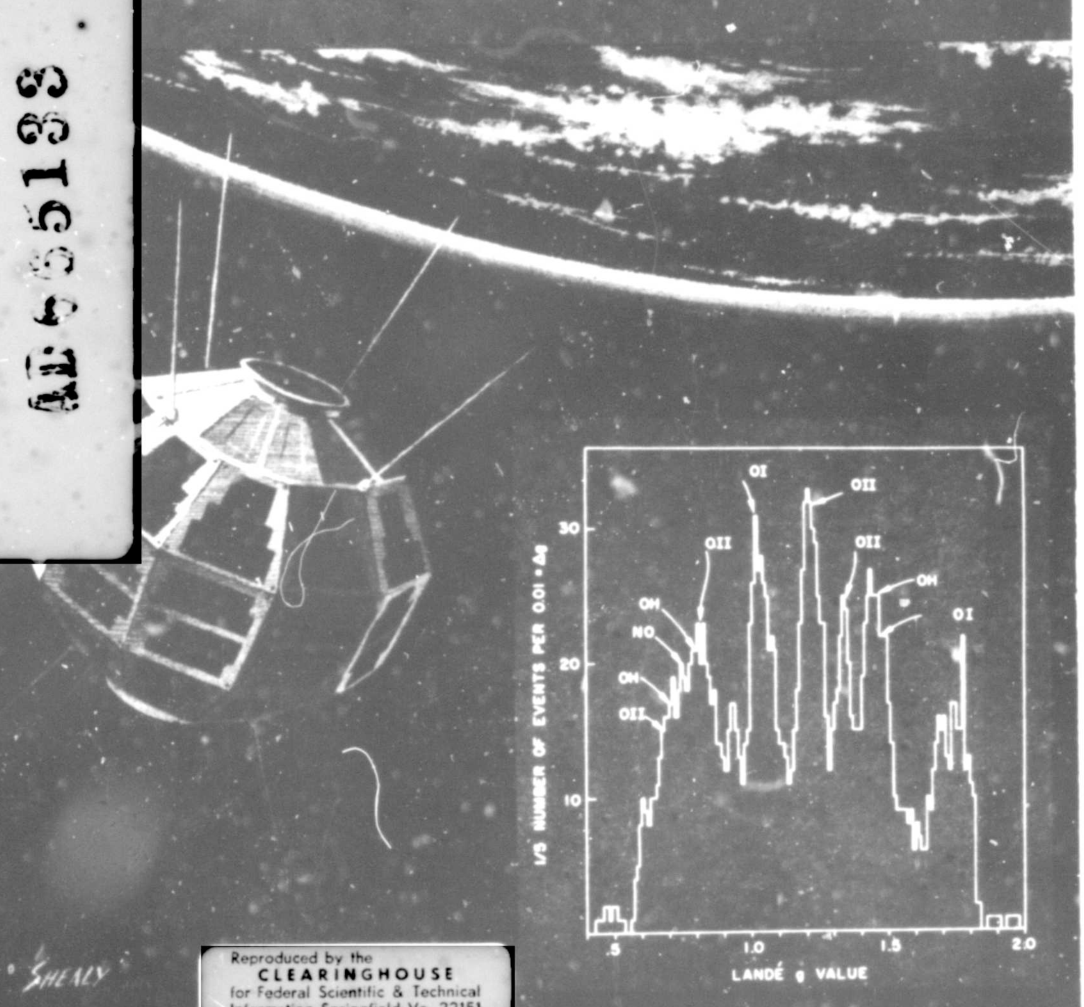
AFOSR 67-2237

13th annual CHEMISTRY program review



AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Office of Aerospace Research ★ United States Air Force
Fiscal Year 1967

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13th annual CHEMISTRY program review 1967

THE COVER

The cover illustration protrays the detection of free radicals in the Earth's atmosphere with satellite borne instrumentation. The various species encountered are identified in the graph. This contribution was made by Prof. Willard Libby and associates (AFOSR Program in Space Chemistry, University of California, Los Angeles) in cooperation with others. A more detailed description of the experiments commences on page 8.

The cover artist was Mr. Charles P. Shealy of the Presentations Division of OAR.

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AFOSR 67-2237
December 1967

DIRECTORATE OF CHEMICAL SCIENCES PROGRAM REVIEW

Fiscal Year 1967

Dr. William L. Ruigh, Scientific Editor
LtCol Edward T. Walford, Managing Editor

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
Arlington, Virginia 22209

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

December 1967

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

Relatively speaking, our AFOSR support of DOD pertinent chemical sciences has steadily declined in the sixties. With the cut in FY 68 funds we returned to less than our FY 65 level of appropriated dollars. Faced with this dilemma, I asked the National Academy of Sciences to suggest what specific areas of chemistry - from Air Force point of view - should have primary emphasis in our future program selection. Their reply is printed in full in the Appendix of this report for your information.

Also for your information we have included in the Appendix a copy of our "Note to Proposers." It tells about our mode of selection and our philosophy of operation.

This 13th Annual Chemistry Program Review is our report to you of our action in response to your kind assistance in the evaluation of significant scientific problems in chemistry and the investigators to carry them out. It is also an account of the accomplishments and the expenditure of public funds. This year we have again emphasized the Air Force relevance of selected accomplishments as well as their scientific significance. We find both factors important and inseparable in our mission-oriented agency.

In our future selections of research efforts, the emphasis will be on the daring and novel, with great potential pay-off to the science of chemistry and therefore to the United States Air Force and our Country's defense.

Sincerely

AMOS G. HORNEY
Director of Chemical Sciences

AFOSR

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December 1967

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*On leave September 1967 - June 1968 for Research and Study at the University of Wisconsin.

MISSION

The mission of the Directorate of Chemical Sciences of the Air Force Office of Scientific Research is 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.

To achieve this mission 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 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 achievement of technological superiority.

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INTRODUCTION

We present our annual Chemistry Program Review. This review provides for a unified account of the research being supported by the Directorate of Chemical Sciences and its relatedness to the AFOSR mission.

Appearing in the first section are a few high-lights from our program written in a style which we hope will be of interest to the non-specialist. In these stories of accomplishments, as in the selection of projects to be supported, the relevance of the research to the future Air Force applications is an important consideration. In the final major section of the review a factual summary is provided for each project which expired during fiscal year 1967.

A written review of this sort requires the time and patience of other individuals in addition to the permanent scientific staff. Major Orville Rollins, on reserve duty in the office, assisted in assembling the statistics which appear in the middle section. Special thanks go to Mrs. Mary Koval, Mrs. Elizabeth Lewis, and Miss Kathryn Miner for the many tedious hours spent in preparing the draft and final copies. Thanks are also due to Mrs. A. G. Horney for the arduous task of proof reading the manuscript for errors in syntax.

ELECTROCHEMISTRY

by Lt. Col. Edward T. Walford

Electrochemistry is one of the great meeting places between chemistry and physics. Advances in this field have traditionally been shared by these sciences since Volta developed the first battery in 1800 and Faraday related this phenomena to chemical change by his electrolysis studies in 1834. Today, civilian, industrial, and military activities are all highly dependent on electrochemical energy conversion devices. The military establishment depends on these devices to perform many of its communications functions such as command, control, and information transfer. Many small and special-purpose vehicles are powered or will be powered by batteries and fuel cells. Auxiliary power is provided for another group of vehicles such as aircraft and space systems. Electrochemical devices are also much in demand as mobile power sources for field use or as remote power sources which require unattended operation. The applications for these devices are extensive and vital to the daily missions of the armed forces. During the present period of rapid advances in electronics, batteries have become even more important. New requirements are constantly developing for batteries of higher energy density, wider range of operating temperature, and longer storage and operating lives.

In view of the above it is interesting historically to note how the electrochemical field has developed since Volta and Faraday. The most important storage battery in use today, the lead-acid battery, was developed by Plante in 1860. Our present dry cell was developed by Leclanche in 1866. The nickel-cadmiun alkaline cell was first developed by Jungner in 1899. While the applications for fuel cells have only appeared in this decade, the original descovery of the principle is credited to Grove in 1839. It seems evident that electrochemical devices in use today are simply improved versions of the discoveries of the last century![1]

The improved batteries and fuel cells of today are based primarily on improved technology rather than new science. These improvements have generally resulted from advances in compositions and forms of the materials used or from new machinery or processing methods. While these innovations sometimes led to a better understanding of the basic phenomena, the electrochemical process has mostly remained shrouded in mystery. A recent important study[2] on this subject has concluded that "the lack of fundamental understanding of the statics and dynamics of electrochemical systems is a substantial deterrent to progress in electrochemical energy conversion."

The general areas which should be emphasized in a fundamental electrochemistry research program can be classified as follows:

(1) Thermodynamic and transport properties
(2) Electrochemical kinetics and catalysis
    (a) Structure of the electrode-electrolyte interface
    (b) Charge-transfer processes
    (c) Mechanism and kinetic studies for specific electrode reactions
    (d) Development of new methods for the study of electrode processes

The Directorate of Chemical Sciences recognizes the relevance of electrochemistry to the Air Force and attempts to maintain a significant program in this area. Some examples of the present efforts are described below.

References

1. "Primary and Secondary Galvanic Cells; History and State-of-the-Art Summary," Euler, VARTA AG, Germany, (1967).

2. "A DOD Research Program for Electrochemical Science with Applications to Energy Storage and Conversion," Editor, G. C. Szego, Institute for Defense Analysis, Study S-208, (1965).

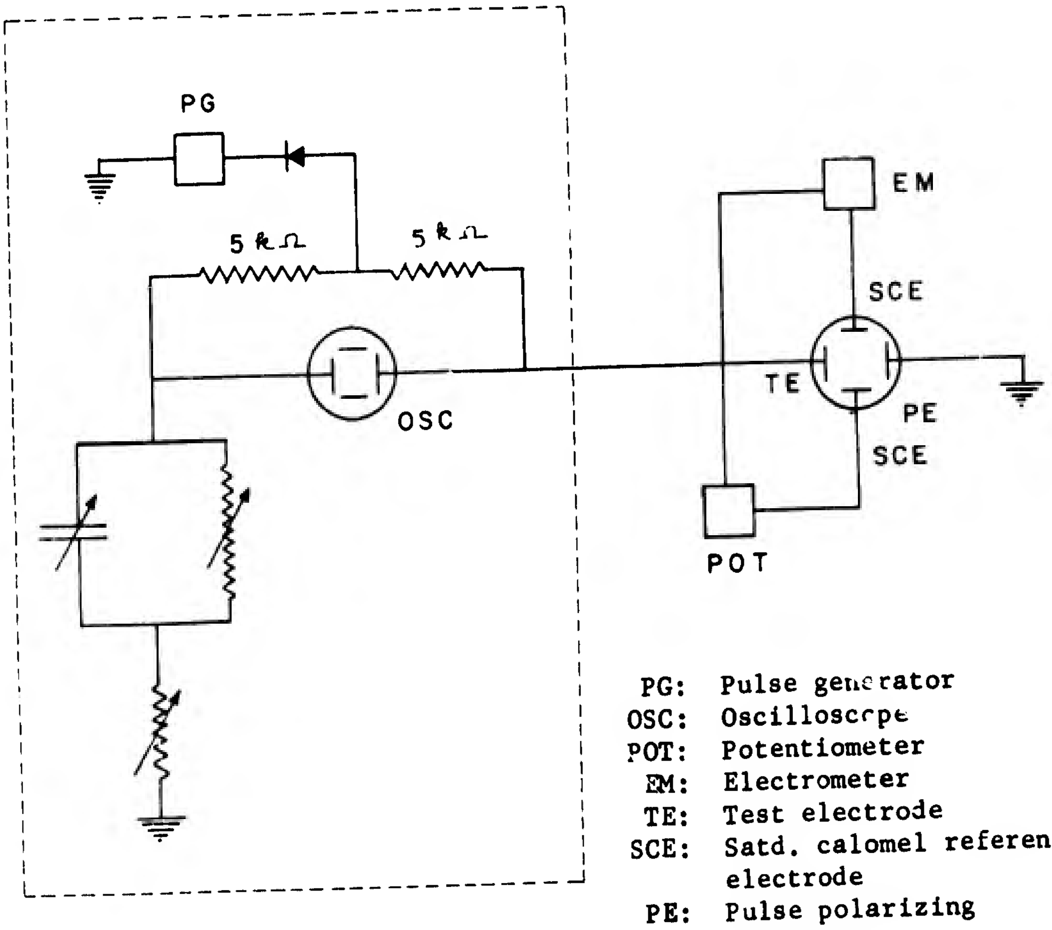
ELECTRICAL DOUBLE LAYER

One of the keys to a better understanding of the electrochemical energy conversion process is what electrochemists have termed the electrical double layer (e.d.l.). It consists of layers of ions of opposite charge immediately adjacent to the electrode and is only a few Å in width. Its structure and the processes which take place within it are complex and little understood.

The e.d.l. can be characterized best by surface tension measurements and by measurements of the differential capacity. However, the peculiar properties of solid electrodes have long posed difficulties in the interpretation of data obtained in kinetics and e.d.l. studies. Surface tension measurements for solids are not sufficiently accurate so that only differential capacity data can be used.

Dr. Schmid at Florida has been investigating the e.d.l. by making a direct comparison of the differential capacities of liquid electrode systems and solid electrode systems. This unusual experiment is being accomplished by using a Hg electrode and a conducting liquid ammonia electrolyte. The measurements are then made at temperatures slightly above and slightly below the melting point of Hg. The systems are therefore identical chemically and only vary in the structure of the electrode surface.

To solve the problems inherent with solid electrode systems Schmid has developed a capacity bridge which operates on high frequency pulses of less than 100μ sec duration. The experimental set-up is shown in Fig. 1.



PG: Pulse generator
OSC: Oscilloscope
POT: Potentiometer
EM: Electrometer
TE: Test electrode
SCE: Satd. calomel reference electrode
PE: Pulse polarizing electrode

Fig. 1 A D.C. Pulsed Bridge for Differential Capacity Measurements

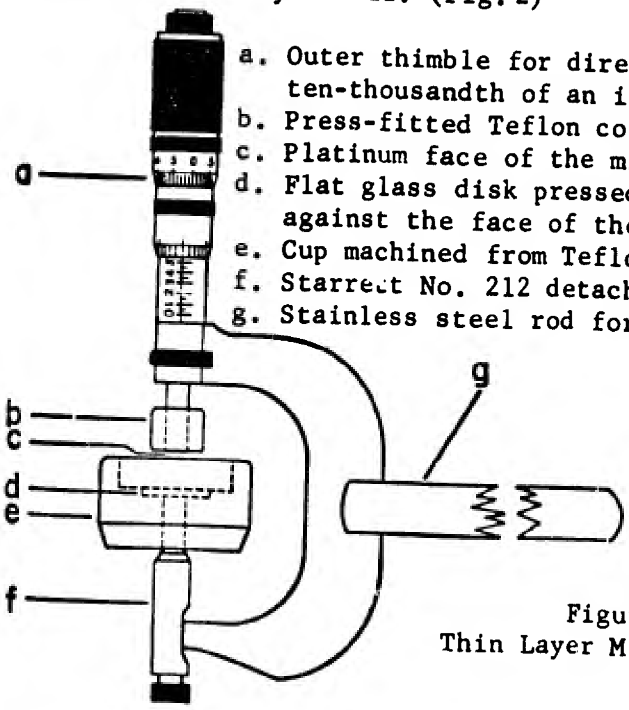
The oscilloscope is used as a null instrument so that the precision of the measurements (presently less than 0.5%) is limited only by the circuit elements of the bridge.

The measurements are then used to obtain a quantitative interpretation of the charge structrue of the e.d.l. It should answer the question as to what extent e.d.l. measurements are influenced by structural characteristics of the electrode surface. In addition Schmid's work should determine to what extent the ideas developed and tested on liquid electrodes can be transferred to solid electrodes.

THIN LAYER ELECTROCHEMISTRY

The chemical nature of the electrochemical process must also be investigated to completely describe the energy conversion process. In particular, kinetic and mechanistic studies must be made of the chemical reactions which occur prior to or following electron transfer. The last decade of electrochemistry has seen the development of a variety of techniques readily adaptable to studies of this nature. One of these methods, thin layer electrochemistry, has been adapted and improved by Drs. Reilly and Murray, co-investigators on an AFOSR grant at North Carolina.

Reilly and Murray have developed a micrometer type twin-electrode thin-layer cell. (Fig. 2)



a. Outer thimble for direct reading to one ten-thousandth of an inch
b. Press-fitted Teflon collar
c. Platinum face of the micrometer spindle
d. Flat glass disk pressed into the Teflon cup against the face of the detachable anvil
e. Cup machined from Teflon
f. Starrett No. 212 detachable anvil
g. Stainless steel rod for mounting cell assembly

Figure 2
Thin Layer Micrometer Electrode

The apparatus provides fast and direct criteria for the diagnosis of systems of interest because of its relatively unique characteristics: rapid mass transfer, large ratio of electrode area to cell volume, and the generation of steady-state rather than transient currents under certain conditions.

In the usual method of operation the cell is loaded with an appropriate electrolyte and the cell thickness is set. (An important advantage of this technique is that the thickness of the solution is accurately known and can be easily varied from 1 cm to 1 x 10^{-3} cm). The electrodes are placed at a potential which does not disturb the system under study. A step potential is then applied to the system and the current response is observed. The current response may be zero, steady state, or changing with time. Under these three types of responses, there exist at least fourteen types of systems which can be studied. The apparatus has been used to obtain equilibrium constants, rate constants, diffusion coefficients and adsorption parameters.

The experimental arrangement of the working electrodes in the thin layer cell allows the simple substitution of different electrodes. The investigators plan to study various electrode materials such as graphite, conducting glass, and silicon carbide. The method should also be ideal for detecting surface oxidation or reduction of the electrode materials.

References

1. "Thin Layer Electrochemical Studies Using Controlled Potential or Controlled Current," Oglesby, Omang, and Reilly, Anal. Chem., 37, 1312 (1965).

2. "Diagnostic Criteria for the Study of Chemical and Physical Processes by Twin Electrode Thin Layer Electrochemistry," Anderson, McDuffie, and Reilly, J. Electroanal. Chem., 12, 477 (1966).

ELECTROLYTIC SOLUTIONS

How does pressure affect the conductance of electrolytic solutions? This is the interesting electrochemical question which Dr. Fuoss of Yale has attempted to answer in his current research. A literature search showed that very little data were available for non-aqueous systems. Dr. Fuoss began by designing and constructing a high pressure apparatus which would permit measurements up to 5,000 atmospheres.

The effect of pressure on electrolytic conductance in solvents of high dielectric constant is primarily hydrodynamic;

viscosity is increased by increased pressure, and ionic mobilities and conductance are thereby decreased. The viscosity effect is especially important in the non-aqueous systems under study. For example, at 5,000 kg/cm^2 and 25°C, the viscosity of water is increased by about 350%.

In solvents of low dielectric constant,however, electrostatic forces between ions can cause association to clusters containing two or more ions. This association phenomena also tends to reduce the conductance of the electrolyte. In the past this effect has been studied by using mixed solvents of varying ratios to vary the dielectric constant of the medium. As the dielectric constant increases with pressure, Fuoss has been able to study the effect of association in a medium whose chemical composition remains unchanged, while its electrical properties are varied in a controlled manner.

The apparatus used consists of a high-pressure chamber with a cylindrical cavity which contains the measuring cell. The principal measurement is conductance as a function of pressure for a variety of electrolytes in a variety of solvents. In order to analyze the conductance data it was also necessary to measure density, viscosity, and dielectric constant. A special torsion pendulum viscometer has been designed for the project.

While the viscosity effect is predominant in causing a decrease in conductance with pressure, the related effect of pressure on association is more complex. Fuoss has shown that in general the association constant for the electrolyte decreases as the dielectric constant of the solvent is increased. Exceptions such as NaBr in CH_3OH have been found which show increased association with increased dielectric constant. It is evident at this time that a large variety of solvents must be investigated before generalizations on the effects of pressure on ionic association can be made. Dr. Fuoss now plans to extend the scope of his work to include studies of ion-dipole and dipole-dipole forces in the solute-solvent system.

Reference

"Effect of Pressure on Conductance," Skinner and Fuoss, J. Phys. Chem., 70, 1426 (1966).

AEROSPACE CHEMISTRY

by Dr. Donald L. Ball and Dr. Alfred Weissler

"Aerospace chemistry" is a term applied to the chemistry of extreme conditions - very high or very low pressure and temperature as well as intense radiation. It encompasses the chemistry of the upper atmosphere: atoms, molecules, and ions in excited states and the reactions which they undergo. It is difficult, in fact, to provide a valid definition. Because of the varied and exhaustive demands of Air Force operations, there is a constant need to expand the list of topics included in the subject category.

In the pages to follow, some of the recent accomplishments in five selected research efforts are reviewed. This is but a partial listing of the extensive AFOSR sponsored activity in the field designated as "aerospace chemistry."

DETECTION OF ATMOSPHEREIC FREE RADICALS WITH RADIO WAVES BY EARTH SATELLITE (DLB)

The upper regions of the earth's atmosphere contain a diverse collection of high energy chemical species called free radicals. They are produced by the interaction of solar radiation and the more common chemical ingredients: N_2, O_2, H_2O. Each of these reaction fragments contain an unpaired electron formerly employed in the bonding of the parent molecules. Some are electrically charged (ions); their occurrence together with free electrons defines the ionosphere. It is quite logical, in fact, to regard these latter electrons as free radicals as well.

The nature of free radicals in the atmosphere, as well as elsewhere in space, has been demonstrated principally by gaps observed in the spectra of radiation emitted by the sun and other stars. Intervening free radicals selectively absorb certain frequencies. Recently, however, an "exciting" and sensitive technique has been applied by Prof. Willard Libby and coworkers at UCLA (AFOSR Program in Space Chemistry) together with his wife, Prof. L. Marshal Libby of the University of Colorado (supported by AEC). In this cooperative effort, aid was provided also by NASA and the Canadian Defense Research Telecommunications Establishment. The observations involved the reflection of radio waves generated within the Canadian Earth satellite Alouette II orbiting above the South Pole. The work is reported in Science, 156, 1730 (30 June 1967).

The basis of the method is that of electron spin resonance (ESR), which has been applied extensively in laboratory studies of free radicals. ESR involves the resonant absorption of microwaves due to the magnetic dipole moment of the unpaired electrons. Two quantum energy states are separated by an imposed magnetic field (Zeeman splitting). These correspond to dipole alignment either parallel or antiparallel to the applied field. The resonant frequency is proportional to the magnitude of this field, for microwave absorption about 3,000 gauss is used. The free radicals in the atmosphere are exposed to the earth's magnetic field--less than one-half gauss. In this case, the appropriate resonant frequency for absorption and reemission (i.e. reflection) is correspondingly less. It requires radiation in the megacycle range (radio waves).

The satellite Alouette II contained an ionosonder which alternately transmitted and "listened for" radio signals whose frequency was increased stepwise. Nine hundred steps were taken in thirty seconds covering the range 0.2 - 14.5 megacycles per second. Those signals, strongly reflected, provided indices for the concentration and identity of the free radicals present. The characteristic resonant frequency is determined by the total electronic environment of the magnetic dipole; in other words, it depends on the particular species in question and its state of electronic excitation. This is defined by the Landé g-factor, which is proportional directly to the resonant frequency and inversely to the magnetic field.

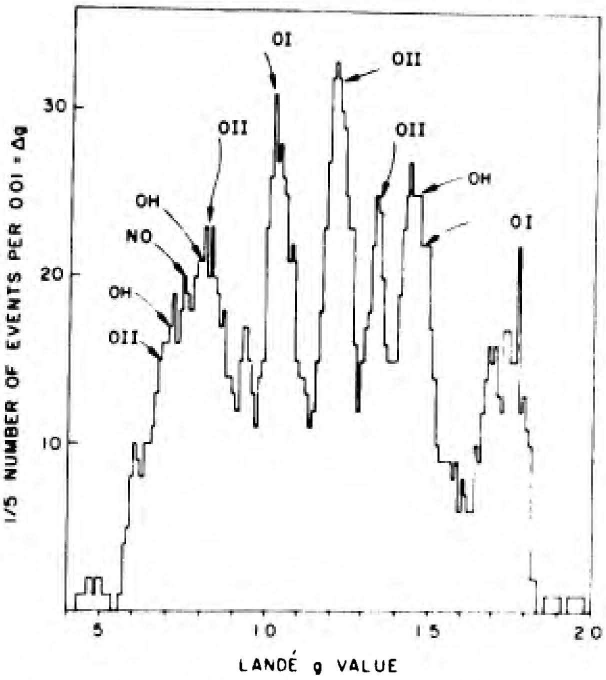


Fig. 3 Distribution of g values for about 500 signals taken from over 100 ionograms recorded above Antarctica.

Fig. 3 reveals the intensity of the reflected radiation as a function of the Landé g value. In most instances assignment is given to the individual free radicals responsible. These include both diatomic and atomic radicals: OH, NO, O, N, O^+, and N^+. The ionic species were principally in excited (metastable) states. The still stronger reflections due to free electrons (observed at g = 2.00) are not shown in the illustration.

The concentrations of free radicals detected by this extremely sensitive method were estimated to be as low as approximately $10^4/cm^3$. Further possible application is foreseen in experiments within more conventional, "Earth-based" laboratories involving free radicals not in their native environment.

THE INFLUENCE OF CHEMISORBED AMMONIA ON THE MOSSBAUER SPECTRUM OF IRON (DLB)

Still another example of resonant absorption of radiation is incorporated in the Mossbauer effect. Here, high frequency, gamma radiation (produced by nuclear decay) is absorbed by atomic nuclei possessing two appropriately separated energy levels. In practice, this match between source and target is sought by varying the relative velocity between them. Although a constant frequency radiation is used, the effective frequency is thus varied by the Doppler effect. The resonant frequency is measurably affected by the electronic environment of the nuclei, i.e., the chemical valence of the total atom and the surrounding electronic bonds. One example of a Mossbauer active isotope is Fe^{57}.

Dr. M. C. Hobson, Jr., of the Virginia Institute for Scientific Research in Richmond, has employed the Mossbauer effect to good advantage as a tool in studies of the chemisorption of ammonia on iron. In this manner the nature of the actual surface is examined; more conventional spectroscopic methods are markedly influenced by the adsorbed molecules themselves (they do not "see" the surface).

In experiments reported recently in Nature, 214, 79 (1967), Dr. Hobson employed iron oxide supported on silica gel. After repeated exposure to hydrogen and outgassing, the "clean" surface was viewed at high vacuum ($1x10^{-6}$ torr). The observed Mossbauer spectrum is given as part A in Fig. 4. Subsequently, ammonia was allowed to adsorb on the iron surface and spectrum B observed. After further outgassing at 100°C and returning to $1x10^{-6}$ torr, spectrum C was observed.

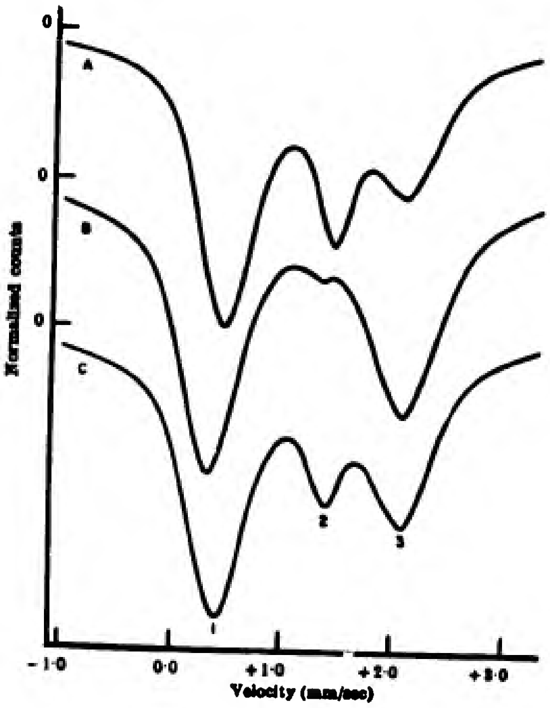


Fig. 4 Mossbauer Effect Spectra of the Adsorption and Desorption of Ammonia on an Iron-on-Silica Gel Catalyst at 25°C.

Spectrum A is identified as the consequence of the superposition of two doublets, one due to ferrous ion and the other to ferric ion. The ferric ion contributes the center peak (inverted in the Figure) and an additional one coincident with one of the outer peaks, assigned to ferrous ion.

When ammonia is presented it adsorbs on the surface and in forming a chemical bond transfers one electron to the iron surface. In effect, ferric ion is reduced to ferrous in producing a surface-ammino complex. Consequently, the center peak of spectrum A is virtually eliminated in spectrum B.

The surface processes are reversible. Removal of the ammonia was apparently not quite complete with spectrum C, but the original condition was closely approached.

HEXAGONAL DIAMOND - A NEWLY DISCOVERED FORM OF CARBON (DLB)

A new chapter has been written at the General Electric Research Laboratories in the continuing story of high-pressure synthesis. A hexagonal modification of diamond was prepared and characterized. The more conventional form, familiar to all, is cubic.

The synthesis and structure analysis are described in a recent publication (J. Chem. Phys., 43, 3437 (1967)) authored by F. P. Bundy and J. S. Kasper of General Electric. Dr. Kasper was supported, in part, by an AFOSR contract entitled "Crystal Chemistry of New High Pressure Phases."

Both cubic and hexagonal diamond, as well as graphite, are different crystallographic modifications of the element carbon. The hexagonal structure bears the same relation to the cubic as, with zinc sulfide, wurtzite does to zinc blende. A closer analogy to carbon is provided by the isoelectronic boron nitride, which occurs in graphitic, hexagonal (wurtzite), and cubic (zinc blende) modifications.

The synthesis of hexagonal diamond from graphite occurs, with various rates of formation, at diverse combinations of pressure and temperature. At pressures above 130,000 atmospheres and 1000°C, transformation is rapid (within milliseconds) and permanent. The product is recoverable as a brittle solid at atmospheric pressure and room temperature.

Significantly, the starting material, graphite, must be oriented with its "c" axis parallel to the applied load (within the high pressure apparatus). The hexagonal product is grown with a particular orientation relative to the parent material. The (100) plane of hexagonal diamond forms parallel to the original (001) basal plane of the graphite. This relation is given in Fig. 5.

Debye-Scherrer X-ray diffraction analysis permits a satisfactory assignment of structure. The unit cell is hexagonal with a = 2.52 Å and C = 4.12 Å. There are four atoms per unit cell, located at 000, 00 3/8, 2/3 1/3 1/2, and 2/3 1/3 7/8. This ideal distribution yields tetrahedral symmetry and 1.54 Å for all C-C distances. The calculated, theoretical density is identical to cubic diamond.

Many questions, however, remain unanswered. Is the hexagonal structure intrinsically semiconducting? Is the hexagonal structure more or less stable than cubic diamond at ambient conditions? Both phases, of course, are less stable than graphite.

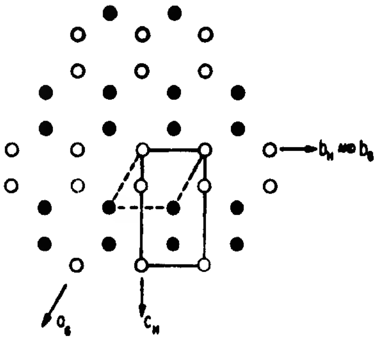


Fig. 5 Basal plane of graphite and the (100) plane of hexagonal diamond showing the relationship between the unit cells of the two structures. If the distinction between the two kinds of circles is ignored, the representation is for the (001) plane of graphite. Only the white circles are in the (100) plane of hexagonal diamond and the black circles must be displaced normal to the plane. The subscripts G and H identify the axes of the unit cells of graphite and of hexagonal diamond, respectively. The b axes of both cells are coincident.

After completion of their work, the G. E. scientists learned of other sources of hexagonal diamond. It was produced by the shock compression of nodular graphite (in iron) to transient pressures as high as 1,400,000 atmospheres. This process was described in a patent release of duPont. Reexamination at G. E. of diamond taken from the Canyon Diablo meteorite then revealed that a sizable portion (over 30%) was hexagonal. It presumably formed on impact with the Earth or during some earlier celestial collision.

PEROXIDE DECOMPOSITION MECHANISMS (DLB)

Significant technological applications are found for inorganic and organic peroxides in such diverse areas as rocket fuels and polymerization initiation. Improved understanding of the general chemical behavior of peroxides logically leads to more effective applications.

The decomposition of peroxyanions in aqueous solution has been the subject of numerous kinetic studies in the laboratory of Prof. John O. Edwards at Brown University. Now under partial sponsorship of the Directorate of Chemical Sciences, AFOSR, a more detailed description of the basic mechanisms has been achieved.

The general, overall reaction under consideration involves the stoichiometry

$$\underset{\text{peroxy-acid}}{2\ R\text{-}OOH} \longrightarrow \underset{\text{oxy-acid}}{2R\text{-}OH} + \underset{\text{oxygen}}{O_2} \ .$$

"R" can represent, for example, the atomic groupings $O\overset{O^-}{\underset{O}{S}}-$ or $H_3C\text{-}C\text{-}^{\neq O}$ in peroxymonosulfuric acid and peroxyacetic acid, respectively.

It had been shown previously with the above, as well as in other cases, that the decomposition reactions are second order in the total concentration of peroxyacid (disregarding the degree of acid dissociation).

$$\text{Rate} = k_{obs} \left[\text{peroxy-acid}\right]_T^2$$

The observed rate 'constant,' k_{obs}, was pH dependent, displaying a maximum value with the pH equal to the pK_a of the reactant acid.

$$ROOH \rightleftharpoons ROO^- + H^+$$

$$K_a = \frac{\left[H^+\right]\left[ROO^-\right]}{\left[ROOH\right]}$$

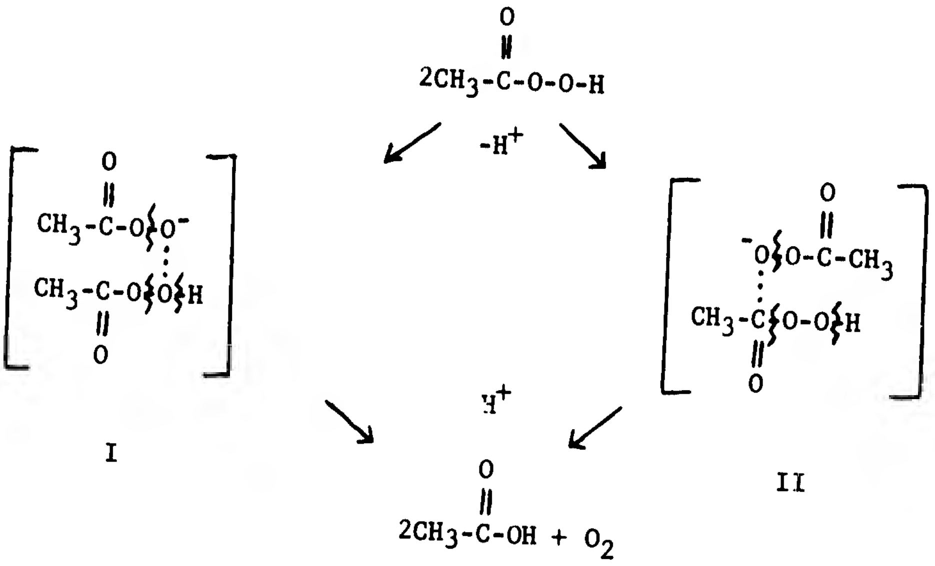
This occurrence afforded the conclusion that the rate determining step in the overall reaction mechanism was bimolecular, involving the completely dissociated anion and its immediate progenitor.

$$ROOH + ROO^- \longrightarrow \text{"transition state"}$$

$$\text{Rate} = k^o\left[ROOH\right]\left[ROO^-\right] = \frac{k^o Ka\left[H^+\right]}{\left\{\left[H^+\right] + Ka\right\}^2} \left[\text{peroxy-acid}\right]_T^2$$

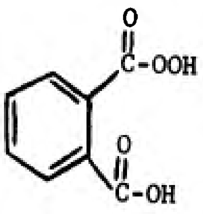
The purpose of recent research at Brown University was a better characterization of the conformation of the transition state. With peroxy-acetic acid, and similarly for the other species, two alternatives might be proposed. (see diagram)

Although Prof. Edwards and co-workers originally favored electrophilic attack at the outer peroxide oxygen atoms (I), other investigators (Goodman and Robson at Proctor and Gamble in England based on their research with peroxybenzoic acids) concluded attack was at the carbonyl carbon atom (II). The crucial experiments to resolve this quandary required isotopic tracer techniques, employing oxygen-18. The peroxyacid reactant was enriched with a doubly labeled species, $R\text{-}O^{18}\text{-}O^{18}\text{-}H$. Inspection of the two alternative transition states, I and II, noting the positions where bonds are ultimately broken, reveals that the product oxygen gas will identify the reaction pathway taken. The product of I would contain isotopically 'scrambled' oxygen, O^{18}-O^{16}. The product of II would contain unscrambled, enriched, oxygen, O^{18}-O^{18}. A mixture of scrambled and unscrambled oxygen would indicate both mechanisms contributed to the overall reaction.



The results obtained so far reveal that, in fact, both mechanisms can occur simultaneously to relative extents depending on the particular system in question. With peroxymonosulfuric acid, over 90% of the decomposition occurs through transition state I. With peroxyacetic acid, on the other hand, approximately 83% of the decomposition occurs through transition state II. Although both competing pathways did occur, I predominated in the first system and II in the second.

After pondering these results, further experiments were undertaken. It was suspected that if the carbonyl carbon site were sterically hindered, then path I would be favored at the expense of II. The example selected for testing this idea was monoperoxyphthalic acid.



In this case, the rate determining, bimolecular step involved a mononegative ion and a dinegative ion. The electrostatic interactions are, therefore, more resemblent of the peroxydisulfate decomposition than the peroxyacetic. In the latter example, the reaction step involved a neutral molecule and a mononegative ion.

The results obtained confirmed expectations. Because of the combined influence of steric and electrostatic factors, mechanism I was found to predominate. Only about 26% of the reaction was assignable to electrophilic attack at the carbonyl carbon atom.

THE HYDRAZINE FLAME (AW)

Dr. Kyle D. Bayes of the University of California at Los Angeles is conducting AFOSR-supported research to learn more about the detailed processes which take place in propulsion and other flames of interest to the Air Force. One of the specific flames which has been studied by Dr. Bayes is that of hydrazine (N_2H_4, a rocket propellent of major importance) burning in a low-pressure stream of oxygen atoms. The research is described in J. Phys. Chem., 71, 371 (1967). Previous workers had identified the light-emitting species in hydrazine flame as NH, NH_2, OH and NO molecules in excited states, but the mechanism of excitation has been unknown. The apparatus used in the present work is shown in Fig. 6.

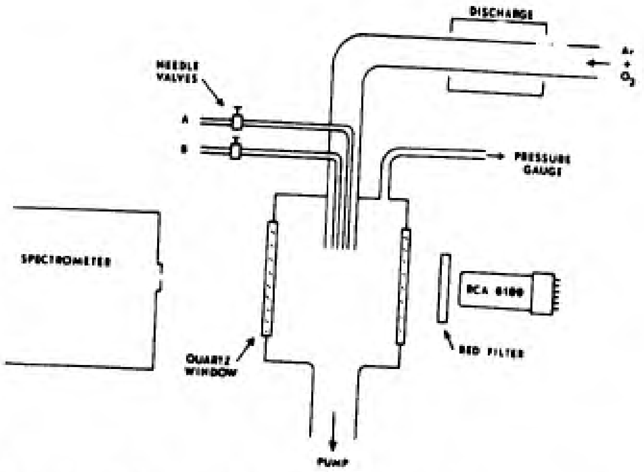


Fig. 6 Schematic Diagram of the Apparatus.

Hydrazine was admitted through needle valve A to the combustion chamber, where it ignited spontaneously when mixed with the stream of oxygen atoms (produced by a microwave discharge) diluted in argon. The light emitted by the flame passed through the quartz window of the combustion chamber and was analyzed by the spectrometer. Fig. 7 shows the flames's spectrum, a prominent feature of which is the ultraviolet gamma bands due to

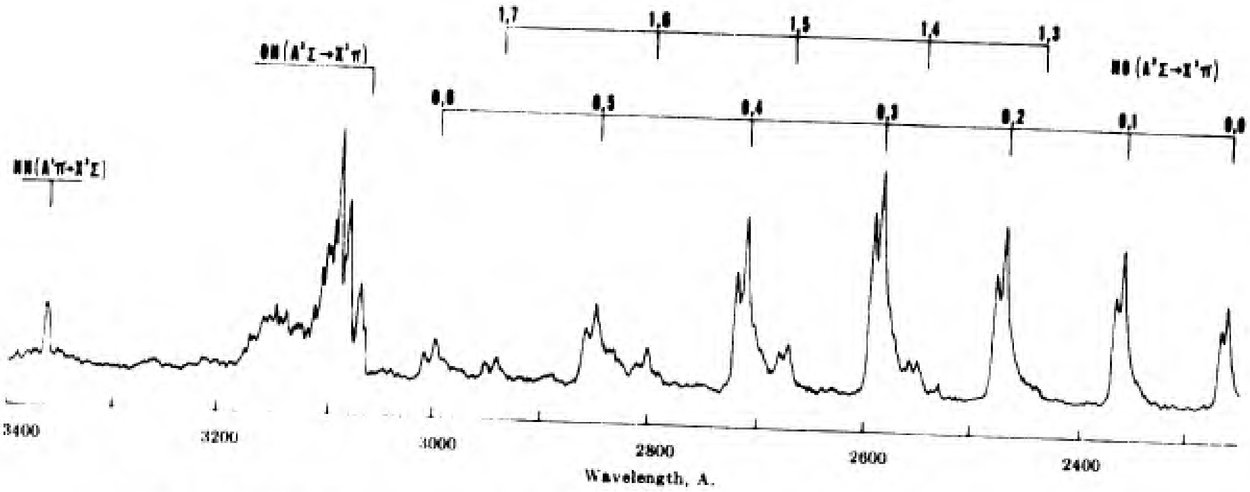


Fig. 7 Emission spectrum from the oxygen atom-hydrazine flame. Partial pressures before reaction: (O) = 14 mtorr; (N_2H_4) = 6.7 mtorr. No added (NO). Total pressure 6 torr. Ebert spectrometer, 0.2-mm slits, EMI 6256S detector.

excited NO (nitric oxide) molecules in the A-doublet-Sigma state. However, the interpretation of this experimental finding ran into difficulties, because there is no obvious reaction between any of the known intermediates and an oxygen atom which releases enough energy to form NO directly in the excited state specified.

Dr. Bayes managed to solve the puzzle, with the help of this clue: he found that adding more NO to the flame (through needle valve B in Fig. 4) increased the emission intensity of the gamma bands of NO and decreased the emission from NH. This suggested that the electronically excited NO responsible for the gamma bands is formed by energy transfer, rather than directly in a chemical reaction. The most likely energy carrier is the lowest triplet state of the nitrogen molecule, the A-triplet-Sigma.

By learning more about energy release reactions in propellant flames, Dr. Bayes's research is helping the Air Force maintain its technological superiority.

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THE CHEMISTRY OF GLASS

by Dr. William L. Ruigh

The relevance of glass research to the Air Force stems from the many varied uses of highly specialized glasses. The Air Force requirements often go far beyond those specified in civilian use. For example the special high strength glass fibre needed for winding Minuteman missile cases was developed under an applied Air Force contract. A very large development effort is being pursued by the Air Force and DoD in the area of composite materials. Not only are glass and vitreous silica being used but also other filamentous materials are embedded in polymer or light metal matrix. These new composite materials have a much higher strength-to-weight ratio than conventional metals or alloys which qualify them for many aerospace uses from turbine compressor blades to helicopter rotors.

Other special but vital glasses are those used in reconnaissance photographic lenses, infrared windows for heat-seeking missiles, radar domes, electrical components for special radar and communication tubes, dielectric material for condensers and heat-proof insulation for winding compact and lightweight electric motors and also heat and impact resistant glasses for the windshields of supersonic vehicles.

The history of glass-making stretches back to 2500 BC with the finding of glass beads in Egyptian archeological sites. Since then the technology and art of glass has gradually expanded until today it is one of the most advanced in our civilization. Perhaps for this same reason, the science of glass is rudimentary and in its infancy. Even such recent developments as Vycor glass and Pyroceram were empirical discoveries.

What is fundamentally lacking in the science of glass is a reasonable knowledge of the structure of glass. The earliest widely accepted concept in glass structure was the Zachariasen continuous three dimensional random network theory. Although very recently seriously challenged, since 1932 it has played a dominant role in the thinking of western glass scientists. In Russia, the diametrically opposed "crystallite theory" propounded by Lebededeff in 1922 and modernized by Porai-Koshits has had a predominant influence. More recently an intermediate view is beginning to be accepted which lies between the complete disorder of Zachariasen and the almost crystalline order of Porai-Koshits.

Today glass is considered to have the "frozen in" structure of the liquid and this structure can vary with the original temperature of the liquid and also the rate of cooling to a solid glass. It is now recognized that glasses, like liquids, have more than short range order and lie between the disordered gaseous state and the regular crystalline solid state.

The glass program of the Directorate of Chemistry of AFOSR is directed toward the central fundamental problem of the chemical structure of glasses. The reservoir of basic knowledge in this area is still almost empty and even the need for such a pool has only recently been recognized. Contributing to this reservoir of basic science is the AFOSR program on the structure of liquids and also the physical chemistry of polymers (particularly regarding the nature of the glass transition point). Less directly contributing is the relatively new effort in the area of "liquid crystals" in which the swarm or cluster theories of structure relate to the cybotactic theory of Stewart regarding liquids.

Dr. Charles G. Dodd at the Technical Center of the Ownes-Illinois Glass Company in Toledo, Ohio, is conducting a research program on "X-ray Absorption-Edge Fine-Structure Spectrometry of Glass and Glass-Crystal Materials." X-ray spectrometry is a comparatively new and undeveloped technique for the analysis of elements in solids both amorphous and crystalline. It is recently being explored as a tool for the determination of atomic and molecular structure. In crystals the X-ray absorption spectra has been divided into the near-edge (2-3 volts) Kossel structure and the far out Kronig structure in the 100-500 w. range above the edge. The spectra up to 40 w. has been related to the atom itself, from 40 to 150 w. the influence of the first and second coordination spheres and above that the influence of the whole lattice or more distant solid environment.

The deductions drawn are still highly speculative and the relationship between structure and spectra largely empirical. The reason for this is partly due to the crude and undeveloped nature of the instrumentation. This is particularly true in the soft X-ray region characteristic of the spectra of the lower molecular weight glass forming elements such as boron, aluminum and silicon. It might be mentioned in passing that pioneer work in the soft X-ray region by Parratt at Cornell and Henke at Pomona and Hawaii have long been supported by the Physics Directorace of AFOSR.

The initial phase of Dr. Dodd's research has been devoted to the design and improvement of both single and two crystal spectrometers. The primary objective is to obtain improved resolution and reliable data on which both empirical and theoretical conclusions can be based.

Exploratory studies on glasses containing Cu, Co, Mn, Cr, and V (the latter with a He atmosphere spectrometer) showed the two crystal spectrometer to be the instrument of choice in studying the Kossel region on which the greatest emphasis was placed. A good correlation was obtained in the case of iron compounds between valence and the first absorption maximum. Kossel spectra on copper, copper oxides and copper glasses suggest that copper may occur in glass as the free metal together with oxides and that the Kossel region spectra may be the most sensitive measure of oxidation states of transition metals in glasses.

With regard to the investigation of silicon and aluminum in glass, Dr. Dodd is spending several months with Dr. F. Laves at the Swiss Federal Institute in Zurich on a cooperative evaluation of the use of an electron microprobe to measure the soft X-ray K emission spectra of glasses.

Another project in the area of glass structure is being conducted by Dr. John H. Mackey, Jr. at the Mellon Institute in Pittsburgh on "Defect States and Structure of Oxide Glasses." This work had its genesis in a ten year program on photochromic glasses at the Mellon Institute sponsored by the Pittsburgh Plate Glass Co. It had been shown that Eu_2O_3 in sodium disilicate glasses prepared in a reducing atmosphere contained Eu^{+2} and on exposure to near UV light, ionization and electron trapping produced coloration occured. The AFOSR research was initiated in the hope of utilizing the solid state approach to the basic chemical problem of glass structures. It was particularly relevant to Air Force interests because many lasers, photographic lenses and photochromic glasses proposed for eye protection against nuclear blast are all based on rare earth containing glasses. It has been shown by absorption spectra that X-rays can form Eu^{+2} in Eu^{+3} containing silicate glasses. In addition to the study of oxide glasses formed by the normal fusion method, novel glasses are now being made using polymerization and silicic acid gelation in the hope of relating the color centers to the structural features of glass.

The viscosity and expansivity of a glass are perhaps the most important physical properties of the material. The very nature of the glassy state as contrasted to the liquid state is characterized by a specific temperature, the "glass transition point," T_G. The first and primary experimental determination of this point is characterized by the temperature at which the thermal expansivity undergoes a relatively abrupt increase with increasing temperature. The "glass transition point" for a given composition of glass is not a fixed constant but varies somewhat with the thermal or "annealing" history of the sample. In an analogous manner glasses can have a "pressure" history as first shown by P. W. Bridgman. The changes in the physical properties of a glass with its thermal and pressure history are a reflection of a fundamental change in structure. Thus, studies of the viscosity and behavior of liquids and glassy solids at different temperatures and pressures are a powerful tool in learning the chemical structures of glasses and their transformation with varying temperature and pressure. Dr. J. D. Mackenzie at Rensselaer Polytechnic Institute in Troy, New York, is directing a contract on "Viscous Flow and Compressibility of Molten Borates at High Pressure." Dr. Mackenzie has had to develop an entirely new technique for this study. He has designed and constructed a unique high pressure, high temperature viscometer based on the rotating cylinder principle. This is the first viscometer constructed in which accurate data are obtainable on high viscosity, corrosive oxide melts at temperatures up to 500°C and pressures of up to 5000 p.s.i. Since pressures were applied by the medium of inert gas atmospheres, solubility studies in boric oxide had to be made with helium, nitrogen and argon. It is unlikely that the small solubility and diffusion of argon will influence the viscosity.

Experimental data on the viscosity of boric oxide and sodium borate melts was obtained in the range 350-500°C and up to 5000 p.s.i. pressures.

In order to obtain constant volume information from this data it was necessary to measure the change of volume of the melts with pressure at high temperatures. This was done by an adaptation of the Bridgman piston displacement method with the material sealed in a copper capsule. The boric oxide and sodium borate melts were studied in the range 350-450°C and pressures up to 1000 bars.

The experimental results constitute the thesis of L. Louis Sperry and the theoretical interpretations of data are being written up for publication in relation to the physical and chemical interpretations of the structure of boric oxide and sodium borate glasses.

BORON CHEMISTRY

by Dr. William L. Ruigh

Why boron chemistry is of importance to the Air Force may not be apparent at first sight. However, a little investigation soon reveals a large number of highly important roles which boron and its compounds play both in current Air Force materials and also in exciting new potential uses. What is surprising is how littlé is known of the fundamental chemical mechanisms by which boron plays its part. Thus, since about 1940 it has been known that minute amounts of boron of the order of about 0.001% particularly in the presence of deoxidizer increases the hardenability index of steel up to 75%. Too much boron makes the steel brittle. Boron in very small amounts refines the grain of aluminum castings. In neither steel nor aluminum is the fundamental mechanism of boron's action thoroughly understood.

The incorporation of substantial amounts of boric oxide to the formulae of inorganic glasses imparts to the glass properties of markedly increased strength, resistance to heat weakening and deformation, chemical or corrosion resistance and other unique properties. These improved glasses are used in heat resistant windshields and the lenses of photographic reconnaissance cameras. Improved high strength boron glasses are used in glass fibers which, incorporated in a resin matrix, are used in winding rocket cases for advanced missiles, light heat resisting insulation for electric motors and other important uses. Boron and boron carbide fibers are being intensively studied by the Air Force as a replacement for glass in new composite materials having high strength and stiffness combined with lightness. Radomes can be constructed of composite materials or out of the new glass ceramic materials of which Pyroceram is an example.

Boron catalysts such as boron fluoride and boron alkyls are used in organic chemistry particularly in the manufacture of polymers in such materials as butyl rubber.

Boron hydrides and metal borohydrides have found wide uses in such diverse areas as organic syntheses (dehydrogenations) and paper bleaches. The remarkable and unique properties of the polyhedral boranes and carboranes with regard to their chemical and thermal stability make them very attractive candidate building blocks and intermediates for unusual polymers having possibliities of meeting the increasingly severe demands of planned and future Air Force requirements in areas such as hydraulic fluids, lubricant , O rings and as the polymeric matrix of fibrous composite materials.

The boron program now being carried out by the Directorate of Chemical Sciences is planned to further fundamental knowledge of boron bonding and structures with a considerable emphasis in the areas of polyhedral boranes and carboranes. This has been planned to back up Air Force and Navy programs in the synthesis of inorganic polymers such as the new extremely stable boronsilicon polymers developed under ONR support.

Dr. Alexander Kaczmarczyk at Dartmouth College in exploring the chemistry of $B_{10}H_{10}^{-2}$ found this normally stable ion to be readily oxidized to boric acid by dilute aqueous potassium permanganate at pH 7 and room temperature. Previous reports had revealed the ion to be transformed under strong acid conditions to higher polyhedral ions such as $B_{20}H_{18}^{-4}$ and $B_{20}H_{18}^{-2}$. Many higher boranes, carboranes and their substitution products required extraordinarily drastic conditions for their oxidation in analytical procedures. One such proceedure required combustion in a fluorine atmosphere under pressure. The new permanganate reaction enabled the development of a simple analytical procedure for the resistant boranes based on oxidation to boric acid followed by a conductometric determination of the liberated boric acid. From this same grant a paper has been published on the action of anhydrous cuprous chloride on $B_{10}H_{10}^{-2}$ in organic solvents to give a highly colored product. Earlier this color was thought to be due to a copper complex, but new data using E.S.R. spectra showed the product to be a $B_{10}H_{10}^{-2}$ free radical with one unpaired electron per cage. Later, radicals having similar optical and magnetic properties were made using $KClO_3$ and similar oxidizing agents in acetic acid. The work is being extended to other polyhedral boranes, carboranes and their substitution products. This work tends to confirm the postulated "aromatic" nature of the cage which has delocalized electrons surround the cage or conducting sphere.

Another effort in the decaborane area is being conducted by Dr. N. N. Greenwood at the University of Newcastle on Tyne in England on the reaction of transition metal carbonyl halides with B_{10} and B_{11} polyhedral ions.

The preparation of polyhedral boron ions depends on the reaction of a borane such as diborane or decaborane with a Lewis base such as triethyl amine. Because of the importance of this reaction, Dr. Greenwood has studied and published a paper on the preparation and properties of monosubstituted triethylamine boranes. NMR and infrared data on all the monohalogenated borane adducts is reported.

Dr. T. E. Haas of Tufts University has a grant on "Inorganic Applications of Nuclear Quadrupole Resonance Spectroscopy." Most of the early work on this grant was on instrumental development and a study of the temperature dependence of chlorine NQR frequencies and pi bonding in K_2PtCl_6 and $K_2I_7Cl_6$. Preliminary work on $B_{10}Cl_{10}^{-2}$ and $B_{12}Cl_{12}^{-2}$ could not be repeated due to inability to find the NQR resonance signal. At present, work is being carried out in the area of carborane derivatives related to ferrocene.

Dr. R. A. Beaudet at the University of Southern California is working on the "Determination of the Molecular Structures of Small Boron Compounds by Microwave Spectroscopy." A large number of isotopically substituted B_4 and B_5 cage-structured carboranes have been studied and the method of microwave spectroscopy developed as a sensitive and accurate tool to determine the structure of these unusual compounds. Much is being learned of the nature of the bonding in these polyhedral structures.

Dr. D. R. Bidinosti at the University of Western Ontario is continuing work which he had earlier carried out with Dr. R. F. Porter at Cornell University under AFOSR grant. Essentially this is a mass spectrometric study of the reaction between BF_3 and B_2O_3.

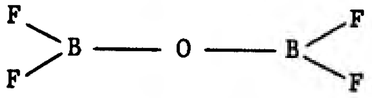
Dr. Bidinosti has completed the construction of a mass spectrometer with an unusually high pumping rate. With this instrument he is able to vary the pressure of BF_3 over a wider range and still get acceptable mass spectrometric results as compared to the Cornell spectrometer. At Cornell he had found one of the major products of the reaction to be the $B_2OF_3^+$ ion whose origin would be difficult to explain from the postulated volatile cyclic $(BOF)_3$ trimer which is presumed to arise from the reaction:

$$BF_3 + B_2O_3 = (BOF)_3$$

Dr. Bidinosti suggests the $B_2OF_3^+$ ion may arise directly from a novel intermediate B_2OF_4 in the reaction:

$$4BF_3 + B_2O_3 = 3B_2OF_4$$

He postulates the following structure for B_2OF_4



The pressure dependence study should differentiate between the two mechanisms of $B_2OF_3^+$ formation. This work has not been completed but a study of the metal-metal bond dissociation energy in cobalt octacarbonyl has been published and the cobalt-cobalt dissociation energy found to be 11.5 ± 4.6 kcal.

Another study on boric oxide is being carried out by Dr. John D. Mackenzie at the Rennsselaer Polytechnic Institute. This is a determination of the viscosity of boric oxide and molten borates under high pressure. Because of its bearing on the structure of glass it will be discussed in the section on glass elsewhere in this annual review. In like manner the work of Dr. M. J. S. Dewar at the University of Texas on the synthesis of "aromatic cyclic organoboron compounds" will be discussed elsewhere. These compounds are of interest in connection with organic semiconductors.

The latest addition to the boron program is a contract with Dr. Michael F. Lappert and Dr. J. Brian Pedley at the University of Sussex in England. Work was initiated in October of 1966 on "Mass Spectrometric Thermochemical and Related Studies on Series of Inorganic Compounds." The primary purpose of this effort is to study problems of bonding in related series of inorganic compounds on an experimental basis and deal with the results by quantum mechanical methods.

Emphasis will be placed on series of Group IV compounds and also boron in Group III. For example, (I) $(CH_3)_3MX$, where M is C, Si, Ge, Sn, and Pb and X is a univalent atom or group such as Cl, Br, I, $N(CH_3)_2$, $P(CH_3)_2$, OCH_3, $OM(CH_3)_3$, SCH_3 and CH_3 and (II) $X_nBX'_{3-n}$ where X and X' have the same meaning as X in (I) and n = 0, 1, 2, or 3.

The experimental techniques are mass spectrometry (primarily for measurements of ionization potentials and bond dissociation energies), calorimetry, electrical dipole measurements, nuclear quadrupole resonance data and other spectroscopic methods.

The objectives of the proposed research are to obtain a closer insight into the nature of chemical bonding and to evaluate as rigorously as possible the physical significance of concepts such as bonding and ionic character in simple model systems. For example the extent of back donation in BCl_3 will be determined and the percentage of ionic character in sigma bonds calculated.

In conclusion the boron program is designed to study the fundamental unanswered problems of bonding and structure in boron compounds and thus support present and future applications of boron in advanced Air Force technology.

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INORGANIC CHEMISTRY

by Denton W. Elliott

Over the past ten years chemistry in general, and inorganic chemistry in particular, has made progress that may be described as almost revolutionary. Certainly one of the areas that has blossomed and continues to be productive is that of coordination chemistry. In the AFOSR chemistry program the part played by this class of compounds, along with the organometallics, has made definite inroads into the synthesis of new compounds, in the understanding of catalytic process, biochemical problems, food and fuel additives, as well as the production of polymeric materials.

With the advent of the more or less fortuitous synthesis of xenon hexafluoride, the interest in the chemistry of the rare gases has flourished. This office has been more concerned with the study of these rare gases involved in the ion-molecule reactions that may occur in the upper atmosphere. Ion-molecule reactions have been proposed as a means of purification in a closed ecological environment.

Many inorganic chemical reactions occur in non-aqueous solvents. Comparatively little is known about these phenomena. A program is underway to study the chemistry of non-aqueous media. Such studies could have important bearing on problems involving hydraulic fluids, heat transfer materials, and the stabilization of polymers.

A necessary part of chemistry is that of determining the properties of a compound by its molecular structure: by the interrelationships of molecules, by the characteristics of their component atoms, by forces that bind atoms together to form molecules, and by the arrangement of the atoms within the molecule. The understanding of everything about the structure should make it possible to predict properties of a compound before it is formed. To help bring this predictive state about in inorganic chemistry, work has been supported on the electronic spectrum and structure of the uranyl and manganese ions. Future efforts are to be extended to other materials, in particular the ions of gallium, indium, thallium,tin and lead. All of these elements have a common, $nd^{10}(n+1)s^2$, electron configuration.

An area of inorganic chemistry that has not been exploited to any great extent is the reaction of metal ions, and iso- and heteropoly anions. Since these have implications in the catalytic and biochemical fields, research that involves them is included in the program.

Aside from gaseous and solution chemistry the program also includes studies on the mechanism of solid state reactions. Aluminum and silicon reactions, as well as the oxides of iron and zinc, are being investigated. Results of work in this area may shed light on the control of brittleness in ceramic materials.

A few selected representative results in the inorganic program are briefly presented below.

RARE GAS, ION-MOLECULE REACTIONS

The role attributed to ion-molecule reactions in the mechanisms of reactions induced by ionizing phenomena has undergone marked changes with time. The significance of ion-molecule reactions in radiation chemistry was recognized as early as 1926 by Lind et al. Lind postulated that the chemical change was produced by the formation of ionic clusters consisting of a central ion surrounded by many neutral molecules and stabilized by polarization forces. After the classical papers of Eyring, Hirschfelder and Taylor, this cluster theory fell into disuse and ions were relegated to minor roles in chemical reaction mechanisms which were then dominated by free radicals.

Since practically the earliest days of mass spectroscopy, ions which arose from reactions of ions and unionized molecules present in the ion source of the spectrometer have been observed in the mass spectra of materials. In recent years, some of these ion-molecule reaction cross sections have been measured and found to be as much as two orders of magnitude larger than corresponding gas collision cross sections. Such observations have reestablished the role of ions in many special areas such as radiation and hot-atom chemistry, mass spectroscopy, reactions in the upper atmosphere, gas discharges, plasmas, etc.

Dr. Walter Koski at Johns Hopkins University under the sponsorship of AFOSR has been investigating experimentally and theoretically various aspects of ion-molecule reactions of significance in various upper atmosphere phenomena.

For studying these ion-molecule reactions, Dr. Koski has used a two-stage mass spectrometer. There are only a very few of these instruments in existence and Dr. Koski and his students have constructed one in their laboratory. The instrument consists of a small mass spectrometer which selects the charge, mass and energy of a beam of ions which are permitted to bombard a gas in the ion source of a second mass spectrometer which is used as an analyzer. The ions to be analyzed are extracted at right angles to the bombarding beam and are detected, counted and recorded using an electron multiplier with appropriate counting and recording instrumentation. The instrument is designed so that the bombarding ions are brought out of the small spectrometer at low energy (8 ev for N^+). They can then be decelerated to about 2 ev or accelerated to about 200 ev before entering the reaction chamber.

The series of reactions that were selected for the initial study were of the type $X^+ + HD$ and $HD^+ + X$, where X is a rare gas. They were interested in obtaining the following type of basic information. Does the ion-molecule reaction proceed through complex formation at low energies? This was an interesting point since in his pioneering theoretical work on ion-molecule reactions, Eyring felt that complexes were not formed because of the long range of the ion-molecule interaction. It appeared from Koski's study that at low energies for the above type reaction there was no doubt that complexes were formed. Another point was that, in deriving the cross section for ion-molecule reactions by conventional methods, no isotope effect was expected in the reactions, i.e., XH^+ should be as abundant as XD^+. Koski and coworkers results indicated a large isotope effect which varied with energy (see Fig. 8). Furthermore, they found that the isotope effect could be accounted for if, in the derivation of the expression for the cross section, the requirement was included that total angular momentum and the energy in the reaction must be conserved.

The reactions of HD^+ with Ar were studied. In the charge transfer reaction

$$HD^+ + Ar \longrightarrow Ar^+ + HD ,$$

a plot of the cross section versus energy of HD^+ showed a number of resonances which were interpreted as being due to reactions of vibrationally excited states of HD^+. If this interpretation is further borne out, it will be the first observation of this type of phenomenon. In the other reactions of this ion, namely

$$HD^+ + Ar \begin{array}{l} \nearrow ArH^+ + D \\ \searrow ArD^+ + H \end{array} ,$$

one finds that at low bombarding energies, the ratio of ArH^+/ArD^+

is not greatly different from unity. Therefore, the isotope effects can be explained by the usual vibrational factors that account for chemical isotope effects. As one increases the bombarding energy, the ratio can attain a value much higher than unity, and the effect cannot be accounted for by the same factors that are important at low energies. This is illustrated in Fig. 8, where ArH^+/ArD^+ is plotted for various Ar^+ ion energies. This type of study has now been extended to Xe, Kr, Ne and He.

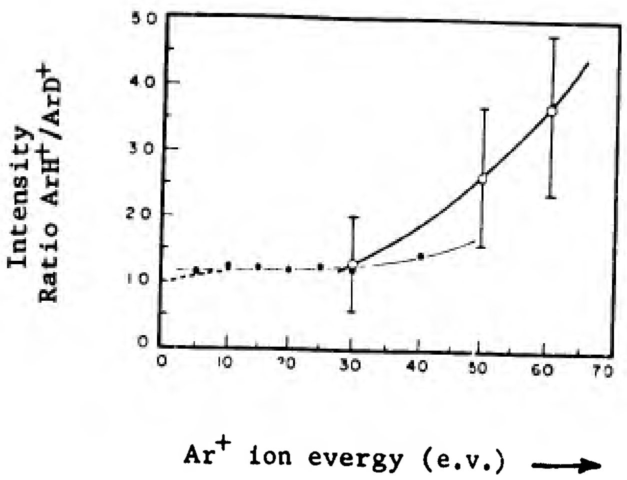

Fig. 8 The ratio of the cross-sections of ArH^+ to ArD^+ as a function of the energy of Ar^+ in the reaction $Ar^+ + HD$

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TRANSITION METAL FLUOROCARBONS

Back in 1960, Professor F. G. A. Stone and his group at Harvard University, under AFOSR support, discovered new fluorocarbon derivatives of manganese, rhenium and iron in which fluorocarbon groups like $C_3F_7^-$, $C_2F_5^-$, or $CF_2{:}CF^-$ are bonded to the metals by electron pair metal-carbon bonds of the type where both the metal and the carbon atom contribute an electron to the bond. Heretofore, transition metal-carbon bonds of this kind had only been observed infrequently. Stone showed that such bonds are stabilized when the carbon atoms bonded to the metal are themselves linked to fluorine atoms.

It is well known that fluorine atoms can substitute for hydrogen atoms in organic molecules, thereby modifying the properties of hydrocarbon groups and affording a range of fluorochemicals, some of which are important as refrigerants, polymers, anaesthetics, and aerosol propellants.

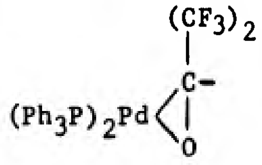
In the last decade, several transition-metal complexes have been prepared in which alkyl or aryl groups are attached to the metals by apparently localized sigma bonds. One example is the methyl group in $CH_3Mn(CO)_5$. However, the outstanding feature of these complexes, indeed the factor that has permitted their successful synthesis, is that specific ligands are also attached to the metals. These ligands can supply the metal with sufficient electrons to fill bonding molecular orbitals. At the same time, by using their own vacant orbitals to accept electron density, they can lower the energy of the non-bonding d-electrons of the metal, thereby removing additional negative charge transferred to the metal atom by the sigma bonded alkyl or aryl groups. However, except for certain complexes of the nickel group metals, these transition-metal derivatives are not chemically robust. They tend to be sensitive to both air and moisture, and to be thermally unstable. The new fluorocarbon derivatives are considerably more robust. This is well illustrated by the thermal stability comparisons made with analogous compounds in the table below, and by the fact that the majority of the fluorocarbon derivatives have been stored as crystals in air for months, or in some cases even years, without decomposition. Moreover, several instances are known in which the fluorocarbon compound, for example $(C_2F_5)_2Fe(CO)_4$, exists, although the hydrocarbon analogue has never been synthesized. Thus, transition metals have been "conditioned" to form localized sigma bonds of reasonable stability by making the attached carbon atom part of a fluorocarbon group.

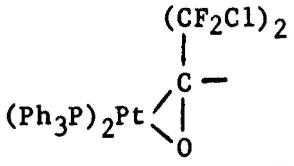
$(C_2F_5)_2Fe(CO)_4$, dec. above 100°	$(C_2H_5)_2Fe(CO)_4$*
$HCF_2CF_2Co(CO)_4$, stable at 25°	$CH_3Co(CO)_4$, dec. −35°
$CF_3Ni(CO)(\pi\text{-}C_5H_5)$, stable at 25°	$CH_3Ni(CO)(\pi\text{-}C_5H_5)$, dec. 0
$C_2F_5Mn(CO)_5$, stable up to 150°	$C_2H_5Mn(CO)_5$, dec. 25
$C_6F_5Mn(CO)_5$, stable up to 170°	$C_6H_5Mn(CO)_5$, dec. 100
$(C_6F_5)_2Zr(\pi\text{-}C_5H_5)_2$, dec. 218	$(C_6H_5)_2Zr(\pi\text{-}C_5H_5)_2$*
$HCF_2CF_2Mo(CO)_3(\pi\text{-}C_5H_5)$, dec. 100	$C_2H_5Mo(CO)_3(\pi\text{-}C_5H_5)$, dec. 80
trans-$(C_6F_5)_2Ni[P(C_2H_5)_3]_2$, not dec. at 213	*trans*-$(C_6H_5)_2Ni[P(C_2H_5)_3]_2$, dec. 125
cis-$(C_6F_5)_2Pt[P(C_2H_5)_3]_2$, not dec. at 160	*cis*-$(C_6H_5)_2Pt[P(C_2H_5)_3]_2$, dec. 151

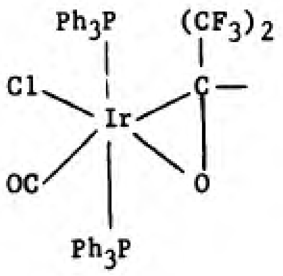
* Compound not known.

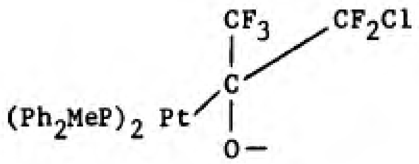
Some comparisons of thermal stability between fluorocarbon complexes and their hydrocarbon analogues.

At Bristol University in England, Professor Stone has continued his study of fluorocarbon complexes of the transition metals. In addition to extending the carbonyl anion reaction to various substrates, he has prepared the first transition metal complexes containing $RF_3C{=}C-$ groups, and made several additional reaction studies which have afforded new organometallic compounds. His group discovered that hexafluoroacetone and other fluorinated acetones could function as ligands to transition metals and have characterized, among others, the following complexes.

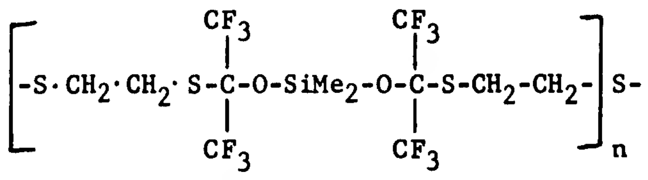








Along with these foregoing studies, Dr. E. W. Abel of this group has been studying the action of perhalogenoacetones on organometallic bases. In the reaction of hexafluoro-acetone with the dithiasilacyclopentane ring, $\overline{S\cdot Si(Me)_2\cdot S\cdot CH_2-CH_2}$, he found that instead of the expected ring expansion, a linear polymer was produced which has the following apparent structure:



$$\left[-S\cdot CH_2\cdot CH_2\cdot S-\underset{CF_3}{\overset{CF_3}{C}}-O-SiMe_2-O-\underset{CF_3}{\overset{CF_3}{C}}-S-CH_2-CH_2-\right] S-{}_{n}$$

This polymer and other products are under further investigation.

It is this type of research, which Professor Stone et al are preforming in the synthesis and characterization of new compounds, that will provide the Air Force with the new materials that are needed to meet their rigorous environmental requirements.

THE SPOILER

Dr. Thomas Dunn, a grantee of the Chemistry Directorate, AFOSR, at the University of Michigan, has been exploiting a technique known as double optical resonance spectroscopy (DOR), in his investigation of the electronic spectrum of the uranyl ion.

Since nearly all molecules are in their lowest electronic state at room temperature,their color depends upon how "high" the excited state lies. However, some molecules possess excited electronic states which have comparatively long lifetimes, so that if one can get a large number of molecules into these states then a beam of light might excite them to even higher excited states and a different "color" 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 millisecond. This may not seem long until compared with the usual lifetime of approximately one millionth of a millisecond. This "metastable" state is obtained when light of blue-green color is absorbed. When a powerful flash-lamp is set off close to the uranyl compound, a large number of these uranyl ions go to the excited state. The "absorption" spectrum of the ions in this state 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.

From the foregoing it becomes apparent that the principle involved in DOR spectroscopy is to populate an electronically excited state of the molecule by exposing it to an intense flash of ultraviolet light, and then to excite those same molecules into an even higher excited state. This is shown diagrammatically in the figure where the primary process is indicated by A, and the final process by D. The intermediate process B is one which is too fast to be observed and corresponds to intersystem crossing.

Excitation to T_1 cannot occur directly because of the forbidden character of the transition between S_1 and T_1 and this, of course, is why the molecules have a long life in the state T_1 before they ultimately fall back to the ground state S_1.

This process has so far been observed for the uranyl ion UO_2^{++} and Mn^{2+} in a spinel lattice. In the case of uranyl ion,

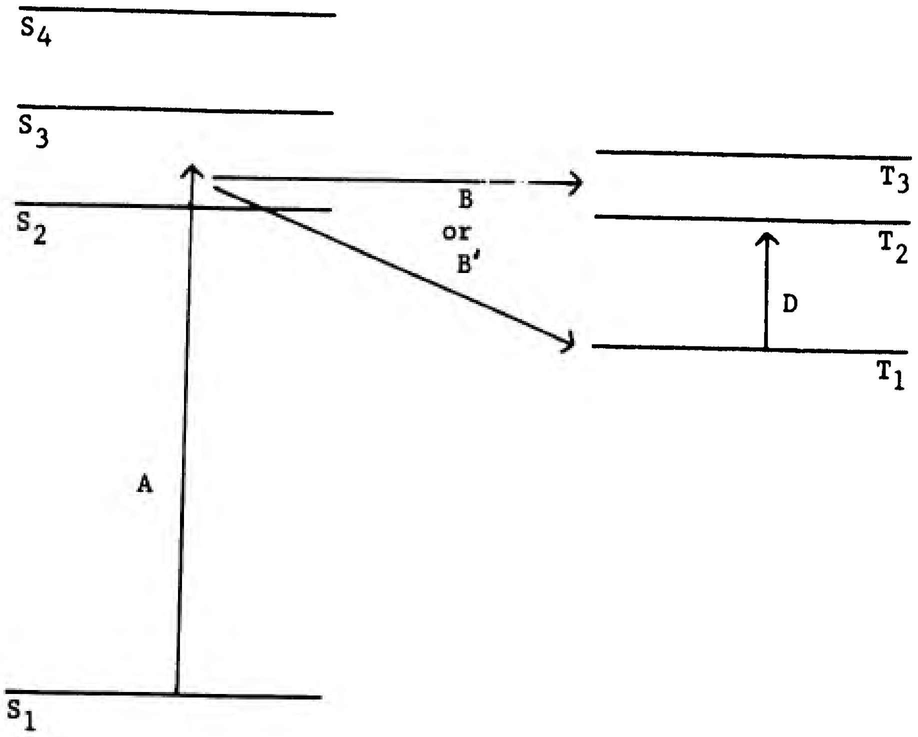


Fig. 9 Population of Excited States

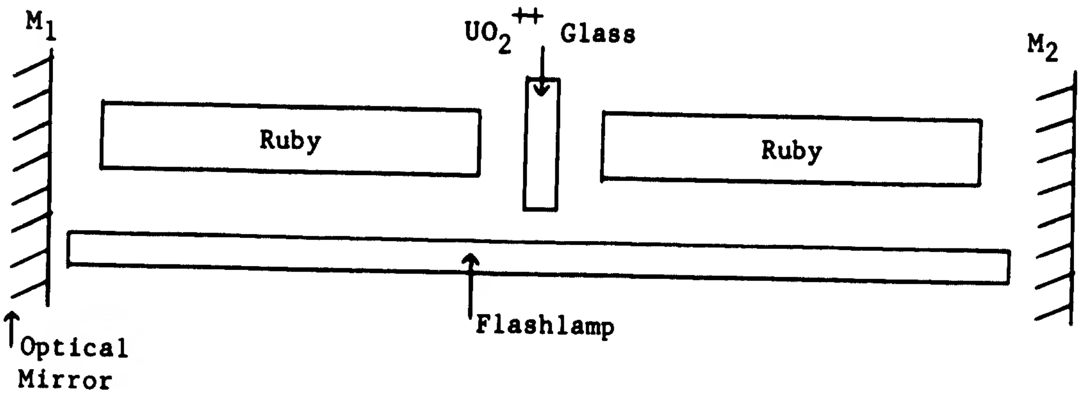


Fig. 10 Laser Apparatus

the effect can be useful in acting as a Q-spoiler for a ruby laser. This can best be seen as follows. Suppose that two ruby rods are arranged in a line as in figure 10, and that they are separated by a piece of glass containing uranyl ion. In addition let us suppose that there are good optical mirrors M_1 and M_2 at each end of this arrangement such that the ruby crystals are in a Fabry-Perot cavity. The flashlamp along the side of the ruby rods is discharged and as it produces an intense flash of light it does two things. First, it excites the Cr III ions of the ruby crystal to excited states from which they can "lase" but second, as soon as the flash starts, it causes UO_2^{++} ions to be excited to the state T_1 discussed above. When the uranyl glass is unexcited it transmits the red ruby laser light easily (since the glass is yellow!), but when large numbers of UO_2^{++} ions start to populate the level corresponding to T_1, these molecules can absorb ruby laser light and go to the level T_2 which just happens to have the right energy. This transition is a reasonably strong one and so, while there are even a few molecules in this state T_1, no ruby laser light will be transmitted from the first ruby rod to the second. Thus, there will be no concerted laser action in the optical cavity.

However, as soon as the flash lamp has finished firing, the excited uranyl ion molecules fall back from the T_1 state to the S_1 state in the 10^{-6} seconds and this now allows the cavity to "resonate" optically since there is now a complete optical path from one mirror to the other. The result is that all the energy which is stored up in the excited Cr III ions in ruby rods, is now released in one giant pulse.

Because the "Q" of the cavity was "spoilt" by the presence of the UO_2^{++} glass when it absorbed, this process of creating giant flashes is called "Q-spoiling" or just "Q-switching." The same thing can also be accomplished by a rapidly rotating mirror or by various dye solutions. The uranyl glass has the advantage that it is very convenient and the glass does not appear to deteriorate as the organic dye solutions do after a while.

It should be possible by testing a variety of materials to find something which will act as a Q switch for almost any frequency of laser light and this is one of the possible by-products of this work on DOR.

THE HYDRIDO COMPLEX

Over a hundred years ago it was noted by Descamps that solutions of cobaltous salts evolved hydrogen in the presence of cyanide ion. Yet it was not until 1942 that Iguchi observed that such solutions were able to absorb molecular hydrogen and transfer it to substrates. This homogeneous catalysis was somewhat of a surprise. In the past decade an ever increasing number of these systems have been recognized and studied.

Homogeneous catalytic reactions are of interest, not only in their own right, but also because they m be studied stoichiometrically on a molecular scale. The results of such studies provide considerable insight into various aspects of the catalytic process. These include factors influencing the rate of reaction due to structure and electron configuration of the catalyst or the substrate, the mechanism of complex formation, the nature of the complex, the mode of product release, selectivity and stereoselectivity, and poisoning and reactivation.

Dr. Jack Kwiatek of U.S.I. Chemicals Company, under support from the Chemistry Directorate, AFOSR, finds that potassium pentacyanocobaltate acts as a catalyst and is effective in reducing carbon-carbon double bonds where they are conjugated with another bond or with an aromatic group, carbonyl, or ester. The catalyst first absorbs hydrogen directly to form a new compound called a hydrido complex. The formation of this hydrido complex is explained by the investigator as follows.

The pentacyanocobaltate (II) anion is a d^7 complex, one electron short of the electron configuration of krypton. Its solutions are paramagnetic with a moment corresponding to one unpaired electron. In a formal sense, the loss of an electron to give cobalt(III) allows a sixth ligand, with its pair of electrons, to coordinate with the metal, which thereby attains the inert configuration.

The high reactivity of this complex toward molecular hydrogen is basic to its function as a catalyst in the hydrogenation of a variety of organic compounds. While some doubt remains concerning the detailed mechanism of this reaction, the net result is a reversible homolytic process in which hydrogen may be reduced to hydride, and cobalt(II) to be oxidized to cobalt(III) (eq. 1).

$$2\ Co(CN)_5^{3-} + H_2 \rightleftharpoons 2\ Co(CN)_5H^{3-} \qquad (1)$$

The reactive hydridocomplex (this name is employed for $Co(CN)_5H^{3-}$) so-formed functions as an intermediate in homogeneous hydrogenation reactions, transferring the hydrogen to various organic substrates.

The hydridocomplex may also derive from sources other than molecular hydrogen. The homolytic cleavage of water by pentacyanocobaltate(II) (eq. 2) permits the reduction of various substrates to take place stoichiometrically in the absence of molecular hydrogen.

$$2\ Co(CN)_5{}^{3-} + H_2O \rightleftharpoons Co(CN)_5H^{3-} + Co(CN)_5OH^{3-} \qquad (2)$$

Since this reaction is reversible, hydrogenation systems which have become "poisoned" (hydrogen-active cobaltous species entirely converted to inactive cobaltic species) may be reactivated autocatalytically in the presence of molecular hydrogen.

References

"Catalytic Reactions of Pentacyanocobaltate," Jack Kwiatek, Catalysis Review, October 1967.

"Factors Involved in Catalytic Hydrogenation and Hydrogenolysis by Pentacyanocobaltate(II)," Jack Kwiatek and Jay K. Seyler, Advances in Chemistry Series (ACS), 1967.

CHEMICAL REACTIVITY AND MECHANISMS

By Dr. Anthony J. Matuszko

Why is AFOSR supporting research in organometallic chemistry? What is the Air Force's interest in organic chemical reaction mechanisms? These are questions often asked by academic and industrial research people interested in our program of basic chemical research. In providing answers to these questions we can point to the many present uses and the anticipated future Air Force applications of organic and organometallic materials. As aircraft reach higher and higher speeds and space exploration continues at its present pace, there is an obvious need for new and improved thermally stable polymeric materials, more versatile elastomers and lubricants which can withstand drastic changes in temperature and pressure, and stronger bonding adhesives (particularly for bonding metal to metal). The systematic approach to these new and better materials depends upon a fundamental understanding of what happens when molecules react and why they react in the manner in which they do. Knowledge of intermediates to be expected and information about the possible effects of reactant concentrations, chemical equilibria, and solvent, temperature and pressure changes on a given reaction can save a tremendous amount of time in the synthesis of a novel and more useful material. Such information can also be useful in providing a better understanding of materials degradation.

A few of the highlights from our program of organic and organometallic research on chemical reactivity and mechanisms are presented in this section of the Annual Review.

FROZEN STATE REACTIONS

Reactions commonly carried out in dilute solutions often proceed more rapidly when the solutions are frozen. This observation seems somewhat startling since it is generally believed that chemical reactions are slowed down when the temperature is lowered. With support from the Directorate of Chemical Sciences, AFOSR, Dr. Richard Pincock of the University of British Columbia is studying the extent of and causes for such apparently anomalous behavior.

The mobility of reacting molecules decreases as the temperature is lowered. However, unlike freezing a pure compound which is converted to a solid at the freezing point, the freezing of a dilute solution will normally initially result in crystallization of the solvent. When thermal equilibrium is attained, a liquid phase containing the solutes may still be present in the frozen mass at temperatures far below the initial freezing point. As the solvent crystallizes out, the reactant solute molecules are squeezed into minute pockets of liquid now containing higher concentrations of solute due to the decrease in volume of the liquid regions. Having been squeezed closer together, the reactant molecules collide more readily despite their decreased mobility. In his investigations, Dr. Pincock has observed accelerated rates of simple bimolecular reactions in frozen organic solvents and in frozen aqueous solutions.

Thus far some interesting general features for frozen systems have become apparent to Dr. Pincock and his coworkers. For example, the reaction of ethylene chlorohydrin with sodium hydroxide (forming ethylene oxide) in frozen solutions follows second order kinetics with rates 1000 times faster than supercooled liquid solutions at the same temperature. Fast reactions at temperatures as low as -80°C are illustrated by the oxidation of iodide ion with arsenic acid in frozen aqueous solutions.

The enhanced reactivity of frozen state reactions is largely attributed to the "concentration effect" by Pincock and other researchers in the field. However, in some instances the concentration effect doesn't tell the whole story. Other factors which have been proposed as contributing to the increase in reaction rates in frozen aqueous systems include molecular orientation by the ice crystals and catalytic activity on the surface of the ice. Dr. Pincock is considering these and other effects in his continuing study of reactions in frozen solutions.

The research on chemical reactions in frozen systems which is being done at the University of British Columbia could have far-reaching consequences. Although Dr. Pincock is concerned only with the chemistry involved, the results obtained are relevant to other scientific and technological areas such as the preservation of human tissues and organs, the storage of foods, and the question of whether life may exist at low temperatures during freezing conditions.

References: (1) J. Am. Chem. Soc., 88, 4455 (1966)
(2) J. Chem. Ed. 43, 358 (1966)

SELECTIVE ELECTROCHEMICAL REACTIONS

At Purdue University, Dr. Robert Benkeser and his coworkers have carried out selective reactions (chemical reductions) of organic compounds by electrochemical means. Employing an undivided cell such as the one shown in Fig. 11, amide groups can be

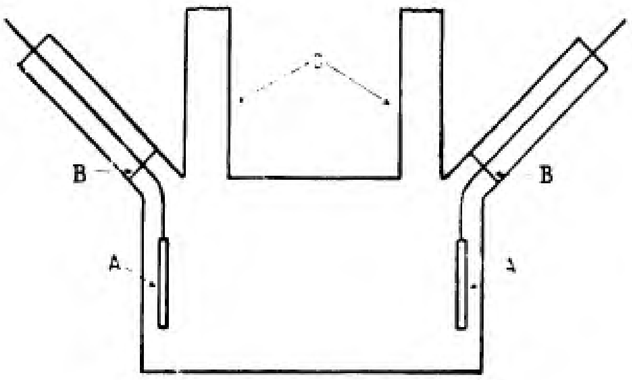
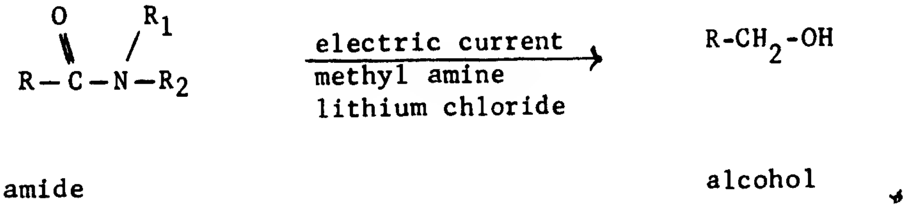


Fig.11 Sketch of the electrolysis cell which is 170mm in length and 100mm in diameter and fitted with platinum electrodes (A), glass seals (B) and dry ice condensers (C)

converted to alcohols and aromatic (benzene) double bonds have been hydrogenated in the presence of the normally more reactive side chain double bonds (olefinic bonds). These electrochemical processes will be useful in making transformations in materials containing other functional groups which would be affected by the usual chemical reducing agents.

Using electrolytic techniques for changing amides into simple alcohols seems like a round-about as well as a costly way of producing alcohols. However, there are times when specific conversions of this kind are desirable in order to improve the physical properties of a material. The replacement of amide by alcohol groups will often make the resulting material more soluble in solvents which may be a desirable property. Also, an alcohol group is chemically more reactive than an amide group. This would allow for modifications in the properties of a substance by the attachment of other chemical groups through reactions with the newly formed alcohol portion of the molecule.

A number of amides were electrochemically converted by the Purdue scientists and the yields of alcohols obtained ranged from 65 to 84%.



$$\underset{\text{amide}}{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{R_1}{|}}{N}{-}R_2} \xrightarrow[\text{methyl amine, lithium chloride}]{\text{electric current}} \underset{\text{alcohol}}{R\text{-}CH_2\text{-}OH}$$

where R_1 and R_2 may be H or alkyl groups

This is the first case of a general reduction of all types of amides (primary, secondary and tertiary amides) to alcohols. Small amounts of the corresponding aldehydes were detected in the crude products suggesting that aldehydes might be intermediates in the reduction processes. When aldehydes were subjected to the same electrolytic conditions as the amides Dr. Benkeser found that much lower yields of alcohols were obtained. Hence, it seemed doubtful that the alcohols were being formed exclusively through the intermediacy of the aldehydes.

In the other phase of this electrochemical investigation the selective reduction of aromatic ring double bonds in the presence of side chain olefinic double bonds was studied. A number of reactions were carried out in which the position of the olefinic bond was varied. When the olefinic bond was located two or more carbon atoms away from the aromatic ring, partial reduction of the ring was effected without altering the side group, as shown by the following example.

45% yield

On the other hand, the normally more reactive olefinic bond was hydrogenated perferentially when present between the first two carbons of the side chain.

63% yield

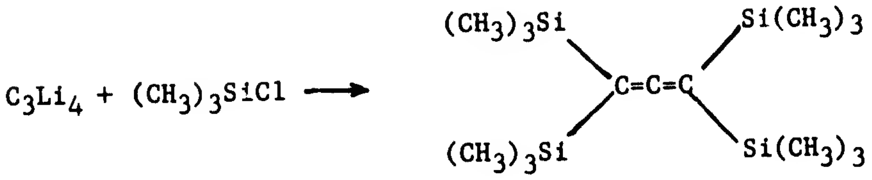
6% yield

Dr. Benkeser and his research group are now looking into the possibility of electrochemically reducing aromatic rings in the presence of other functional groups.

These electrochemical investigations will be useful in improving the properties of existing materials and in the synthesis of new materials for various Air Force applications.

POLYLITHIATED ORGANIC COMPOUNDS

At the University of Wisconsin Dr. Robert West and his coworkers have reported the preparation of perlithiopropyne, C_3Li_4. This is the first example of an organometallic compound in which all the hydrogens are displaced by lithium atoms. The C_3Li_4 was obtained in the reaction of propyne, $CH_3C{\equiv}CH$, with n-butyllithium, $CH_3CH_2CH_2CH_2Li$, in hexane. The product is a red-brown solid which reacts with trimethylchlorosilane(I) to give the unique silicon derivative, tetrakis (trimethylsilyl) allene(II).



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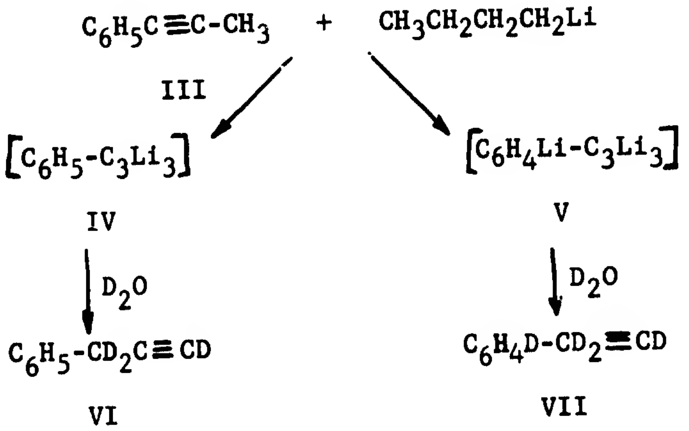
It is hoped that the C_3Li_4 will prove to be the first of a family of completely lithiated hydrocarbons. The compound has potential application as a catalyst for polymerization of dienes to make synthetic rubber and as an intermediate in the synthesis of novel organic and organo metallic materials.

Another AFOSR investigator actively doing research on organolithium compounds is Dr. James Mulvaney at the University of Arizona. Prompted by West's observations in forming C_3Li_4, Mulvaney carried out the reaction of 1-phenylpropyne(III) with an excess of n-butyllithium.

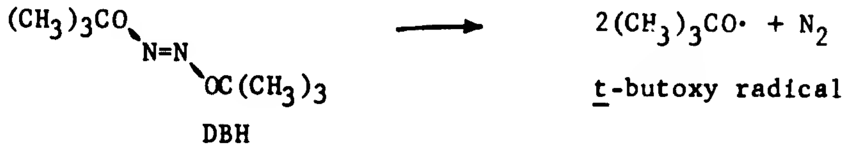


Although IV and V were not isolated by Dr. Mulvaney, he believes that these polylithiated intermediates were present in the reaction mixture prior to the addition of deuterium oxide, D_2O, and the formation of compounds VI and VII.

Results obtained from basic chemical studies such as those described above are useful to the Air Force in better understanding polymerizations catalyzed by organometallic substances and in the synthesis of new materials for aerospace applications.

NEW INITIATOR FOR POLYMERIZATION

In an AFOSR supported study at the University of California (1) (San Diego), Dr. T. G. Traylor has reported the synthesis of di-t-butyl hyponitrite (DBH), a convenient new source of t-butoxy radicals.



The properties of this compound should make it an excellent initiator for free radical polymerizations.

Dr. Traylor's research has been concerned with mechanisms of reaction of oxy radicals (RO·) and peroxyradicals (ROO·) which are formed when organic materials react with oxygen upon exposure to the atmosphere (autoxidations). One of the least understood reactions involved in all such oxidations is the bimolecular interaction of the peroxy radicals formed as intermediates. The process may lead to termination of the reaction (Equation 1) involving removal of the free radicals by a variety of mechanisms or may continue a chain reaction (Equation 2).

$$\underset{\text{alkylperoxy radical}}{2ROO\cdot} \rightarrow \text{non-radical products} \qquad (1)$$

$$\searrow \underset{\text{alkoxy radical}}{2RO\cdot} + O_2 \qquad (2)$$

Tetroxides (R-O-O-O-O-R) are believed to be among the intermediates formed in such oxidation reactions. Since tetroxides themselves are not sufficiently stable, isosteric systems of the general formula R-O-N=N-O-R, where two oxygen atoms are replaced by nitrogens, were selected for study. This led to the synthesis of the DBH and other hyponitrites.

A few hyponitrites described in the literature are used as initiators for polymerizations. However, their usefulness is severely limited since they decompose explosively. The DBH reported by the University of California research group is easily prepared, safely handled, and decomposes cleanly and efficiently to form t-butoxy radicals and nitrogen gas. It seems to be insensitive to scratching and is far less sensitive to shock than di-t-butylperoxyoxalate (DBPO), another source of t-butoxy radicals which Traylor is using in his study. The mechanisms of decomposition of DBH and DBPO under the same conditions appear to be identical.

The di-t-butyl hyponitrite should be useful as a new free radical initiator in the synthesis of polymeric materials. The results of the mechanism studies (2) done by Dr. Traylor and his research team will provide the Air Force with a better understanding of the processes which cause air oxidation of materials. The knowledge obtained may be used to prevent or retard such oxidation processes.

References:

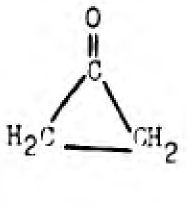
(1) Tetrahedron Letters No. 49 pp6163-6168 (1966).

(2) Dr. Traylor presented a paper on "Mechanisms of Peroxy Radical Interactions" at the Peroxide Symposium in Berlin - Adlershof in September 1967; also, a paper has been submitted to the Journal of the American Chemical Society on "Cage Reactions of t-Butoxy Radicals."

SMALL RINGS WITH GREAT POTENTIAL

The chemistry of small ring organic molecules (three or four membered cyclic structures) poses a challenge to the research chemist interested in fundamental studies of reaction mechanisms or in the synthesis of complex molecules. Characteristic reactions with these molecules proceed at relatively low temperature. Synthetic chemists can use the release of the high energy contained in these systems as a driving force for desired reactions under mild conditions.

Among the reactive small ring systems being investigated by Dr. Nicholas Turro of Columbia University are the three membered ring cyclopropanones. Dr. Turro and his research group during the past year reported a simple, high yield preparation of cyclopropanone (1) and two of its derivatives (II and III).



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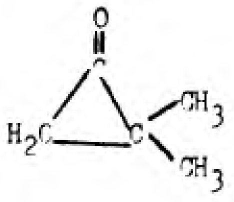
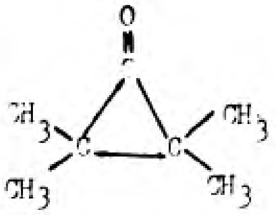
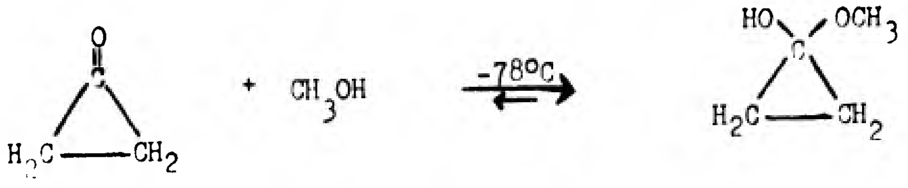


II



III

As a result of severe strain energies, these compounds have large amounts of energy waiting to be released. Activation energies are therefore low and many reactions of these ketones occur smoothly at room temperature and below. Every bond in the ring system is labile and the carbonyl group is exceptionally reactive. For example, the reaction with methyl alcohol proceeds quite readily and almost quantitatively at -78°C.



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Due to its high degree of reactivity cyclopropanone polymerizes rapidly at room temperature. It was found that acetic anhydride or acetyl chloride when added to methylene chloride solutions of I retarded polymerization substantially, thus making it possible to study reactions of I at room temperature.

Small ring systems with their "excess" energy waiting to be released will provide the Air Force with novel reactive intermediates for the synthesis of new materials for various aerospace applications.

THE CHARACTERIZATION OF LIQUIDS

By Dr. Donald L. Ball

Significant technological benefits would obviously derive from improved understanding of the liquid state of matter. Endless examples could include not only direct applications but indirect as well. Most engineering materials inevitably pass through the liquid state on the path from raw material to finished product. It is not practical, in this basic regard, to isolate the special needs of the Air Force.

The goal of any theory of liquids must be to understand and predict the macroscopic properties (e.g., viscosity, compressibility, heat capacity, boiling and freezing point) in terms of the microscopic properties (the configuration of component atoms and the forces between them). This translation has been attempted by a variety of theoretical approaches, but none of these can claim other than limited success even with a relatively simple liquid, such as argon.

The solid and gaseous states are assisted in their interpretation by idealized limits which real systems approach. These are conditions of complete order (for solids) and complete disorder (for gases). No such convenient comparison is to be found for liquids. This situation has been admirably described by E. A. Moelwyn-Hughes. (1)

> The liquid state of matter is thus an intermediate one. Like a central party in politics or a moderate denomination in religion, it is less rigorously defined and more difficult to understand than either of the extremes that flank it.

In this most fundamental area the Directorate of Chemical Sciences, AFOSR, sponsors a select group of research efforts. It includes theoretical as well as experimental contributions. In the pages to follow, the interdependence of both approaches should be made clear.

In the subject area, the theoretical contributions of Professor Stuart A. Rice and co-workers, at the James Franck Institute, University of Chicago, have been outstanding. Professor Rice, of course, restricts his efforts neither to the liquid state nor theoretical analysis alone. In total, during the initial two year period of AFOSR support (ending [illegible] October [illegible]), over sixty technical papers were published by this group.

An important, but difficult task of theory lies in the prediction of liquid transport properties: thermal conductivity, viscosity, diffusion. To achieve this, appropriate means are required to introduce the element of irreversibility. Building upon the [illegible] microscopic equations of motion, the time-irreversible macroscopic flow equations must be constructed.

The theory of Rice and Allnatt has enjoyed considerable success in reaching the indicated objective. No attempt will be made to outline the precise mathematical formulation of the Rice-Allnatt theory. No derivations will be made of its precise consequences. Instead, the qualitative distinctions will be summarized and later the comparison of its predictions with available experimental data will be made (in the case of liquid argon). For the reader who is not content with this necessarily brief description, reference is made to available detailed discussions in the literature.(2)

The theory was developed for monatomic dense fluids. The interatomic potential energy is viewed in a special way. It is taken to be the superposition of a rigid core, very-short-range repulsion and a relatively weak, longer-range interaction. The fundamental dynamic event consists of a strongly repulsive encounter followed by a quasi-Brownian motion of the atom in the flucuating force field due to all remaining atoms in the system. Small, but frequent energy and momentum transfers characterize the second stage. In total they "erase all memory" of the first stage encounter. Successive repulsive encounters are thus statistically independent; in this manner the element of irreversibility is introduced.

The Rice-Allnatt theory accounts separately for the three components in the overall thermal conductivity and viscosity due to particle transfer, rigid core encounters, and longer-range interactions. Special difficulties are involved in the computation of the self-diffusion coefficient due to uncertainties about a fundamental parameter, the friction constant. All cases require knowledge of both the radial distribution function and the interatomic potential. The more accurate this knowledge is, the more meaningful will be predictions and tests of this or any theory. More will be said later on this important consideration.

The comparison of theory and experiment, as regards the thermal conductivity of liquid argon, is summarized in Table I. It should be noted that the first state listed provides a density of 1.374 g/cc; the three remaining high pressure states provide the same density, 1.12 g/cc. Overall, the agreement of theory with experiment is remarkable indeed.

TABLE I

The Thermal Conductivity of Liquid Argon, x 10^4, cal/deg-sec-cm

	90°K 1 atm	128°K 50 atm	133.5°K 100 atm	185.5°K 500 atm
K (obs)	2.96	1.89	1.86	1.87
K (calc)	1.65	1.69	1.59	1.70

Application of the theory to bulk and shear viscosity follows a similar mathematical formalism to that employed with the above. Again calculations were made for liquid argon; they are summarized in Table II.

TABLE II

The Bulk Viscosity, ϕ, and Shear Viscosity, η, for Liquid Argon Millipoise

	90°K 1 atm	128°K 50 atm	133.5°K 100 atm	185.5°K 500 atm
ϕ (obs)	---	---	---	---
ϕ (calc)	7	0.9	1.0	1.1
η (obs)	2.39	0.835	0.843	0.869
η (calc)	1.74	0.73	0.73	0.78
ϕ/η (calc)	4	1.3	1.3	1.3

The agreement for shear viscosity is excellent for the high pressure, constant density states (1.12 g/cc). The constancy of the ratio of bulk to shear viscosity predicted for the high pressure states is noteworthy. The different value for the single state at atmospheric pressure could be solely a reflection of the density difference. The calculations for this state, however, are regarded as the least reliable.

When the Rice-Allnatt predictions were first announced, no suitable experimental measurements of bulk viscosity were available for comparison. However, stimulated by the theoretical predictions, two experimental programs were initiated (at Texas A&M and the U. S. Naval Ordnance Laboratory). In both cases, splendid agreement was found; the precise states listed in Table II, however, were not measured directly. In the first-mentioned study (J. Chem. Phys., 45, 4669 (1966), extensive determinations of bulk viscosity were made in the density range 1.06-1.41 g/cc. The ratio of bulk to shear viscosity was found constant (±10%) at constant density (but with variable pressure and temperature). For 1.12 g/cc, the interpolated value for the viscosity ratio is 1.9 (in comparison with the Rice-Allnatt prediction of 1.3). Even closer agreement with theory was found in the second-mentioned study (J. Chem. Phys., 46, 4441 (1967). At -38.6°C, 0.5-1.0 g/cc, the measured values of bulk viscosity were, within experimental error, all in agreement with calculated Rice-Allnatt predictions.

The final example of Rice-Allnatt prediction considered here will be the self-diffusion coefficient for liquid argon. Here special difficulties arise because of the separate knowledge required of the interatomic friction constant. Table III presents a comparison of experiment with a series of predictions (each based on a different approach to determining the friction constant).

TABLE III
Self-Diffusion Coefficient for Liquid Argon
(Units of D are 10^{-5} cm^2 sec^{-1})

	84°K	90°K	100°K
D (obs)*	1.84	2.35	3.45
D (calc)[a]	1.43	1.80	2.25
D (calc)[b]	3.91	4.11	--
D (calc)[c]	2.25	2.49	--
D (calc)[d]	2.80	3.25	3.85
D (calc)[e]	2.46	2.70	3.34

* Naghizadeh and Rice

a. Square Well, exponentially decaying correlation function.

b. Small Step Diffusion Theory.

c. Small Step, isotope separation data.

d. Linear trajectory theory with no cross correlations.

e. Linear trajectory theory with inclusion of cross correlations.

The Rice-Allnatt theory is assuredly at least an adequate first order representation of the properties of real systems. The success enjoyed is not based on adjustable parameters (none are employed) nor on the use of models (except in the case of diffusion for the calculation of the friction constant).

The significance of the comparisons of calculations with experiment is really difficult to identify. As noted, the necessary calculations employ both the radial distribution function and the interatomic potential. Available knowledge of these quantities is deemed inadequate. Significant assistance to rectify this situation is being provided elsewhere under AFOSR support.

The necessary experimental approach is emphasized in the diverse activities of Professor C. J. Pings, California Institute of Technology (AFOSR Program for Research on Liquid Structure). Some recent developments in this program will be described.(3)

Employing x-ray diffraction measurements, Professor Pings and coworkers investigated the structure of argon at thirteen separate states of temperature and pressure in the general critical region (143° - 163°K, 40 - 98 atmospheres). These states were carefully selected so as to fall on a grid of lines of constant density and temperature. For the first time, the independent influences of these two variables were delineated.

The structural description is made in terms of the net radial distribution function, G(r). This function reveals the variation in local density (relative to the average value) as a function of distance, r, from the center of an arbitrary reference atom in the fluid. G(r) is determined by computation, through a Fourier transform, based on the experimentally measured intensities of scattered x-rays as a function of angle.

Representative examples of the results, in Fig. 12 show G(r) at various densitites. As seen, the probability of finding a neighboring atom is a damped, cyclic function of distance; at small enough distances (because of interatomic repulsion) this probability is zero (G(r) = -1).

The structural features of argon are regarded, based on this study, to be predominantly related to the sample density. The density influence on the longer range order can be seen in Fig. 12. Also, in the present curves, subpeaks reported in previous investigations are absent. These irregularities, to which special structural features

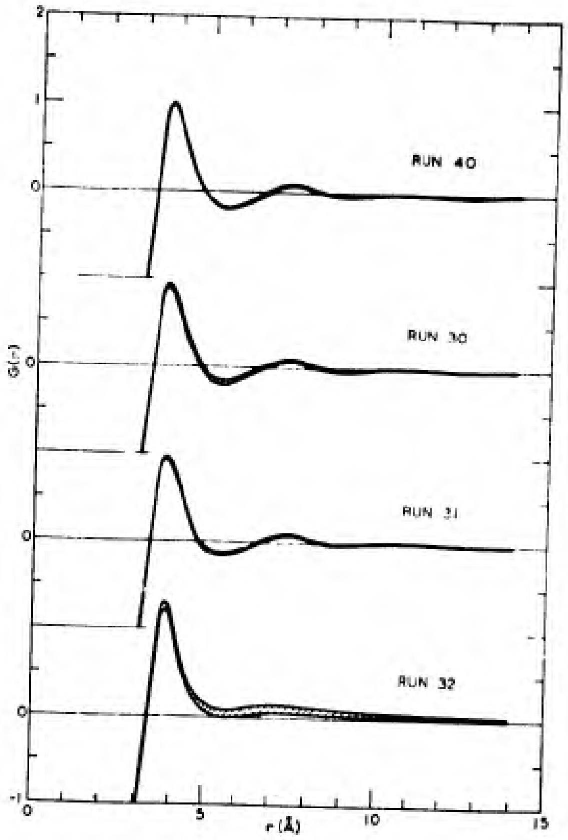

Fig. 12 The atomic radial distribution function of argon at $t = -125^{o}C$. Run 40, $\bar{\rho} = 0.982$ g/cc; Run 30, $\bar{\rho} = 0.910$ g/cc; Run 31, $\bar{\rho} = 0.780$ g/cc; Run 32, $\bar{\rho} = 0.280$ g/cc.

had been ascribed, are now believed to have been due to experimental error as well as computational difficulties. However, even with more modern detection systems and data processing methods, the recent results still retain some notable uncertainty (indicated by the shaded areas).

Another important contribution by the Caltech program is represented by efforts to compute the interatomic potential energy function, U(r), from the data obtained for the radial distribution function. This analysis is based on the available expansion of G(r) in a power series involving the density and the Mayer cluster integrals. By neglecting terms higher than first order, with iterative computational techniques, the result shown in Fig.13 was obtained. It is regarded to be in good agreement with currently accepted estimates. However, the data used were appropriate to densities about one-half the critical value. The neglect of second order terms in the expansion is hardly realistic.

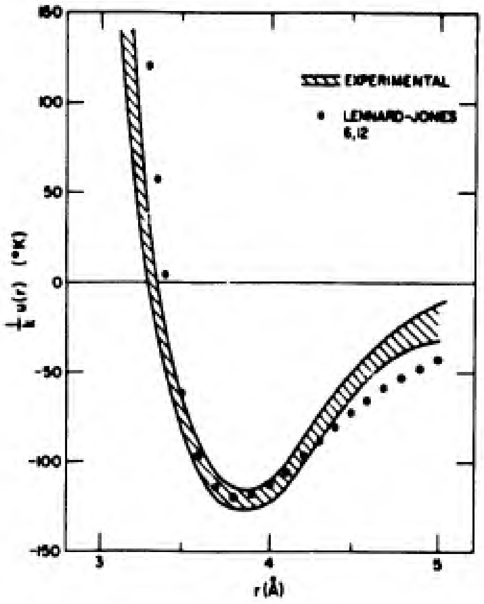

Fig. 13 Intermolecular potential function for argon. The Shaded area represents uncertainty arising from the experimental determination of the radial distribution function.

In future efforts, using more extensive data obtained in a selected density range, it should be possible to include second order terms and obtain an improved potential energy curve without relying on an iterative procedure.

In the past, using the above mentioned series expression for G(r) in terms of U(r), radial distribution functions have been derived from assumed approximations to the potential energy curve. However, the efforts of Professor Pings are apparently the first aimed in the opposite direction, employing experimentally determined radial distribution functions.

In the remarks above, the interdependence of theory and judicious experiment have been stressed. The two research programs described have been noteworthy in their separate contributions, which are seen to complement one another exceedingly well. Limitations on space preclude the inclusion of still other AFOSR sponsored research efforts which also contribute significantly to the characterization of the liquid state.

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CHEMISTRY PROGRAM STATISTICS

PROJECTS

	Number	Amount
New Projects	19[1]	$ 958,576
Renewals	48	$2,472,959
Continuing Projects	76	
Completed Projects	33	
TOTAL	176	
Completed Projects	33	
Active Projects end FY67	143	
(Including 6 with European Office, 6 in Canada, 3 in Australia, 3 in New Zealand, 1 in Chile, and 1 in Hawaii)		
Total Monies Committed During FY67		$3,431,535
Dollars Spend per Contract or Grant Year $3,431,535/105		$ 32,681

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[1] Three funded with ARPA money; One Interagency

SYMPOSIA

The Directorate of Chemical Sciences supported five symposia during fiscal year 1967. In general, these symposia served to bring together a selected group of participants who are actively engaged in a particular area of research. Those symposia marked with an asterisk (*) are described more fully in the Completed Project Summary section of this book.

GORDON RESEARCH CONFERENCE ON INORGANIC CHEMISTRY*, New Hampton School, New Hampshire, 8 - 10 August 1966

CHARACTERIZATION OF MACROMOLECULAR STRUCTURE, National Academy of Sciences, Washington D. C., 2 - 7 April 1967 (Co-sponsored with Air Force Materials Laboratory)

COLLOQUIUM ON THE PHOTOINTERACTION BETWEEN RADIATION AND MATTER*, Society of Photographic Scientists and Engineers, Washington, D. C., 26 - 29 October 1966

GORDON RESEARCH CONFERENCE ON HIGH TEMPERATURE CHEMISTRY*, Tilton School, Tilton, New Hampshire, 22 - 29 July 1966

SIXTH RARE EARTH RESEARCH CONFERENCE, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 3 - 5 May 1967

The following symposia are presently scheduled for support in the near future.

GORDON RESEARCH CONFERENCE ON INORGANIC CHEMISTRY, New Hampton, New Hampshire, 7 - 11 August 1967

SIXTH INTERNATIONAL SYMPOSIUM ON THE REACTIVITY OF SOLIDS, General Electric Research Laboratory, Schenectady, New York, August, 1968

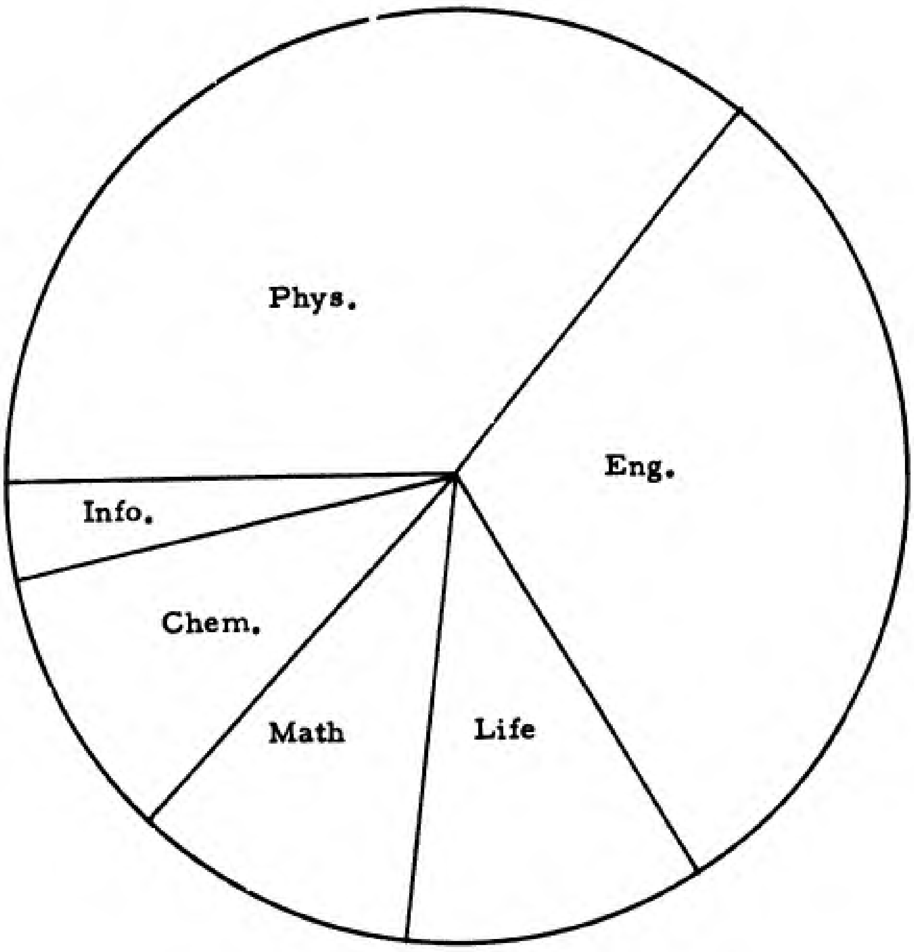
INORGANIC CHEMICAL NOMENCLATURE, National Academy of Sciences, Washington, D. C., Continuing

AFOSR BUDGET FY 67

Directorate	Symbol	Amount in Thousands	Percent
Physical Sciences	Phys.	$ 13,035	36.1
Engineering Sciences	Eng.	10,851	30.1
Life Sciences	Life	3,873	10.7
Mathematical Sciences	Math.	3,651	10.1
Chemical Sciences	Chem.	3,480	9.6
Information Sciences	Info.	1,220	3.4
		$ 36,110[1]	100.0

[1] As of 16 June 1967

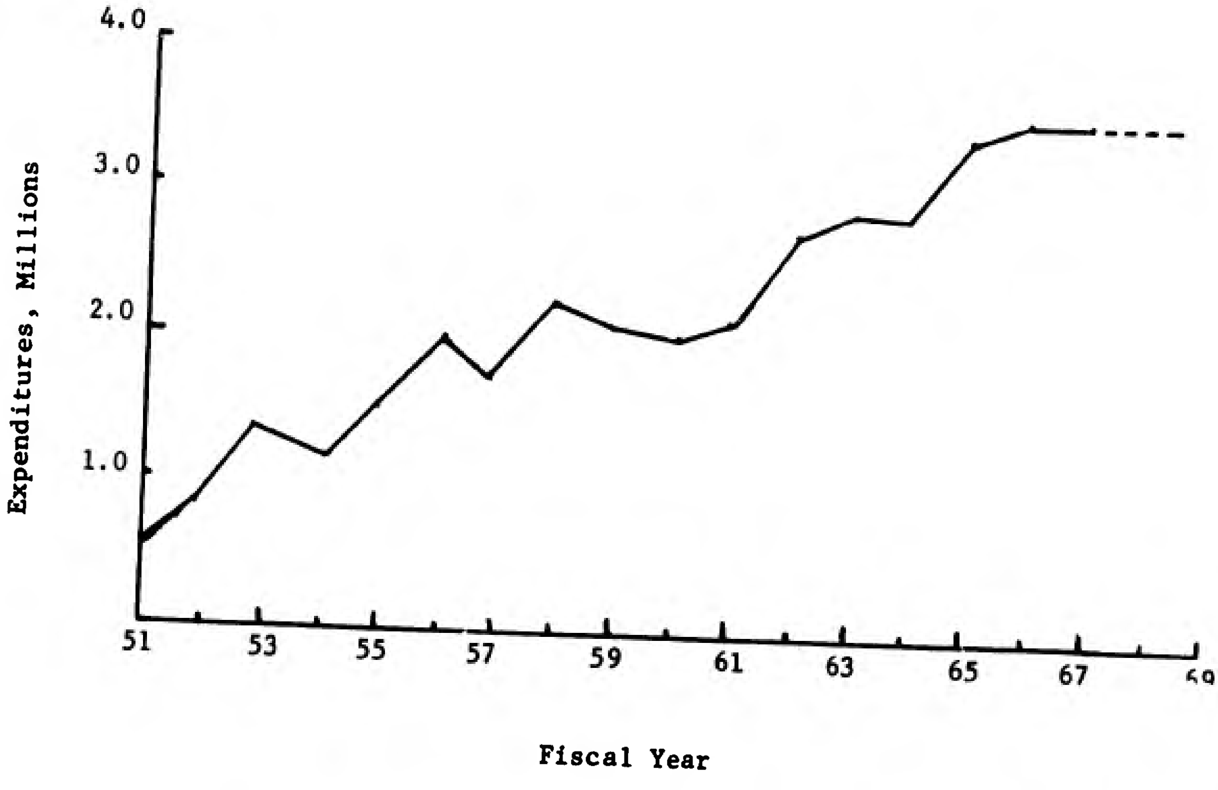
This information is depicted below.



CHEMISTRY BUDGET

FY	Amount in Thousands	FY	Amount in Thousands
51	$ 596	60	$1,964
52	835	61	2,086
53	1,310	62	2,700
54	1,150	63	2,922
55	1,451	64	2,959
56	1,976	65	3,356
57	1,732	66	3,475
58	2,205	67	3,480
59	2,066	68(est.)	3,311

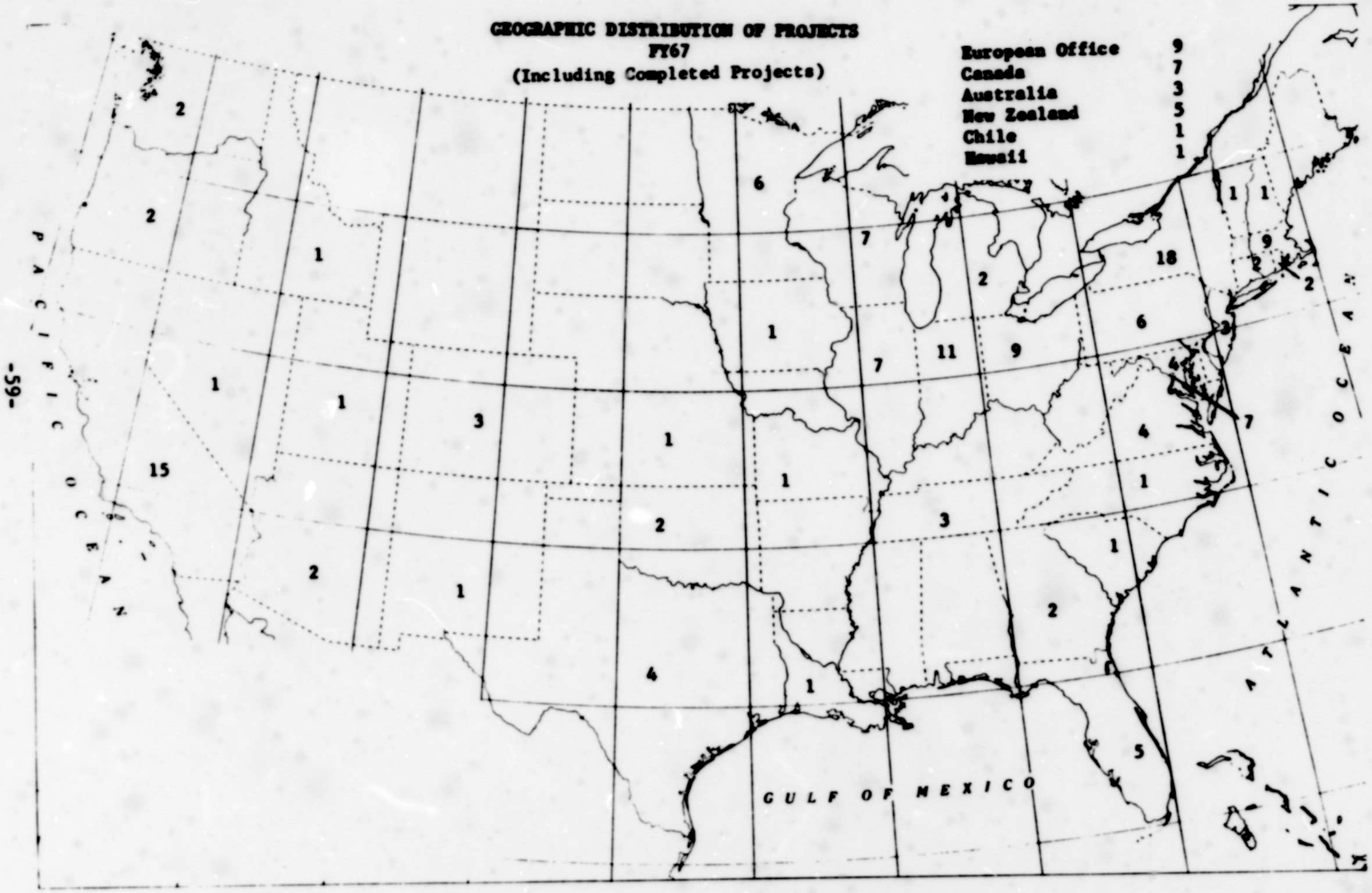
This information is displayed graphically below.



DISTRIBUTION OF SRC FUNDS BY FISCAL YEAR PERIODS
(FIGURES ARE THOUSANDS OF DOLLARS)

		Period of 1951-1955	Period of 1956-1959	Period of 1960-1963	Period of 1964-1967	Total
1.	California	254.7	819.0	1349.4	2579.9	5003.0
2.	New York	381.4	1047.2	1729.9	1286.9	4445.4
3.	Illinois	297.2	837.5	682.5	1066.9	2884.1
4.	Massachusetts	389.6	759.4	292.9	683.2	2125.1
5.	Indiana	65.4	414.0	518.1	1078.4	2075.9
6.	Pennsylvania	290.4	309.5	764.7	580.7	1945.3
7.	New Jersey	607.7	428.8	512.1	277.6	1826.2
8.	Ohio	539.4	411.7	283.5	400.8	1635.4
9.	Maryland	190.9	417.6	316.2	498.1	1422.8
10.	Texas	163.7	45.2	352.9	655.0	1216.8
11.	Washington	112.2	269.2	519.0	223.5	1123.9
12.	Florida	103.6	155.4	318.5	357.9	935.4
13.	Minnesota	99.0	217.6	342.5	209.7	868.8
14.	Wisconsin	61.1	241.5	164.9	400.5	868.0
15.	Connecticut	414.8	54.3	231.9	39.8	740.8
16.	District of Columbia	90.8	228.9	99.4	316.1	735.2
17.	Colorado	38.9	189.5	190.3	184.3	603.0
18.	Oklahoma	175.2	200.4	23.9	82.7	482.2
19.	Kansas	0	23.1	312.3	89.2	424.6
20.	Michigan	14.2	110.6	49.3	193.5	377.6
21.	Alabama	13.9	151.8	192.8	0	358.5
22.	Virginia	119.7	56.6	48.1	125.1	349.5
23.	Utah	161.3	83.6	14.8	54.3	314.0
24.	Oregon	0	44.7	195.1	51.3	291.1
25.	North Carolina	45.2	70.5	0	144.6	260.3
26.	Georgia	0	0	46.5	192.8	239.3
27.	New Mexico	0	0	75.3	103.4	178.7
28.	Tennessee	12.0	0	0	128.0	140.0
29.	Iowa	0	0	29.9	91.4	131.3
30.	New Hampshire	0	35.3	15.1	69.5	119.9
31.	Arkansas	72.1	9.4	0	0	81.5
32.	South Carolina	0	34.6	13.1	27.9	75.6
33.	Kentucky	0	69.6	0	0	69.6
34.	Arizona	0	0	6.0	57.3	63.3
35.	Louisiana	0	0	24.5	29.9	54.4
36.	Rhode Island	0	0	15.0	37.5	52.5
37.	Mississippi	0	0	46.0	4.6	50.6
38.	Missouri	0	0	23.8	24.8	48.6
39.	Idaho	0	0	18.2	27.4	45.6
40.	Vermont	0	0	0	33.3	33.3
41.	North Dakota	0	0	22.6	5.0	27.6
42.	Hawaii	0	0	0	15.0	15.0
43.	Nevada	0	0	0	13.6	13.6

GEOGRAPHIC DISTRIBUTION OF PROJECTS
FY67
(Including Completed Projects)



European Office	9
Canada	7
Australia	3
New Zealand	5
Chile	1
Hawaii	1

PROPOSAL DATA

	FY 65	FY 66	FY 67
New Proposals Received	271	322	327
Renewal Proposals Received	24	48	53
Total	295	370	380
New Proposals Declined, Withdrawn, or transferred	213	291	281
New Proposals Awaiting Action	0	0	10
New Proposals Funded	58	31	14
Percent Funded	21%	10%	4%
Renewal Proposals Funded	24	48	53
Percent Funded	100%	100%	100%
Overall Percent Declined	72%	79%	80%
Overall Percent Awaiting Action	0	0	3%
Overall Percent Funded	28%	21%	17%
Total	100%	100%	100%

PROFESSIONAL ACTIVITIES BY

MEMBERS OF THE DIRECTORATE OF CHEMICAL SCIENCES

Professional Meetings and Conferences Attended	23
Attendance by DCS Members	55
DOD Laboratories and Related Installations Visited	16
Visits by DCS Members	22
Papers Presented at Professional Meetings and and Conferences (ETW)	1
Professional Courses Completed (ETW)	1
Professional Courses Taught (ETW)	2
Symposia Chaired (AGH)	1
DCS Projects Visited (in the laboratories)	133
Potential Investigators Briefed on DCS Program at:	
(a) Universities, Colleges, Research Laboratories, National Meetings of the American Chemical Society, Symposia, etc.	175
(b) The Washington Office	120
TOTAL	295

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Mains, G.
Carnegie Institute of Technology
Pittsburgh, Pa.
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Stanford Research Institute
Menlo Park, California
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Myers, R. T.
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University of Chicago
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Newman, M. S.
Ohio State University
Columbus, Ohio
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Smith, W. T.
University of Kentucky
Lexington, Kentucky
AF49(638)-49

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Schmidt, H. H.
University of California
Riverside, California
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Shine, H. J.
Texas Technological College
Lubbock, Texas
AF-AFOSR-23-63

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Streitwieser, A.
University of California
Berkeley, California
AF-AFOSR-554-64

"Acidity of Hydrocarbons, XXI. Equilibrium Acidities of Some Hydrocarbons towards Lithium Cyclohexylamine in Cyclohexylamine," A. Streitwieser, E. Ciuffarin, J. H. Hammonds, and J. I. Brauman,
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Texas Technological College
Lubbock, Texas
AF-AFOSR-23-63

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Yaffe, L.
McGill University
Montreal, Canada
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DIRECTORATE OF CHEMICAL SCIENCES
AFOSR ARLINGTON, VA.

RESEARCH EFFORTS

As of 1 July 1967

(Alphabetical by Institution or Place)

Chemistry of Organolithium Compounds and Acetylenes M4 (968) 62/720-65	James Mulvaney Department of Chemistry University of Arizona Tucson, Arizona
Sixth Rare Earth Research Conference M1 (1067) 10/1-67	Wallace C. Koehler Solid State Division Atomic Energy Commission (ORNL) Oak Ridge, Tennessee
Chemistry of Radiation Protecting Agents B2 (1067) 60/950-65	John Packer Department of Chemistry University of Auckland Auckland, New Zealand
Far Infrared Studies of the Hydrogen Bond E3.5 (1068) 60/911-67	Robert Jakobsen Organic Chemistry Division Battelle Memorial Inst. Columbus, Ohio
Study of N_2 A-Triplet-Sigma State Generated by 1849 Å Mercury Photosensitization B4 (569) 60/765-65	Norman N. Lichtin and Morton Z. Hoffman Department of Chemistry Boston University Boston, Massachusetts
Photochemistry of Azo Compounds and Studies in Unimolecular Reactions B4 (1267) 60/583-66	Colin Steel Department of Chemistry Brandeis University Waltham, Massachusetts
Organometallic Chemistry E3 (1068) 10/61 (052) 847	F. G. A. Stone Department of Chemistry University of Bristol Bristol, England

Chemical Reactions in Frozen Solutions M2 (268) 62/1102-66	Richard E. Pincock Department of Chemistry University of British Columbia Vancouver 8, Canada
Kinetics of Ion-Complex Formation in Mixtures of Fused Salts Studied by Ultrasonic Absorption R2 (968) 60/1185-67	Sergio Petrucci Department of Chemistry Brooklyn Polytechnic Institute Brooklyn, New York
Isotope Study of the Decomposition of Inorganic Peroxides B2 (1067) 10/1027-66	John O. Edwards Department of Chemistry Brown University Providence, Rhode Island
Study of the Light Emitted by Atomic Flames B5 (967) 60/687-64	Kyle D. Bayes Department of Chemistry University of California Los Angeles, California
The AFOSR Program in Space Chemistry at UCLA W1 (168) 60/1255-67	Willard F. Libby Department of Chemistry University of California Los Angeles, California
Ultrarapid-scan Infrared Spectroscopy E2 (1/68) 60/1074-66	George C. Pimentel Department of Chemistry University of California Berkeley, California
Quantum Organic Chemistry M2 (9/67) 62/1002-66	Andrew Streitwieser, Jr. Department of Chemistry University of California Berkeley, California
Carbonium Ion Radicals and Oxy Radicals M4 (967) 62/514-66	Teddy G. Traylor Department of Chemistry University of California San Diego, La Jolla, California

Transfer of Excitation in Solution B3 (1067) 62/1479	George S. Hammond Department of Chemistry California Institute of Tech. Pasadena, California
The AFOSR Program for Research on Liquid Structures B4 (967) 10/1273	Cornelius J. Pings Department of Chemical Engineering California Institute of Tech. Pasadena, California
High-Resolution Spectroscopy of Small Molecules in the Gaseous State E2 (1/68) 60/1644	G. Wilse Robinson Department of Chemistry California Institute of Tech. Pasadena, California
Gas Phase Reaction of Atoms, Radicals and Simple Molecules B2 (269) 60/1265-67	Leon F. Phillips Department of Chemistry University of Canterbury Christchurch, New Zealand
Photo-Induced Redox Reactions B3.5 (969) 10/226-63	Jay K. Kochi Department of Chemistry Case Institute of Technology Cleveland, Ohio
Electronic Structures of Molecules by Variational Methods and Correlation Corrections B2 (10/67) 60/1030-66	Donald R. Whitman Douglas Carlson Department of Chemistry Case Institute of Technology University Circle Cleveland, Ohio
Structure of Molten Salts and Glasses E2 (1/68) 10/1086-66	Norman H. Nachtrieb Department of Chemistry University of Chicago Chicago, Illinois
Theoretical and Experimental Studies in Chemical Physics B3 (1067) 60/781-67	Stuart A. Rice Department of Chemistry University of Chicago Chicago, Illinois

Development of a Molecular Beam Accelerator B3 (468) 10/866-67	Lennard Wharton Department of Chemistry University of Chicago Chicago, Illinois
Salt Effects on Several Acidity Functions M2 (11/67) 62/999-66	Mario Ojeda Department of Chemistry University of Chile Santiago, Chile
NMR Studies of Intra- and Inter-Molecular Interactions W4 (867) 10/216-65	Melvin W. Hanna Department of Chemistry University of Colorado Boulder, Colorado
Vapor Phase Calorimetry W4 (369) 62/810-65	Joseph D. Park and John R. Lacher Department of Chemistry University of Colorado Boulder, Colorado
Electron Spin Resonance of Free Radicals E4 (767) 10/285-65	George K. Fraenkel Department of Chemistry Columbia University New York, New York
Chemistry of Strained Ring Compounds M2 (12/67) 60/1000-66	Nicholas J. Turro Department of Chemistry Columbia University New York, New York
Concentration Fluctuations in the Vicinity of the Critical Point B2 (1267) 60/1253-67	Benjamin Widom Department of Chemistry Cornell University Ithaca, New York
The Solution Chemistry of Polyhedral Boron Hydride Ions R4 (368) 10/589-66	Alexander Kaczmarczyk Department of Chemistry Dartmouth College Hanover, New Hampshire

Kinetic Energy of Ionic Products from Electron and Ion-Molecule Reactions W2 (9/67) 60/990-66	Eugene R. Weiner Department of Chemistry University of Denver Denver, Colorado
Plasma Pinch Flash Photolysis B4 (869) 60/980-67	Gilbert J. Mains Department of Chemistry University of Detroit Detroit, Michigan
Multicharge Aromatic Ions M4 (1068) 62/738-67	Merle A. Battiste Department of Chemistry University of Florida Gainesville, Florida
Synthesis of Triple Strand Polymers M4 (369) 62/817-67	George B. Butler Department of Chemistry University of Florida Gainesville, Florida
Differential Electrical Double Layer Capacities on Liquid and Solid Electrodes W2 (1067) 60/1034-66	Gerhard M. Schmid Department of Chemistry University of Florida Gainesville, Florida
Flame Spectrometry and Gas Chromatographic Detectors R2 (967) 10/1033-66	James D. Winefordner Department of Chemistry University of Florida Gainesville, Florida
Atomic and Molecular Kinetics on Solid Surfaces H,R4 (168) 60/1362	Gert Ehrlich General Electric Research Lab. P. O. Box 1088 Schenectady, New York
Crystal Chemistry of New High Pressure Phases H,R4 (1267) 10/1361	John S. Kasper General Electric Research Lab. P. O. Box 1088 Schenectady, New York

Sixth International Symposium on the Reactivity of Solids W,H1.5(468) 60/67-C-0078	A. M. Bueche Department of Chemistry General Electric Research Lab. Schenectady, New York
Reactions of Metallic Ions E2.25(1268) 60/1225-67	Joseph E. Earley Department of Chemistry Georgetown University Washington, D. C.
Heteropoly Compounds of Group VB Elements E2 (268) 10/1066-66	Michael T. Pope Department of Chemistry Georgetown University Washington, D. C.
ESR Thermal Decomposition Studies of Nitroaromatic Compounds and Inorganic Salts M2 (268) 62/1069-66	Edward G. Janzen Department of Chemistry University of Georgia Athens, Georgia
Transition Metal Complexes Containing Nitrogen, Phosphorus, or Sulfur E5 (1267) 10/1211-67	R. Bruce King Department of Chemistry University of Georgia Athens, Georgia
Studies in Ring Expansion M5 (968) 62/67-13	George L. Buchanan Department of Chemistry University of Glasgow Glasgow, Scotland
Gordon Research Conference on Inorganic Chemistry E1 (369) 10/1103-67	Seymour Yolles Grant W. Urry Gordon Research Conference University of Rhode Island Kingston, Rhode Island
X-Ray Crystallographic Methods R4 (168) 62/1059-66	J. Zanos Gougoutas Department of Chemistry Harvard University Cambridge, Massachusetts
Instrument Grant for Chemical Structure Determination R2 (168) 62/1060-66	J. Zanos Gougoutas Department of Chemistry Harvard University Cambridge, Massachusetts

The Solvent Extraction Behavior of Inorganic Complexes E2 (1067) 10/983-65	Ray L. McDonald Department of Chemistry University of Hawaii Honolulu, Hawaii
Transition Metal Ammine Complexes at High Pressures and Temperatures E2 (1067) 10/1190-67	Wesley W. Wendlandt Department of Chemistry University of Houston Houston, Texas
The Acid-Base Characteristics of Phototropism M4 (967) 62/1264	J. David Margerum Hughes Research Labs. 3011 Malibu Canyon Road Malibu, California
Liquid Crystal Reactions by Ellipsometry E.33 (867) 67-C0091	E. L. Grove Department of Chemistry Illinois Institute of Tech. Chicago, Illinois
Kinetic Spectroscopy of Chemically Active Systems E2 (168) 60/1703	Edward J. Bair Department of Chemistry Indiana University Bloomington, Indiana
Theoretical and Experimental Analysis of Electron Scattering from Atoms and Molecules B2 (168) 60/1681	Russell A. Bonham Department of Chemistry Indiana University Bloomington, Indiana
Electronic Computer Calculations on Simple Diatomic and Polyatomic Molecules E1 (1267) 60/1242-67	Harrison Shull Stanley A. Hagstrom Department of Chemistry Indiana University Bloomington, Indiana
Quantum Chemistry Program Exchange W4 (1068) 60/767-67	Harrison Shull Department of Chemistry Indiana University Bloomington, Indiana

Reactions and Structures of Metal-Olefin Complexes and Related Substances W4 (1268) 10/763-67	John R. Doyle and Norman C. Baenziger Department of Chemistry State University of Iowa Iowa City, Iowa
Upper Atmosphere Ion-Molecule Reactions E4 (867) 60/1301	Walter S. Koski Department of Chemistry Johns Hopkins University Baltimore, Maryland
Studies of Liquid Crystals as Related to Electro-Optical and Other Devices E1 (568) 67-C-0103	Glenn H. Brown Department of Chemistry Kent State University Kent, Ohio
Surfaces States in Pure Palladium H5 (368) 60/144-65	Richard W. Zuehlke Department of Chemistry Lawrence College Appleton, Wisconsin
Structure and Reactivity of Solutions of Metals in Non-metallic Solvents W6 (967) 10/64-80	M. C. R. Symons Department of Chemistry University of Leicester Leicester, England
Displacement Reactions by Free Radicals on S-S and O-O Bonds M4 (867) 62/540-66	William Pryor Department of Chemistry Louisiana State University Baton Rouge, Louisiana
Surface Stabilized Free Radicals R4 (168) 60/642-66	Hyman Gesser Department of Chemistry University of Manitoba Winnipeg, Canada
Phosphorus Coordination Compounds R4 (1068) 10/782-67	Samuel O. Grim Department of Chemistry University of Maryland College Park, Maryland

The Chemistry of Carbanions M4 (1267) 62/573-66	Herbert O. House Department of Chemistry Massachusetts Institute of Tech. Cambridge, Massachusetts
Organometallic Synthesis of Reactive Intermediates M4 (1067) 62/502-66	Dietmar Seyferth Department of Chemistry Massachusetts Institute of Tech. Cambridge, Massachusetts
Electrochemistry of Transition Metal Ions in Acetonitrile W4 (1068) 10/777-67	John W. Olver Department of Chemistry University of Massachusetts Amherst, Massachusetts
Rates of Exchange of Solvent Molecules with Paramagnetic Ions M4.5 (867) 60/212-65	Thomas R. Stengle and Cooper M. Langford Department of Chemistry University of Massachusetts (and Amherst College) Amherst, Massachusetts
Inorganic N. M. R. Spectroscopy R2 (368) 10/1127-66	R. J. Gillespie Department of Chemistry McMaster University Hamilton, Ontario, Canada
Photolytic and Pyrolytic Free Radicals R2 (268) 10/1085-66	A. S. Buchanan Department of Chemistry University of Melbourne Parkville, N. 2, Melbourne Australia
Kinetic Spectroscopy in the Infrared R2 (767) 10/976-66	Robert M. Hexter Clifford W. Hand Mellon Institute Pittsburgh, Pennsylvania
Defect States and Structure of Oxide Glasses R3 (768) 10/974-67	John H. Mackey, Jr. Mellon Institute Pittsburgh, Pennsylvania

Excited States of Uranium and Heavy Metals E4 (168) 60/865-67	Thomas Dunn Department of Chemistry University of Michigan Ann Arbor, Michigan
Acid-Base Equilibria and Titrations and Electrochemical Equilibria in Acetonitrile W1 (967) 10/1223-67	I. M. Kolthoff Department of Chemistry University of Minnesota Minneapolis, Minnesota
Polynuclear Hydroxo Complexes R2 (968) 10/691-67	R. Stuart Tobias Department of Chemistry University of Minnesota Minneapolis, Minnesota
Vibrational Anharmonicity and Rotation-Vibration Interaction in Polyatomic Molecules E1 (967) 60/570-67	John Overend Department of Chemistry University of Minnesota Minneapolis, Minnesota
Characterization of Macromolecular Structure M1 (1167) 60/1179-66	Martin A. Paul National Research Council National Academy of Sciences Washington, D. C.
Conference on Current and Future Problems in Chemistry at High Temperatures E1 (867) 60/1040-66	Martin A. Paul National Research Council National Academy of Sciences Washington, D. C.
Research on Inorganic Chemical Nomenclature W2 (268) 10/890-65	Martin A. Paul National Research Council National Academy of Sciences Washington, D. C.
Kinetics of Transition-Metal Ions of d^8 Electronic Configuration B2 (1067) 10/994-66	David J. MacDonald Department of Chemistry University of Nevada Reno, Nevada
Chemistry of Decaborane R3 (169) 10/910	Norman N. Greenwood Department of Chemistry King's College University of Newcastle Newcastle-upon-Tyne, England

Fundamental Investigations of Luminescent Materials R4 (967) 10/269-67	G. A. Crosby Department of Chemistry University of New Mexico Albuquerque,New Mexico
Sigma Pi Rearrangement M4 (367) 62/824-67	Minoru Tsutsui Department of Chemistry New York University New York, New York
Photochemically Generated Valence Tautomers B4 (469) 62/837-67	Theodore D. Goldfarb and Robert S. Boikess Department of Chemistry State University of New York Stony Brook, Long Island, N.Y.
Photochemical Generation of Divalent Carbon Derivatives M4 (269) 62/1213-67	Albert Padwa Department of Chemistry State University of New York Albany, New York
Electrochemical Studies of Kinetics, Adsorption, and Excited Electronic States E4 (368) 60/584-66	Royce W. Murray and Charles N. Reilley Department of Chemistry University of North Carolina Chapel Hill, North Carolina
Heterogeneous Catalysis in Liquid Systems E6 (968) 60/97-63	Robert L. Burwell, Jr. Department of Chemistry Northwestern University Evanston, Illinois
Energy Transfer in Hot Molecules B2 (668) 60/1155-66	Edward W. Schlag Department of Chemistry Northwestern University Evanston, Illinois
Quantitative Conformational Analysis M2 (1068) 62/772-67	Ernest L. Eliel Department of Chemistry University of Notre Dame Notre Dame, Indiana

Molecular Structure of Carbanions and Kinetics of their Exchange Processes in Solution W4.5 (1267) 62/251-65	Gideon Fraenkel Department of Chemistry Ohio State University Columbus, Ohio
Density of Cryogenic Liquid Mixtures W2 (967) 60/1020-66	Frank B. Canfield Department of Chemistry University of Oklahoma Norman, Oklahoma
Nucleophilic Displacements on Trivalent Phosphorus R5 (967) 62/132-67	K. Darrell Berlin Department of Chemistry Oklahoma State University Stillwater, Oklahoma
An Investigation of the Mechanism of the Reaction Between Boron Trifluoride and Nitrogen (III, IV, V) Oxides E2 (568) 10/1152-66	P. R. Ogle, Jr. Department of Chemistry Otterbein College Westerville, Ohio
X-Ray Adsorption-Edge Fine-Structure Spectrometry of Glass and Glass-Crystal Materials R,H2 (1267) 10/1670	Charles G. Dodd General Research Division Owens-Illinois Technical Center Toledo, Ohio
High Pressure (3-5Kb.) Inorganic and Organometallic Syntheses R4 (169) 10/1519	Alan G. MacDiarmid Department of Chemistry University of Pennsylvania Philadelphia, Pennsylvania
Solvent Isotope Effects for CH_3OH vs. CD_3OH M4 (1067) 62/431-65	Edward R. Thornton Department of Chemistry University of Pennsylvania Philadelphia, Pennsylvania
Spectroscopic Studies of Chemical Reactions in the Solid State E2(867) 60/907-65	I. C. Hisatsune Department of Chemistry Pennsylvania State University University Park, Pennsylvania
Atomic Chemistry M2 (1167) 62/1245-67	P. S. Skell Department of Chemistry Pennsylvania State University University Park, Pennsylvania

Chemical Electronic Structure Theory B2 (967) 60/1625	Leland C. Allen Department of Chemistry Princeton University Princeton, New Jersey
Inorganic Structure and Spectra R5 (1267) 10/1492	William D. Horrocks, Jr. Department of Chemistry Princeton University Princeton, New Jersey
Studies in Stereochemistry M1.5 (1167) 62/1188-67	Kurt Mislow Department of Chemistry Princeton University Princeton, New Jersey
Electrolytic Reduction of Organic Compounds W4 (369) 62/822-67	Robert A. Benkeser Department of Chemistry Purdue University Lafayette, Indiana
Study of Kinetic Methods of Chemical Analysis E2 (1068) 10/11212-67	Dale W. Margerum Harry L. Pardue Department of Chemistry Purdue University Lafayette, Indiana
Hot Atom Chemistry of Oxygen and Nitrogen B2 (1067) 10/1031-66	Friedrich Schmidt-Bleek Department of Chemistry Purdue University Lafayette, Indiana
Charge and Energy Transfer in Organic Systems E2 (967) 62/863-65	Lawrence E. Lyons Department of Chemistry University of Queensland St. Lucia, Brisbane, Australia
Reaction Rate Studies of Gaseous Unimolecular Isomerizations E4 (867) 60/119-65	Frederick D. Tabbutt Department of Chemistry Reed College Portland, Oregon

Viscous Flow and Compressibility of Molten Borates at High Pressure R4 (968) 10/1460	John D. Mackenzie Department of Chemistry Rensselaer Polytechnic Inst. Troy, New York
Bibliographic File of Abstracts on Photographic Science H2 (468) 10/1112-66	Thomas Hill Rochester Institute of Tech. 69 Plymouth Avenue South Rochester, New York
Unimolecular Decomposition of Cyclobutane Derivatives at High Pressure W4 (1267) 60/575-66	David J. Wilson and Winston D. Walters Department of Chemistry University of Rochester Rochester, New York
The Solvolytic Reactivity of Pi-Complexed Compounds M2 (867) 62/991-66	Robert S. Bly, Jr. Department of Chemistry University of South Carolina Columbia, South Carolina
Physical Adsorption of Vapors W2 (568) 60/1097-66	Arthur W. Adamson Department of Chemistry University of Southern Calif. Los Angeles, California
Microwave Spectroscopy of Boron Compounds R4 (769) 60/849-67	Robert A. Beaudet Department of Chemistry University of Southern Calif. Los Angeles, California
Electrochemistry of Solids W2 (967) 10/986-66	Ferdinand A. Kroger Department of Chemistry University of Southern Calif. Los Angeles, California
The AFOSR Center for Macromolecular Research at Stanford University M6 (168) 60/1341	Paul J. Flory Department of Chemistry Stanford University Stanford, California

Mass Spectrometric, Thermochemical and Related Studies on Series of Inorganic Compounds R2 (869) 10/67-C-0005	Michael F. Lappert Department of Chemistry University of Sussex Falmer, Brighton, Sussex, England
High Resolution Raman Spectroscopy E3 (369) 60/1092-67	William H. Fletcher Department of Chemistry University of Tennessee Knoxville, Tennessee
Organic Chemical Physics M3 (1168) 62/1050-67	Michael J. S. Dewar Department of Chemistry University of Texas Austin, Texas
Reactions of Molecules in Excited States with Paramagnetic Gases W4 (1268) 60/778-67	W. Albert Noyes, Jr. Department of Chemistry University of Texas Austin, Texas
Ion-Radicals of Organic Sulfur, Selenium, Tellurium and Phosphorus Compounds M2 (967) 62/975-66	Henry J. Shine Department of Chemistry Texas Technological College Lubbock, Texas
Kinetics of Atomic Association Reactions Using Flash Photolysis Over a Wide Temperature Range R4 (1067) 60/506-66	George Burns Department of Chemistry University of Toronto Toronto, Canada
Kinetics of Ion Formation in Shock Waves R4 (1067) 60/504-66	John E. Dove Department of Chemistry University of Toronto Toronto, Canada
Molecular Interactions and Crystal Structures at Low Temperatures W2 (967) 10/1010-66	Stanley Nyburg Department of Chemistry University of Toronto Toronto, Canada

Inorganic Applications of Nuclear Quadrupole Resonance Spectroscopy R4 (169) 10/859-67	Terry E. Haas Department of Chemistry Tufts University Medford, Massachusetts
Laser Temperature-Jump Studies of Fast Reactions R4 (967) 10/476-66	Edward M. Eyring Department of Chemistry University of Utah Salt Lake City, Utah
Coordination, Ligand Reactivity, and Catalysis W4 (668) 60/630-66	Mark M. Jones Department of Chemistry Vanderbilt University Nashville, Tennessee
Interaction of Molecules with Solid Surfaces B2 (967) 60/993-66	A. D. Crowell Department of Physics University of Vermont Burlington, Vermont
Use of Mössbauer Effects in Chemistry E2 (369) 60/1236-67	J. F. Duncan Department of Chemistry Victoria University of Wellington Wellington, New Zealand
Theoretical Studies on the Structure of Inorganic and Organometallic Compounds H,M2 (1068) 62/1184-67	J. E. Bloor Department of Chemistry University of Virginia Charlottesville, Virginia
Mössbauer Effect Studies of Surface Reactions B1 (1066) 60/1049-66	Melvin C. Hobson, Jr. Virginia Institute for Scientific Research Richmond, Virginia
Chemical Characterization of Molecules Adsorbed on a Foreign Solid B4 (1069) 60/734-67	Melvin C. Hobson, Jr. Department of Chemistry Virginia Inst. Sci. Research Richmond, Virginia

Oxidation of Arsenic (III) and Antimony (III) E4 (967) 10/210-65	John G. Mason Department of Chemistry Virginia Polytechnic Inst. Blacksburg, Virginia
Intermolecular Energy Transfer B2 (967) 60/1633	B. S. Rabinovitch Department of Chemistry University of Washington Seattle, Washington
Acidity Dependence of Reaction Rates and Equilibria in Strong Aqueous Acids M4 (1267) 62/590-66	William M. Schubert Department of Chemistry University of Washington Seattle, Washington
Mechanism of Nitrogen Fixation by Ultrasonic Radiation in Water E4 (569) 60/67-24	Michael Anbar Department of Chemistry Weizmann Institute of Science Rehovoth, Israel
Properties of Solid, Non-Stoichiometric Lanthanide Oxide Phases E4 (269) 60/853-67	Bruce G. Hyde Department of Physical Chemistry University of Western Australia Nedlands, W. A., Australia
Some Thermochemical Studies by Mass Spectrometry R2 (967) 10/977-66	D. R. Bidinosti Department of Chemistry University of Western Ontario London, Ontario, Canada
Chemistry of Strained Olefins M2 (967) 62/1006-66	Jerome A. Berson Department of Chemistry University of Wisconsin Madison, Wisconsin
Structural Chemistry and Bonding in Inorganic Compounds E4 (1167) 10/518-66	Lawrence F. Dahl Department of Chemistry University of Wisconsin Madison, Wisconsin

Stereochemical Aspects of Ionization Processes M4 (769) 62/847-67	Harlan L. Goering Department of Chemistry University of Wisconsin Madison, Wisconsin
Novel Organometallic Compounds M2 (268) 62/1061-66	Robert C. West Department of Chemistry University of Wisconsin Madison, Wisconsin
Pressure Dependence of Electrolytic Conductance R4 (667) 60/244-65	Raymond M. Fuoss Department of Chemistry Yale University New Haven, Connecticut
Nucleophilic Displacements by Organophosphorus Compounds R4 (569) 62/1170-66	Irving J. Borowitz Department of Chemistry Yeshiva University New York, New York

DIRECTORATE OF CHEMICAL SCIENCES
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RESEARCH PROJECTS COMPLETED IN FY 1967

(Alphabetical by Institution or Place)

Complexing Properties of Inorganic Solvents EW2 (1266) 10/96-63	R. D. Peacock Department of Chemistry The University of Birmingham Birmingham, England
Atom Recombination W4 (1266) 60/158-65	E. A. Ogryzlo Department of Chemistry University of British Columbia Vancouver, B.C. Canada
Models for Asymmetric Induction In Polymerization M4 (966) 62/124-63	Donald J. Cram Department of Chemistry University of California Los Angeles, California
AFOSR Program in Space Chemistry at UCLA H4 (167) 10/245-65	Willard F. Libby Department of Chemistry University of California Los Angeles, California
Gas-phase Reactions W4 (267) 60/264-65	Leon F. Phillips Department of Chemistry University of Canterbury Christchurch, New Zealand
Theoretical and Experimental Studies in Chemical Physics B2 (1066) 60/781-65	Stuart Rice Department of Chemistry University of Chicago Chicago, Illinois
Critical Opalescence and Molecular Forces M5 (966) 60/750/65	Peter J. Debye Department of Chemistry Cornell University Ithaca, New York
Symposium on Electrode Processes R1 (1066) 60/1647	Ernest Yeager The Electrochemical Society 30 East 42nd Street New York, New York

Colloquium on the Photographic Interaction Between Radiation and Matter EW1 (367) 60/1713	James E. LuValle Society of Photographic Scientist and Engineers Fairchild Space and Defense Systems 300 Robbins Lane Syosset, New York
Small Ring Compounds M4 (966) 62/488- 64	Emil J. Moriconi Department of Chemistry Fordham University New York, New York
Reactions of Metallic Ions E4 (1066) 10/133-65	Joseph E. Earley Department of Chemistry Georgetown University Washington, D. C.
Gordon Research Conference on High Temperature Chemistry W1 (267) 60/1083-66	LeRoy Eyring Gordon Research Conferences Department of Chemistry University of Arizona Tucson, Arizona
Gordon Research Conference on Inorganic Chemistry R1 (367) 10/1103-66	Edwin M. Larsen Gordon Research Conferences Department of Chemistry University of Wisconsin Madison, Wisconsin
Studies of the Infrared Spectra of Compressed Gaseous Mixtures R4 (1066) 10/167-65	George C. Turrell Department of Chemistry Howard University Washington, D. C.
Rearrangements of Carbonium Ions and Free Radicals in the Bicyclo (3,1,0) Hexyl System M4 (966) 62/875-65	Peter K. Freeman Department of Chemistry University of Idaho Moscow, Idaho

Chemical Reactions of Secondary Electrons R4 (965) 60/1104	Paul Y. Feng Department of Chemistry Illinois Institute of Tech. Chicago, Illinois
Preparation and Properties of Reactive Intermediates E4 (1266) 60/362-64	Harrison Shull Department of Chemistry Indiana University Bloomington, Indiana
High Resolution Studies in the Far Infrared R4 (267) 10/93-63	Dean W. Robinson Department of Chemistry Johns Hopkins University Baltimore, Maryland
Coincidence Measurements of Molecule-Ion Reactions H4 (167) 10/1365	William H. Johnston Marvin L. Vestal Wm. H. Johnston Labs. Inc. 3617 Woodland Avenue Baltimore, Maryland
Synthesis and Chemistry of Acetals and Mercaptals of Formyl Halides E4 (1066) 62/145-65	Richard N. McDonald Department of Chemistry Kansas State University Manhattan, Kansas
Conference on Liquid Crystals E1 (766) 60/971-65	Glenn H. Brown Department of Chemistry Kent State University Kent, Ohio
Studies in the Cyclobutane Series M3 (866) 62/123-63	Irving Lillien Department of Chemistry University of Miami Coral Gables, Florida
Complex Formation, Ion Conjugation and Unusual Valence States in Acetonitrile W4 (1266) 10/28-65	I. M. Kolthoff Department of Chemistry University of Minnesota Minneapolis, Minnesota

Mixed Heteropoly Acid Formation E4 (167) 10/205-65	John C. Guyon Department of Chemistry University of Missouri Columbia, Missouri
Oxidation-Reduction Reactions of Organic Sulfur Compounds M4 (1166) 62/106-65	John L. Kice Department of Chemistry Oregon State University Corvallis, Oregon
Chemical Research on Matter E,C2 (167) 60/64-32	Egil A. Hylleraas Institute of Theoretical Physics University of Oslo Blindern PR, Oslo, Norway
Preparation and Properties of Nitronic Esters M4 (966) 62/122-65	Nathan Kornblum Department of Chemistry Purdue University Lafayette, Indiana
Ultra Trace Analysis by Coordination Chain Reactions R4 (1066) 10/134-65	Dale W. Margerum Department of Chemistry Purdue University Lafayette, Indiana
Solution Chemistry R4 (966) 10/65-22	Lars Gunnar Sillén Division of Inorganic Chemistry Royal Institute of Technology Stockholm 70, Sweden
Hydrogen Transfer Reactions in Catalytic Homogeneous Systems E4 (1266) 62/1214	Jack Kwiatek Research Laboratory U. S. Industrial Chemicals Co. Cincinnati, Ohio
The Use of Mössbauer Effect in Chemistry E4 (367) 10/27-65	James F. Duncan Department of Chemistry Victoria University Wellington, New Zealand

Steric Effects in Conjugated Systems M5 (367) 62/389-63	Jerome A. Berson Department of Chemistry University of Wisconsin Madison, Wisconsin
Instrument Grant for Electrolytic Conductions R1 (567) 60/1148-66	Raymond M. Fuoss Department of Chemistry Yale University New Haven, Connecticut

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COMPLETED PROJECT SUMMARY

1. TITLE: Complexing Action of Inorganic Solvents

2. PRINCIPAL INVESTIGATOR: Dr. R. D. Peacock
Department of Chemistry
University of Birmingham
Birmingham, England

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

4. GRANT NO: AF-EOAR-63-96

5. COSTS AND FY SOURCE: $15,000 FY63

6. SENIOR RESEARCH PERSONNEL: Dr. R. D. Peacock
Dr. B. Cohen

7. JUNIOR RESEARCH PERSONNEL: T. R. Hooper
D. Hugill
D. Nichols
P. Watkins

8. PUBLICATIONS:

"Preparation of Thiazyl Fluorides," B. Cohen, T. R. Hooper, D. Hugill, and R. D. Peacock, Nature, 207 748 (1965).

"Pentafluorosulphur Iminosulphur Difluoride," B. Cohen, T. R. Hooper and R. D. Peacock, Chemical Communications, 32, (1966).

"The Preparation of Tetrasulphur Tetranitride and Thiazyl Fluoride from Sulphur Tetrafluoride," B. Cohen, T. R. Hooper, and R. D. Peacock, J. Inorg. Nucl. Chem., 28, 919 (1966).

"Complexing Action of Inorganic Solvents," Final Report, AFOSR-66-2706.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objective of this research was to make a general study of inorganic compounds containing the elements, nitrogen, fluorine, and sulfur. In addition, a general study of the solvent action of carbon dioxide, chlorine, and ammonia, under pressures of 10 to 200 atmospheres, was planned.

A new method was developed for the preparation of tetrasulfur tetranitride. This method involves the reaction of ammonia with sulfur tetrafluoride. Thiazyl fluoride was also produced from these reactants (in 20% yield) by varying the conditions.

Tetrasulfur tetranitride was subjected to fluorination using fluorine, hydrogen fluoride, and disulfur decafluoride. In each case the results were different from those reported by other workers. The most significant difference was noted in the case of fluorine where, inter alia, the novel compound pentafluorosulfur iminosulfur difluoride, SF_5NSF_2, and thiazyl fluoride were obtained. The former is the first inorganic iminosulfur difluoride. It is the second compound known to contain the pentafluorosulfur group bonded to nitrogen, SF_5NF_2 being the other. The molecule contains sulfur in both the tetra- and hexavalent states. In the case of hydrogen fluoride, the main product of the fluorination was thiotrithiazyl fluoride. When disulfur decafluoride was used as the fluorinating agent, thiazyl trifluoride was obtained in low yields together with other compounds as yet unidentified.

This group of researchers also did prelininary work with hydrides and fluorides of selenium and tellurium. Selenium nitride, Se_4N_4, was found to react explosively with selenium tetrafluoride.

In studying the solvent action of liquid carbon dioxide it was found that this solvent dissolves iodine to give a purple-colored solution. From this is was concluded that the double bonds in carbon dioxide are not available for coordinate linkages.

Project Scientist: LtCol E.T.Walford

COMPLETED PROJECT SUMMARY

1. TITLE: Atom Recombination

2. PRINCIPAL INVESTIGATOR: Dr. E. A. Ogryzlo
   Department of Chemistry
   University of British Columbia
   Vancouver, Canada

3. INCLUSIVE DATES: 2 October 1962 - 30 April 1967

4. GRANT NO: AF-AFOSR-158-65

5. COSTS AND FY SOURCE: \$16,169 FY63; \$18,515 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. E. A. Ogryzlo
   Dr. A. Pearson

7. JUNIOR RESEARCH PERSONNEL: R. J. Browne
   K. Mintz
   S. J. Arnold

8. PUBLICATIONS:

"Recombination of Chlorine Atoms," L. W. Bader and E. A. Ogryzlo, Nature, <u>201</u>, 491 (1964).

"Reactions of O_2 ($^1\Delta g$) and O_2 ($^1\Sigma_g^+$)," L. W. Bader and E. A. Ogryzlo, Discussions of the Faraday Soc., <u>37</u>, 46 (1964).

"Halogen Atom Reactions II. Luminescence from the Recombination of Chlorine Atoms," L. W. Bader and E. A. Ogryzlo, J. Chem. Phys., <u>41</u>, 2926 (1964).

"Halogen Atom Reactions III. Luminescence from the Recombination of Bromine Atoms," D. B. Gibbs and E. A. Ogryzlo, Can. J. Chem., <u>43</u>, 1905 (1965).

"Pressure Dependence of the Visible Absorption Bands of Molecular Iodine," E. A. Ogryzlo and G. Thomas, J. Molecular Spectroscopy, <u>17</u>, 198 (1965).

"The Yield of Singlet Oxygen in the Reaction of Chlorine with Hydrogen Peroxide," R. J. Browne and E. A. Ogryzlo, Can. J. Chem., <u>43</u>, 2915 (1965).

"The Red Emission Bands of Molecular Oxygen," S. J. Arnold, R. J. Browne and E. A. Ogryzlo, J. Photochem. and Photobiol., <u>4</u>, 963 (1965).

"Some Novel Energy-Pooling Processes Involving O_2 (${}^1\Delta_g$)," S. J. Arnold, N. Finlayson and E. A. Ogryzlo, J. Chem. Phys., 44, 2529 (1966).

"Some Reactions Forming O_2 (${}^1\Sigma_g^+$) in the Upper Atmosphere," S. J. Arnold and E. A. Ogryzlo, Canad. J. Physics, 45, June (1967).

"Atom Recombination: I. Halogen Atoms, II. Singlet Molecular Oxygen," Final Report, AFOSR-67-1290.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Halogen Atoms

The recombination of chlorine atoms was found to produce a red emission (luminescence) composed of a series of bands extending into the infrared. Studies of the influence of changing pressure and atom concentration on the emission spectrum suggest that it is made up of at least two components of assignable sources. These results are consistent with a bimolecular radiative recombination involving the ${}^1\Pi_{1u}$ repulsive state and a termolecular recombination into the ${}^3\Pi_{0+u}$ state, which is rapidly quenched by chlorine atoms.

A red glow was also detected from the recombination of bromine atoms. The explanation proposed is similar to that used for chlorine. Luminescence was observed also in the case of atomic iodine recombination, but not with sufficient precision to identify the emitter.

Detailed measurements were made of the kinetics of the atomic recombination of both chlorine and iodine. Using the former as an example, the observed third order rate law is

$$\frac{-d(Cl)}{dt} = 2k_{exp}\,(Cl)^2(Cl_2).$$

However, the rate "constant," k_{exp}, was found to be dependent on pressure and atom concentration in a manner consistent with the following mechanism.

$$Cl + Cl_2 + M \underset{k_2}{\overset{k_1}{\rightleftarrows}} Cl_3 + M$$

$$Cl_3 + Cl \xrightarrow{k_3} Cl_2 + Cl_2$$

The observed rate constant, assuming a steady-state concentration of the intermediate complex Cl_3, is given by

$$k_{exp} = \frac{k_1 k_3}{k_2} \bigg/ \left(\frac{k_3}{k_2} \cdot \frac{(Cl)}{(M)} + 1 \right)$$

Here, "M" is the "third body" to which energy is transferred. In these studies of atomic chlorine and bromine recombination, no dilute gas was employed; "M" was, in fact, respectively, chlorine and bromine molecules. Based on the observed dependence of k_{exp} on $(Cl)/(Cl_2)$ or $\left((Br)/(Br_2)\right)$, k_1 and k_3/k_2 were determined for both chlorine and bromine atom recombination.

Singlet Molecular Oxygen

Extensive investigations were made of the quenching of excited oxygen molecules. The conclusions reached include the following:

Excited oxygen molecules $O_2(^1\Delta_g)$ were prepared in an electric discharge. Excited molecules $O_2(^1\Sigma_g^+)$ were formed by an energy disproportionation process

$$O_2(^1\Delta_g) + O_2(^1\Delta_g) \longrightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-).$$

The reactant molecules can also combine their energy and emit it as a single photon.

$$O_2(^1\Delta_g) + O_2(^1\Delta_g) \longrightarrow O_2(^3\Sigma_g^-) + O_2(^3\Sigma_g^-) + h\nu$$

Quenching of $O_2(^1\Sigma_g^+)$ by added foreign gases was investigated (for water, deuterium oxide, ammonia, hydrogen sulfide, carbon dioxide, chloroform, and methane). A positive correlation was noted between quenching efficiency and polarity (as well as boiling point) of the added substance. Polyatomic molecules are, on the average, more effective quenchers than diatomic molecules. However, quenching efficiency could not be attributed to resonance mechanism.

Project Scientist: Dr. D. Ball

COMPLETED PROJECT SUMMARY

I. TITLE: Models for Asymmetric Induction in Polymerization

2. PRINCIPAL INVESTIGATOR: Dr. Donald J Cram
Department of Chemistry
University of California
Los Angeles, California

3. INCLUSIVE DATES: 1 October 1962 - 30 September 1966

4. GRANT NO: AF-AFOSR-124-63 and 124-65

5. COSTS AND FY SOURCE: $50,642 FY63; $54,976 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. H. P. Muller
Dr. R. Guthrie
Dr. H. Fischer
Dr. F. Willey
Dr. S. Janiak

7. JUNIOR RESEARCH PERSONNEL:

T. Buckman
R. Uyeda
F. Wudl
A. Cohen
J. Day
T. Hoffman
J. Almy
S. Cheng
W. Ford
W. Kollmeyer
T. Leitereg
S. Ela
J. Roitman
L. Bock
M. Brown
W. Larson

8. PUBLICATIONS:

"Base-Catalyzed Intramolecular 1,3- and 1,5-Proton Transfers," D. J. Cram, F. Willey, H.P. Fischer and D. A.Scott, J. Am. Chem. Soc., 86,5370 (1964).

"Electrophilic Substitution at Saturated Carbon. XXII. Intramolecular Hydrogen Transfer Reactions in Base-Catalyzed Allylic Rearrangements," D. J. Cram and R. T. Uyeda, J. Am. Chem. Soc., 86, 5466 (1964).

"Electrophilic Substitution at Saturated Carbon. XXII. Stereochemical Stability of Allylic and Vinyl Anions," D. H. Hunter and D. J. Cram, J.Am. Chem. Soc., 86, 5478 (1964).

"On the Claim of a Bimolecular Mechanism of Prototropy," D. J. Cram and R. D. Guthrie, J. Am. Chem. Soc., 87, 397 (1965).

"Formation of a Cyclopropane Ring from an α, β-Unsaturated Carboxylic Acid," R. T. Uyeda and D. J. Cram, J. Org. Chem., 30, 2083 (1965).

"Electrophilic Substitution at Saturated Carbon. XXVI. Base-Catalyzed Intramolecular 1,3- and 1,5-Proton Transfer," D. J. Cram, F. Willey, H. P. Fischer, M. Relles and D. A. Scott, J. Am. Chem. Soc., 88, 2759 (1966).

"Electrophilic Substitution at Saturated Carbon. XXVII. Carbanions as Intermediates in the Base-Catalyzed Methylene-Azomethine Rearrangement," D. J. Cram and R. D. Guthrie, J. Am. Chem. Soc., 88, 5760 (1966).

"Electrophilic Substitution at Saturated Carbon. XXIX. Relationships between Position of Protonation of Allylic Anions and the Kinetic and Thermodynamic Stabilities of the Olefinic Products," S. W. Ela and D. J. Cram, J. Am. Chem. Soc., 88, 5791 (1966).

"Models for Asymmetric Induction in Polymerization," Final Report, AFOSR-66-2571.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to develop one-stage chemical reactions that could serve as models for multistage polymerization chain reactions leading to stereoregular polymers. Polymers such as polypropylene can be regarded as composed of units strung together which possess the symmetry properties of hands. Thus, polymers are known that resemble an assembly of left hands (isotactic), that approximate an assembly of alternating left and right hands (syndiotactic), and that can be described as an assembly of randomly oriented left hand and right hands (atactic). The physical properties of these polymers vary remarkably with the "handedness" of the chains, and therefore the utility of the polymers depends on an ability to regulate the "handedness" or stereoregularity of the chain.

Two theories of why stereoregular polymers form have evolved: 1) the handedness of the last unit in the growing chain induces left or right handedness in the next unit added to the chain; 2) a catalyst (sometimes a solid) acts as a templet which in effect "stamps out" left or right handed chains. In their model work, Dr. Cram and his research group obtained permissive evidence that applies, and determined what variables favor stereoregular and stereorandom processes. Reactions were discovered in which a "right handed" molecule underwent reaction to produce a new molecule in which the "old hand" was destroyed and a new "hand" introduced which was essentially 100% "right."

Many examples of 1, 3- and 1, 5-base-catalyzed intramolecular proton transfers were discovered, and the factors that govern these reactions were studied. Allylic, azoallylic or benzylic anions were invariably intermediates in the reaction. Intramolecularity was found to vary within wide limits as changes were made in the polarity and nature of the cations of the medium. The relative pK_a's of the substrate and the direction of isotope transfer also influenced the intramolecularity. Hydrogen bonding and ion-pairing were demonstrated to be the organizational factors which led to the intramolecular proton transfers.

Project Scientist: Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: The AFOSR Program for Space Chemistry

2. PRINCIPAL INVESTIGATOR: Dr. Willard F. Libby
Department of Chemistry
University of California, Los Angeles
Los Angeles, California

3. INCLUSIVE DATES: 1 January 1963 - 30 December 1966

4. GRANT NUMBER: AF-AFOSR-245-63; AF-AFOSR-245-64; AF-AFOSR-245-65

5. COSTS AND FY SOURCE: $152,731 FY63; $152,506 FY64; $291,273 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. John W. Root

7. JUNIOR RESEARCH PERSONNEL: Dr. Fred Aldridge
Dr. Alfred J. Darnell
Dr. Donald R. Davis
Dr. Roger H. Ide
Dr. Carl A. Jensen
Dr. Armen R. Kazanjian
Dr. Larry Kevan
Dr. Jeremy Sprung
Dr. Lowell L. Wood

Saul Alkaitis
John Griffiths
Martin Hackendorf
Peter Hamlet
Howard Katzman
Joel Leventhal
David Lichtenstein
Michelle Meyers
Allen Minton
Patrick Payton
Richard Shafer
Lewis Solomon

8. PUBLICATIONS:

"Electron Transfer Among the Transition Elements. The Controlling Role of the Franck-Condon Principle on Rates," W. F. Libby, J. Chem. Phys., 38, 420 (1963).

"Indium Antimonide: The Metallic Form at Atmospheric Pressure," A. J. Darnell and W. F. Libby, Science, 139, 1301 (1963).

"Indium Antimonide: Superconductivity of the Metallic Form," H. E. Bonnel, A. J. Darnell, W. F. Libby and B. R. Tittmann, Science, 139, 1301 (1963).

"Theory of Metallic Diamond," W. F. Libby, Phys. Rev., 130, 548 (1963).

"Moratorium Tritium Geophysics," W. F. Libby, J. Geophys. Res., 68, 4485 (1963).

"Indium Telluride Metal," A. J. Darnell, A. J. Yencha, and W. F. Libby, Science, 141, 713 (1963).

"Superconductivity of Metallic Indium Telluride," H. E. Bonnel, A. J. Darnell, W. F. Libby, B. R. Tittmann and A. J. Yencha, Science, 141, 714 (1963).

"Chemistry of Positive Ions III. The Radiation Chemistry of Solid n-Hexane at 77^{o}K," Larry Kevan and W. F. Libby, J. Chem. Phys., 39, 1288 (1963).

"Search for Natural Curium 247," G. W. Wetherill, W. F. Libby and G. W. Barton, J. Geophys. Research, 69, 1603 (1964).

"Positive-Ion Chemistry: High Yields of Heavy Hydrocarbons from Solid Methane by Ionizing Radiation," D. R. Davis and W. F. Libby, Science, 144, 991 (1964).

"The Chemistry of Ionic States in Solid Saturated Hydrocarbons," Larry Kevan and W. F. Libby, Advances in Photochemistry, Volume 2, Interscience Publishers, New York, 183 (1964).

"Superconductivity in the Artificial Metals: Metallic Indium Antimonide, the Indium-Antimonide-Tin Alloys, and Metallic Indium Telluride," B. R. Tittmann, A. J. Darnell, H. E. Bonnel and W. F. Libby, Phys. Rev., 135, A1460 (1964).

"Artificial Metals: InSb, the Sn Alloys with InSb, and Metallic InTe," A. J. Darnell and W. F. Libby, Phys. Rev., 135, A1453 (1964).

"Intense 584-Å Light from a Simple Continuous Helium Plasma," C. A. Jensen and W. F. Libby, Phys. Rev., 135, A1247 (1964).

"Metallic Diamonds: Pressure-Produced Metals," A. J. Darnell and W. F. Libby, Progress in Solid State Chemistry, 2, (1965).

"Nature of the Chemical Reactivity of Radiobromine Atoms Produced by Isomeric Transition," A. R. Kazanjian and W. F. Libby, Chem. Phys., 42, 2778 (1965).

"Science and Manned Spacecraft," W. F. Libby, Astronautics and Aeronautics (1965).

"Reactions of Thermal Carbon Atoms," Jeremy L. Sprung, S. Winstein and W. F. Libby, J. Am. Chem. Soc., 87, 1812 (1965).

"Electron and Energy Transfer in Irradiated Xenon-Hexane Liquid Solutions," Donald R. Davis, W. F. Libby and Larry Kevan, J. Am. Chem. Soc., 2766 (1965).

"Tritium in Mt. Everest Ice-Annual Glacier Accumulation and Climatology at Great Equatorial Altitudes," Maynard M. Miller, Joel S. Levanthal and W. F. Libby, J. Geophys. Res., 70, 3885 (1965).

"Space Chemistry," W. F. Libby, Science in the Sixties, University of New Mexico, 175 (1965).

"The Nature of Long Range Interaction in Hemoglobin," W. F. Libby, Science in the Sixties, University of New Mexico, 200 (1965).

"Chimica spaziale," W. F. Libby, La Chimica E L'Industria, 48, 471 (1966).

"Melting Points at High Compressions from Zero-Compression Properties Through the Kennedy Relation," W. F. Libby, Phys. Rev. Letters, 17, 423 (1966).

"Chemistry of Positive Ions, VI. Positive-Ion Chemistry in Solid Methane," Donald R. Davis, W. F. Libby and W. G. Meinschein, J. Chem. Phys., 45, 4481 (1966).

"Electron in Box Theory for Metal Atom Clusters," W. F. Libby, J. Chem. Phys., 46, 399 (1967).

"The Effects of High Hydrostatic Pressure on Coliphage T-$_4$," Louis Solomon, Pete Zeegan and Fred Eiserling, Biochim. Biophys. Acta, 112, 102 (1966).

"The AFOSR Program for Space Chemistry," Final Report, AFOSR 67-1494.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The AFOSR Program in Space Chemistry at UCLA consists of the investigation of chemical phenomena under the conditions of outer and inner space together with peripheral but pertinent activities.

A. High Pressure Chemistry

New metals were produced by collapsing the Group IV elements and their analogous binary compounds into the hexagonal tin metallic lattice. The new metals were removed from the press at one atmosphere by chilling with liquid nitrogen and their properties measured.

It was learned in these studies that the pressure of collapse of the tetrahedral diamond type lattice to the hexagonal tin lattice is related to the electronic energy gap in the diamond solid such that the $P\Delta V$ work is half of the electronic energy gap. This relationship, together with the known six electron volt energy gap of diamond, indicates that the pressure of collapse of the diamond to the metallic diamond lattice probably would occur somewhat in excess of three million atmospheres, the pressure at the center of the earth. It is planned to bind diamond with a binder which has an expansion coefficient and compressibility similar to that of diamond itself in order to make a diamond matrix similar to the cobalt bound tungsten carbide matrix now used in nearly all high pressure apparatus. This will be done to build a press capable of one million atmospheres.

The high pressure chemistry of the biochemical DNA was studied with the coliphage $T\text{-}_4$ virus where it was discovered that the double helix of deoxyribonucleic acid uncoiled, presumably as a result of the rupture of the linking hydrogen bonds between the two chains. Crude experiments on aliphatic hydrocarbons and foodstuffs have shown interesting effects on the application of pressures of 50,000 atmospheres. Phenomena which occur above 10,000 atmospheres are relatively unexplored, in particular the violent explosions which occur with branched chained hydrocarbons subjected to pressure plus shear.

It was found that the application of pressures to foodstuffs in the range of 5 - 10 kilobars was similar to thermal cooking. However, even the weakest ordinary chemical bond could not be ruptured under these conditions, apparently only hydrogen bonds. This suggests an application to the synthesis of biochemicals where the application of pressure would accomplish a selective rupture of the hydrogen bonds only.

B. Radiation Chemistry

Studies of the chemistry of ions were continued to learn more of the effects of ionizing radiation on matter, so that the great problems in radiobiology and in the commercial application of atomic radiation could be attacked successfully. Ions are an excited state of molecules which are relatively long-lived under many conditions and it seems likely that much of the chemistry occurring as a result of ionizing radiation could occur in the ionic state. In earlier work a large part of the behavior of hydrocarbon ions was explained on the principle that the ion chemistry should be chemically similar to the analogous neutral atom or molecule. Thus CH_4^+ behaves as fluorine atom does and CH_5^+ is thought of as a Bronsted acid, like HF, etc. This theory predicts that aromatic ions will be relatively inert and has very little to say about the properties of such highly stripped ions as CH_2^+, CH^+.

In addition to the chemistry of positive ions, the chemical effects of Auger explosions were investigated. These extraordinary events follow on the creation of a vacancy in an inner shell of an atom, preferably the K shell, and in the case of heavy atoms like bromine may result in as many as a dozen positive charges being placed on the single atom. These charges then, by intra-electron transfer within the molecule, diffuse over the molecule and by virtue of the resultant strong repulsive electrical forces explode the molecule. These explosions have strong consequences. Studies were made on bromine compounds in which it was shown that the chemical nature of the products was determined by the ionization potential of the environment being above or below that of atomic bromine - supposedly determining whether the chemistry was ionic and due to Br^+ or neutral and due to Br.

The ability of electrons to transfer over large distances (tens of angstroms) from a neutral molecule of lower ionization to the ion of a molecule of higher ionization potential affords a very promising method of concentrating ionization energy on a minor constituent and thus increasing the effeciency. This may make certain atomic radiation uses economic. It also may have application to radiobiology where groups of lower ionization potential (such as aromatic structures) may have a protective effect because their ions are chemically unreactive.

C. High Vacuum Chemistry

The principle purpose in high vacuum chemistry is to test the usefulness of the vacuum which is characteristic of interplanetary space. The LEED (Low Energy Electron Diffraction) Apparatus of Varian Associates was used to examine the nature of the effects on the diamond surface by carbon vapor treatments. The elimination of air, 10^{-13} atmospheres, should give the required cleanliness. If successful, this technique may provide the first serious and straightforward application of space satellites for chemical manufacturing purposes.

D. High Temperature Chemistry

Several high temperature plasma torches were built capable of heating nearly any gas to temperature of about 100,000°K. These flames have many uses - from growing sapphires and other crystals to the study of the spectrum of the sun by making a flame of the supposed composition of surface solar matter.

Primary efforts during this period have been to study the chemical reaction between benzene (in the form of a film at liquid nitrogen temperatures) and carbon vapor. The principal result was the formation of a high molecular weight polymer even at the low temperature. The polymer was seen to grown even though the apparatus is surrounded by boiling liquid nitrogen.

Project Scientist: Lt Col. E. T. Walford

COMPLETED PROJECT SUMMARY

1. TITLE: Gas-phase Reactions

2. PRINCIPAL INVESTIGATOR: Dr. Leon F. Phillips
Chemistry Department
University of Canterbury
Christchurch, New Zealand

3. INCLUSIVE DATES: 15 February 1963 - 14 February 1967

4. GRANT NO: AF-AFOSR-264-63; AF-AFOSR-264-65

5. COSTS AND FY SOURCE: $23,900 FY63; $25,000 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. Maxwell M. Sutton
Dr. William M. Litchman

7. JUNIOR RESEARCH PERSONNEL: C. G. Freeman
K. S. Raxworthy
M. J. McEwan
M. R. Grigor
D. I. Walton
T. S. Wauchop
G. J. Smith
A. J. McNaughton

8. PUBLICATIONS:

"Photometric Study of the Reaction of Iodine with Active Nitrogen," C. G. Freeman and L. F. Phillips, J. Phys. Chem., 68, 362 (1964).

"Photometric Observations on the Reactions of Active Nitrogen with Chlorine and Bromine," K. S. Raxworthy and L. F. Phillips, Can. J. Chem., 42,2928 (1964).

"The Lifetime of the A. $^3\Sigma_u^+$ State of N_2," L. F. Phillips, Can. J. Chem., 43, 369 (1965).

"Mass Spectrometric Studies of Atomic Reactions. V. The Reaction of Nitrogen Atoms with NO_2," L. F. Phillips and H. I. Schiff, J. Chem. Phys., 42, 3171 (1965).

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"Direct Observation of $A^3\Sigma^+_u$ Nitrogen Molecules in the N-I_2 Flame," D. I. Walton, M. J. McEwan and L. F. Phillips, Can. J. Chem., 43, 3095 (1965).

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"The Dissociation Energy of NaO_2," M. J. McEwan and L. F. Phillips, Trans. Faraday Soc., 62, 1717 (1966).

"Reaction Flames of Active Nitrogen with IBr and ICl," M. R. Grigor and L. F. Phillips, 11th Symposium (International) on Combustion, p. 751. Pittsburgh: The Combustion Institute, in press.

"Radical Concentrations and Decays in Lean $H_2/N_2/O_2$ Flames," M. J. McEwan and L. F. Phillips, Combustion and Flame, in press.

"Mass Spectrometric Study of the Reaction of Hydrogen Atoms with Cl_2O," C. G. Freeman and L. F. Phillips, in preparation.

"Gas-phase Reactions," Final Report, AFOSR-67-0919.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research effort can be classified into three main areas, namely: (a) studies of chemiluminescence from atom reactions in conventional discharge-flow systems at pressures near 3 torr; (b) kinetic measurements on fast reactions in discharge-flow systems at total pressures near 0.3 torr, using a mass spectrometer to monitor the partial pressures of reactants and products; and (c) photometric observations on reactions and equilibria in oxygen-rich $H_2/N_2/O_2$ flames at atmospheric pressure.

In chemiluminescence studies of the reaction of iodine with atomic nitrogen evidence was obtained for the production of an intermediate excited nitrogen molecule in the $A^3\Sigma^+_u$ state. It was postulated that these excited A-state molecules collide with nitrogen molecules to form excited iodine molecules, I_2^*, which decay to produce an intense blue chemiluminescence. The decay of the blue emission at low iodine pressures was found to follow precisely the decay of the atomic nitrogen concentration and bore no relation to the natural lifetime of the excited A-state nitrogen molecules. This suggests strongly that these A-state molecules were present in a steady state condition.

Kinetic studies of the hydrogen atom-oxygen dichloride system were performed with a mass spectrometer which was built with funds from the AFOSR grant. The rate constant for the primary reaction step

$$H + Cl_2O \longrightarrow HCl + ClO$$

was found to be 1.0 ± 0.3 x 10^{13} ml per mole per sec at 300°K. The instrumentation could be used to study the reactions of Cl_2O with oxygen and nitrogen atoms as well and with very little modification to study analogous reactions of ClO_2. Several of these reactions are of interest in connection with the use of perchlorate oxidizers in solid rocket fuels.

Based on photometric studies of oxygen-rich $H_2/N_2/O_2$ flames, the reaction

$$O + O + Na \longrightarrow O_2 + Na^*$$

was found to be the most important source of chemiluminescence from traces of sodium. This reaction may be responsible for the sodium chemiluminescence in the upper atmosphere. Excess O_2 was found to react with sodium to form NaO_2. Based on measured values for the equilibrium constant of the reaction

$$Na + O_2 + M \longrightarrow NaO_2 + M$$

the dissociation energy of gaseous NaO_2 (to form Na and O_2 at 0°K) was computed to be 65 ± 3 kcal/mole.

Project Scientist: Dr. D. Ball

COMPLETED PROJECT SUMMARY

1. TITLE: Theoretical and Experimental Studies in Chemical Physics

2. PRINCIPAL INVESTIGATOR:
Stuart A. Rice
Institute for the Study of Metals
University of Chicago
Chicago, Illinois

3. INCLUSIVE DATES: 1 November 1964 - 31 October 1966

4. GRANT NO: AF-AFOSR-781-65

5. COSTS AND FY SOURCE: $188,314 FY65

6. SENIOR RESEARCH PERSONNEL:
R. Stephen Berry
Jean-Pierre Boon
Sang-il Choi
Morrel H. Cohen
H. Ted Davis
Peter Gray
Ian H. Hillier
Kazuo Hiroike
Joshua Jortner
Neil R. Kestner
John C. Mackie
Lothar Meyer
Norman H. Nachtrieb
Stuart A. Rice
Brian E. Springett
E. G. Wilson

7. JUNIOR RESEARCH PERSONNEL:
Bruce J. Berne
Leon M. Glass
Jon E. Haebig
Andrew U. Hazi
Norman Hurt
Joseph L. Katz
John Lekner
Eugene S. Pysh
Harold Schnyders
Robert Silbey
Huei-Ying Sun
Martin T. Vala, Jr.
Stephen Webber
David A. Young

8. PUBLICATIONS:

"A Brief Review of Some Aspects of the Molecular Theory of Liquids," in Liquids: Structure, Properties, Solid Interactions. Proceedings of the Symposium on Liquids: Structure, Properties, Solid Interactions, General Motors Research Laboratories, Warren, Michigan, 1963. Ed. by Thomas J. Hughel. Elsevier Publishing Company, Amsterdam (1965), pp. 51-141.

"Comments on the Theory of Ionic and Electronic Mobility in Liquids," in Progress in Dielectrics, Vol. VI, ed. by J. B. Birks. Temple Press Books, Ltd., London (1965), p. 183. With Joshua Jortner.

"Energy Transfer Phenomena in Liquid Helium," Phys. Rev. Letters 12, 415 (1964). With Joshua Jortner, Lothar Meyer and E. G. Wilson.

"Guest-Host Interactions: An Examination of the Solvent Induced Spectral Shift in a Model System," J. Chem. Phys. 41, 3779(1964). With Huei-Ying Sun and Joshua Jortner.

"Ion-Pair Exciton States and the Optical Spectrum of Crystalline Neon," J. Chem. Phys. 41, 2911 (1964). With Stephen Webber and Joshua Jortner.

"On the Kinetic Theory of Dense Fluids. XVIII. The Bulk Viscosity," J. Chem. Phys. 41, 3689 (1964). With Peter Gray.

"Charge Transfer Exciton States in Aromatic Molecular Crystals," J. Chem. Phys. 41, 3294 (1964). With Sang-il Choi, Joshua Jortner and Robert Silbey.

"On the Singlet Exciton-States of Crystalline Anthracene," J. Chem. Phys. 42, 1515 (1965). With Robert Silbey and Joshua Jortner.

"On the Excited Electronic States of Isotactic Polystyrene and Polyvinylnaphthalene," J. Chem. Phys. 41, 2846 (1965). With Martin T. Vala, Jr., Robert Silbey and Joshua Jortner.

"Comments on the Use of Carbon SCF Atomic Orbitals in Aromatic Molecules," J. Chem. Phys. 42, 444 (1965). With Robert Silbey, Neil R. Kestner and Joshua Jortner.

"Localized Excitations in Condensed Neon, Argon, Krypton, and Xenon," in Low Temperature Physics, LT9, Proceedings of the Ninth International Conference on Low Temperature Physics. With Joshua Jortner, Lothar Meyer and E. G. Wilson. Edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqut, Plenum Press, New York (1965), pp. 356-359.

"Exchange Effects on the Electron and Hole Mobility in Crystalline Anthracene and Naphthalene," J. Chem. Phys. 42, 733 (1965). With Robert Silbey, Joshua Jortner and Martin T. Vala, Jr.

"Erratum: Exchange effects on the Electron and Hole Mobility in Crystalline Anthracene and Naphthalene," (J. Chem. Phys. 42, 733 (1965). J. Chem. Phys. 43, 2925 (1965). With Robert Silbey, Joshua Jortner, and Martin T. Vala, Jr.

"Triplet Excitons in Crystals of Aromatic Molecules," J. Chem. Phys. 42, 309 (1965). With Joshua Jortner, Joseph L. Katz and Sang-il Choi.

"The Chemistry of Xenon," Chem. Rev. 65, 199 (1965). With John G. Malm, Henry Selig and Joshua Jortner.

Reply to M. Blander Re: "A Perturbation Theory of the Heats of Mixing of Fused Salts." J. Chem. Phys. 42, 810 (1965). With H. Ted Davis.

"Deep Impurity States in Molecular Crystals: The Optical Excitation of a Substitutional Argon Atom in Crystalline Neon," J. Chem. Phys. 42, 1907 (1965). With Stephen Webber and Joshua Jortner.

"Photoconductivity in Crystals of Organic Molecules," in Modern Quantum Chemistry, Istanbul Lectures, Part III: Action of Light and Organic Crystals. Ed. by Oktay Sinanoglu, Academic Press, Inc., New York (1965), pp. 235-48. With J. Jortner.

"Search for a Charge Transfer State in Crystalline Anthracene," J. Chem. Phys. 42, 1535 (1965). With R. S. Berry, Joshua Jortner, John C. Mackie and Eugene S. Pysh.

"The Electron-Helium Atom Pseudopotential," in Modern Quantum Chemistry, Istanbul Lectures, Part II: Interactions. Ed. by Oktay Sinanoglu, Academic Press, Inc., New York (1965), pp. 129-32. With Joshua Jortner, Neil R. Kestner and Morrel H. Cohen.

"Experimental Study of Luminescence and Excitation Trapping in Vinyl Polymers, Paracyclophanes, and Related Compounds," J. Chem. Phys. 43, 886 (1965). With Martin T. Vala, Jr. and Jon Haebig.

"Theoretical Studies of Transannular Interactions. I. Benzene Excimer Fluorescence and the Singlet States of the Paracyclophanes," J. Chem. Phys. 44, 23 (1966). With Ian H. Hillier, Martin T. Vala, Jr., and Joshua Jortner.

"On the Electronic States of Crystalline Naphthalene," J. Chem. Phys. 42, 2948 (1965). With Robert Silbey, Joshua Jortner, and Martin T. Vala, Jr.

"On the Kinetic Theory of Dense Fluids. XIX. Comments on and a Rederivation of the Kinetic Equations," J. Chem. Phys. 42, 3134 (1965). With Kazuo Hiroike and Peter Gray.

"Chemical Predictions by M.O. Theory: The Rare Gas Halides," in Modern Quantum Chemistry, Istanbul Lectures, Part I: Orbitals. Ed. by Oktay Sinanoglu, Academic Press, Inc., New York (1965), pp. 15-47. With Joshua Jortner.

"Excitons and Energy Transfer in Molecular Crystals," in Modern Quantum Chemistry, Istanbul Lectures, Part III: Action of Light and Organic Crystals. Ed. by Oktay Sinanoglu Academic Press, Inc., New York (1965), pp. 139-59. With J. Jortner and R. Silbey.

"Electrons in Liquids," in Modern Quantum Chemistry, Istanbul Lectures, Part II: Interactions. Ed. by Oktay Sinanoglu, Academic Press, Inc., New York (1965), pp. 133-62. With J. Jortner and N. R. Kestner.

"On the Equation of State of the Rigid Sphere Fluid," J. Chem. Phys. 42, 3559 (1965). With John Lekner.

"Low Energy Elastic Scattering of Electrons and Positrons from Helium Atoms," Phys. Rev. 140, A56 (1965). With Neil R. Kestner, Joshua Jortner, and Morrel H. Cohen.

"A Conjecture on Conformations Leading to Energy Trapping in Helical Polymers," Proc. Natl. Acad. Sci. 53, 973 (1965). With Ian H. Hillier.

"Comment on the Rice-Allnatt Kinetic Equations," J. Chem. Phys. 42, 4061 (1965). With Norman Hurt.

"Possible Uses of High Pressure Techniques for the Study of the Electronic State of Molecular Crystals," in Physics of Solids at High Pressures. Ed. by C. T. Tomizuka and R. M. Emrick, Academic Press, Inc., New York (1965), pp. 63-164. With Joshua Jortner.

"Conjecture on the Rate of Vibrational Relaxation of a Diatomic Molecule in a Monatomic Lattice," J. Chem. Phys. 42, 3826 (1965). With H. -Y. Sun.

"On the Quantum Mechanical Fokker-Planck Equation," J. Chem. Phys. 43, 2633 (1965). With H. Ted Davis and Kazuo Hiroike.

Statistical Mechanics of Simple Liquids. John Wiley and Sons, Inc., New York (1965). With Peter Gr .

"Theoretical Studies of Solvated Electrons," in The Solvated Electron. Ed. by Robert F. Gould, Advances in Chemistry Series, Vol. 50, A.C.S. Publications, Washington, D.C. (1965), pp. 7-27. With Joshua Jortner.

"Localized Excitations in Condensed Ne, Ar. Kr, and Xe," J. Chem. Phys. 42, 4250 (1965). With Joshua Jortner, Lothar Meyer, and E. G. Wilson.

"Excited Electronic States of Crystalline Benzene," J. Chem. Phys. 43, 3336 (1965). With Robert Silbey and Joshua Jortner.

"Antiresonances in Doped Molecular Solids--Experimental Evidence for Configuration Mixing of Impurity States and Conduction-Band States," Phys. Rev. Letters 15, 289 (1965). With E. S. Pysh and Joshua Jortner.

"Study of the Properties of an Excess Electron in Liquid Helium. I. The Nature of the Electron-Helium Interactions," J. Chem. Phys. 43, 2614 (1965). With Joshua Jortner, Neil R. Kestner, and Morrel H. Cohen.

"Study of the Properties of an Excess Electron in Liquid Helium. II. A Refined Description of Configuration Changes in the Liquid," J. Chem. Phys. 43, 2625 (1965). With Kazuo Hiroike, Neil R. Kestner, and Joshua Jortner.

"Electron Mobilities in Liquid Argon," Phys. Rev. Letters 15, 187 (1965). With Harold Schnyders and Lothar Meyer.

"The Reflection Spectra of Liquids Hg, In and Bi from 2-20 eV," Phys. Rev. 145, 55 (1966). With E. G. Wilson.

"The Reflection Spectrum of Liquid Hg from 2-20 eV," in Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, September (1965), pp. 271-282. North-Holland Publishing Company. With E. G. Wilson.

"Molecular Rydberg Transitions in Rare Gas Matrices--Evidence for Interaction between Impurity States and Crystal States," J. Chem. Phys. 43, 2997 (1965). With E. S. Pysh and Joshua Jortner.

"Conjecture on Resonant Transfer of Vibrational Energy and Radiationless Transitions in the Solid Phase: The Lifetime of Triplet Anthracene," J. Chem. Phys. 44, 2539 (1966). With H. -Y. Sun and Joshua Jortner.

"On the Kinetic Theory of Dense Fluids," J. Chem. Phys. 44, 2155 (1966). With Norman Hurt.

"Electron Drift Velocities in Liquefied Argon and Krypton," Phys Rev. (In Press). With Harold Schnyders and Lothar Meyer.

"Comments on the Experimental and Theoretical Study of Transport Phenomena in Simple Liquids," in Simple Dense Fluids: Data and Theory. Ed. by H. L. Frisch and Z. W. Salsburg, Academic Press, Inc., New York. (In Press). With J. P. Boon.

"Cooperative Exciton States in Molecular Crystals," J. Chem. Phys. 44, 3364 (1966). With Joshua Jortner.

"Do Exciton States Exist in the Liquid Phase?" J. Chem. Phys. 44, 4470 (1966). With Joshua Jortner.

"On the Calculation of Autocorrelation Functions for Dynamical Variables," J. Chem. Phys. 45, 1086 (1966). With Bruce Berne and Jean-Pierre Boon.

"A Pseudopotential Theory of Atomic and Molecular Eydberg States," With Andrew U. Hazi. Submitted to J. Chem. Phys.

"Intensity Distribution of Excimer Emission," With L. Glass and I. H. Hillier. J. Chem. Phys. (In Press).

"Theoretical Studies of Transannular Interactions. II. The Triplet States of the Paracyclophanes," With I. H. Hillier and L. Glass. J. Chem. Phys. (In Press).

"Theoretical Studies of Transannular Interactions. III. The Absorption and Emission Spectra of a Multi-Layered Paracyclophane," With Ian H. Hillier and Leo Glass. J.A.C.S. (In Press).

"Theoretical Studies of Transannular Interactions. IV. The Electronic States of the Paracyclophane Anion," With Ian H. Hillier. Submitted to J. Chem. Phys.

"Comments on the Influence of Intermediate Excitons and Exchange Forces on the Interaction in Molecular Crystals: The Crystal Sturcture of Chlorine," With Ian Hillier. Submitted to J. Chem. Phys.

"Some Comments on the Properties of Triplet Excitons in Molecular Crystals," Submitted to the Proceedings of the Symposium on the Triplet State, to be held at the American University of Beirut, February (1967).

"On the Equation of State of the Rigid-Disk Fluid," With David A. Young. Submitted to J. Chem. Phys.

"Comments on the Theory of the Exciton States of Molecular Crystals," With Joshua Jortner. Submitted to Physics and Chemistry of the Organic Solid State.

"A Comment on Self-Diffusion in Liquid Metals," With Norman H. Nachtrieb. Paper presented at the Symposium on the Properties of Liquid Metals, Brookhaven National Laboratory, September 1966. To be published in Advances in Physics.

"Supplement: Other Aspects of the Equilibrium Properties of Liquids," In Statistical Theory of Liquids by I. Z. Fisher. With Peter Gray. University of Chicago Press, Chicago, Illinois (1964), pp. 235-330.

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 extension of the theory of excitons to circumstances where charge delocalization is important.

(b) The development of a deeper understanding of the nature of dynamical coherence in classical many-body systems and its role in transport phenomena.

(c) Successful completion of a set of experimental studies designed to elucidate the nature of excess electron states in very simple liquids and the development of a zeroth order theory to describe the experimental data.

(d) The development of a theory of electron atom scattering and of the Rydberg states of molecules based upon a pseudopotential approach.

(e) The development of a new approximation in the equilibrium theory of liquids, its testing against experiment, and the initiation of a study of its implications for the theory of phase transitions.

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.

Project Scientist: Dr. D. L. Ball

COMPLETED PROJECT SUMMARY

1. TITLE: Critical Opalescence and Molecular Forces

2. PRINCIPAL INVESTIGATOR: Dr. Peter J. W. Debye
Department of Chemistry
Cornell University
Ithaca, New York

3. INCLUSIVE DATES: 1 October 1961 - 30 September 1966

4. GRANT NO: AF-AFOSR-62-12; AF-AFOSR-750-65

5. COSTS AND FY SOURCE: $95,954 FY62; $73,200 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. Benjamin Chu
Dr. Helmut Kaufmann
Dr. Klaus Kleboth
Dr. Dietrich Woermann
Dr. Daniel Caufield
Dr. John Bashaw
Dr. Claude C. Gravatt, Jr.
Dr. Robert T. Jacobsen
Dr. Masayuki Ieda

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Critical Opalescence of Binary Liquid Mixtures: Methanol-Cyclohexane," P. Debye, B. Chu and H. Kaufmann, J. Chem. Phys., 36, No. 13, 3373 (1962).

"Critical Opalescence of Polystyrene in Ethylcyclohexane," P. Debye, D. Woermann and B. Chu, J. of Polymer Science: Part A Vol. 1, 255 (1963).

"Viscosity of Critical Mixtures," P. Debye, B. Chu and D. Woermann, J. of Polymer Science: Part A Vol. 1, 249 (1963).

"The Priestley Medal Address," P. Debye, Chem. and Eng. News, Vol. 41, 92-27 (1963).

"Molecular Configuration of Polystyrene in Benzene," P Debye, B. Chu and H. Kaufmann, J. Polymer Science: Part A Vol. 1, 2387-2394 (1963).

"Light Scattering and Molecular Forces," P. Debye, reprinted from I.C.E.S. Pergamon Press (Electromagnetic Scattering, edited by Milton Kerker) (1963).

"Further Study on the Angular Dissymmetry of Critical Mixtures: Aniline-Cyclohexane: Aniline-1-Hexane," P. Debye, H. Kaufmann, K. Kleboth and B. Chu, Transactions of the Kansas Academy of Science, 66, No. 2, (1963).

"Critical Opalescence of Binary Mixtures: Perfluorotributylamine Isopentane," P. Debye, D. Caulfield and J. Bashaw, J. Chem. Phys., 41, 3051 (1964).

"An Electric Field Effect on the Critical Opalescence," P. Debye, K. Kleboth, J. Chem. Phys., 42, 3155 (1965).

"Spectral Width of the Critical Opalescence Due to Concentration Fluctuations," P. Debye, Phys. Rev. Letters, 14, 783 (1965).

"Critical Opalescence of the Polystyrene-Cyclohexane System: Small-Angle X-ray Scattering," P. Debye, J. Bashaw, B. Chu and D. M. Tan Creti, J. Chem. Phys., 44, 4302 (1966).

"Light Scattering as a Tool," The Official J. of the International Union of Pure and Appl. Chem., Butterworths, London, Vol. 12, (1966).

"Electric Field Effect on the Critical Opalescence. II. Relaxation Times of Concentration Fluctuations," P. Debye, C. C. Gravatt and M. Ieda, J. Chem. Phys., in press.

"Critical Opalescence and Molecular Forces," Final Report, AFOSR-67-0934.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The phenomenon of critical opalescence and the resulting distribution of electromagnetic scattering have been used to study molecular structure and interactions in binary systems. This work was extensively reported in the open literature during the course of the AFOSR grants.

The "range of molecular forces" is defined as the second moment of the potential energy distribution curve for two molecules and can be related to the electromagnetic scattering properties of the system. In the vicinity of the critical solution point these forces and the resulting range of their effects get very large. This effect has been studied and the range of molecular interaction measured for several binary liquid systems.

The effect of an electric field on the critical opalescence was predicted and measured for the system nitrobenzene-isooctane.

The extensive study of polystyrene in several solvents was continued. The critical opalescence of the polystyrene-ethylcyclohexane system was investigated for comparision with previous work in cyclohexane while the intramolecular configuration of the polymer was studied in benzene.

The effects of intermolecular interactions on the viscosity and the small angle x-ray scattering of a critical solution of polystyrene in cyclohexane was also reported.

A short theoretical publication on the spectral width and time dependence of the critical opalescence [Phys. Rev. Letters, 14, 783 (1965)] indicates one of the avenues of Professor Debye's thought and intentions at the time of his death.

After the untimely death of Dr. Debye, the direction of the research was undertaken by Dr. Benjamin Widom. A new grant, AF-AFOSR-1253-67 was made to Cornell University with Dr. Widom as principal investigator and Dr. R. T. Jacobsen, Dr. C. C. Gravalt Jr., and Dr. Y. Balta as research associates.

This was for the purpose of bringing an orderly end to the project and writing up of the results. This termination grant will be reported in the next annual review.

Project Scientist: Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Symposium on Electrode Processes

2. PRINCIPAL INVESTIGATOR: Dr. Ernest Yeager
The Electrochemical Society, Inc.
30 East 42nd Street
New York, New York 10017

3. INCLUSIVE DATES: 1 November 1965 - 31 October 1966

4. CONTRACT NO: AF49(638)-1647

5. COST AND FY SOURCE: $11,990 FY66

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Symposium on Electrode Processes of the Theoretical Division," Preprints of Complete Papers -- Printed, but not Published, The Electrochemical Society, Inc., 30 East 42nd Street, New York, New York 10017, May 1966

"Electrode Processes, Transactions of the 1966 Symposium," Edited by E. Yeager, H. Hoffmann and E. Eisenmann, Published by The Electrochemical Society, Inc., 30 East 42nd Street, New York, New York, 10017. Reprinted in part from the Journal of The Electrochemical Society, October and November Issues, Vol. 113, 185 (1966).

"Electrode Processes," Final Report, AFOSR 67-0651 (Identical to previous reference).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The "Symposium on Electrode Processes," sponsored jointly by the Directorate of Chemical Sciences, AFOSR and the Theoretical Electrochemistry Division of the Electrochemical Society was held on May 1 - 6, 1966, at Cleveland, Ohio. It was part of the spring meeting of the Electrochemical Society and was a sequel to the first "Symposium on Electrode Processes" held in Philadelphia in 1959 and also sponsored by AFOSR.

The overall purpose of this symposium was to further fundamental research in electrochemistry in the United States. Specifically the objectives were: (1) to present to American electrochemists involved in fundamental and applied electrochemical research the important new concepts and approaches which have been introduced in the study of electrode processes in recent years; (2) to promote the development of new concepts in electrochemistry through the exchange of ideas between American electrochemists and their foreign counterparts; (3) to encourage greater interest among American scientists in the fundamental approach to the study of electrode processes and to attract the interest of capable young faculty members and graduate students in the major universities of this country.

The program of the symposium placed emphasis on various problems associated with electrode processes, such as: (1) theoretical and experimental studies of the structure of electrochemical interfaces; (2) kinetic studies of adsorption phenomena; (3) theoretical treatments of charge transfer at electrode surfaces; (4) new approaches to the study of electrode processes and electrochemical catalysis.

A better understanding of electrode processes is of importance to the Air Force in connection with applied research on the improvement and development of energy conversion sources such as primary and secondary batteries and fuel cells.

Project Scientist: Dr. W.L.Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Colloquium on the Photographic Interaction Between Radiation and Matter

2. PRINCIPAL INVESTIGATOR: Dr. James E. LuValle
Fairchild Space and Defense Systems
Syosset, New York

3. INCLUSIVE DATES: 1 April 1966 - 31 March 1967

4. CONTRACT NO: AF49(638)-1713

5. COSTS AND FY SOURCE: $9,043 FY66

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS: None

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The Colloquium was co-sponsored with the Society of Photographic Scientists and Engineers. Its purpose was to bring together the leading international photographic scientists and engineers to discuss their progress and to stimulate ideas for future research. The subject of this colloquium was of considerable interest to the DOD, as well as the photographic industry.

The colloquium consisted of theoretical and experimental papers on the interaction of radiation and matter to yield a memory. Fourteen papers were presented on silver halide systems and thirteen papers on non-silver halide systems. The large active attendance (around 600) indicated that the objectives were met.

Project Scientist: Lt Col E. T. Walford

COMPLETED PROJECT SUMMARY

1. TITLE: Small Ring Compounds

2. PRINCIPAL INVESTIGATOR: Dr. Emil J. Moriconi
Department of Chemistry
Fordham University
New York, N. Y. 10458

3. INCLUSIVE DATES: 1 October 1961 - 30 September 1966

4. GRANT NO: AF-AFOSR-62-18; AF-AFOSR-488-64

5. COSTS AND FY SOURCE: $41,552 FY62; $46,440 FY64

6. SENIOR RESEARCH PERSONNEL: Dr. Francis J. Creegan
Dr. Albert J. Fritsch, S.J.
Dr. Paul Mazzocchi
Dr. John J. Murray
Dr. John St. George, S.J.
Dr. Francis A. Spano

7. JUNIOR RESEARCH PERSONNEL: Thomas E. Brady
Albert A. Cevasco
John F. Kelly
Robert Misner
James W. Young

8. PUBLICATIONS:

"Ring Expansion of 2-Alkyl-1-indanones to Isocarbostyril Derivatives," E. J. Moriconi, F. J. Creegan, C. K. Donovan and F. A. Spano, J. Org. Chem., 28, 2215 (1963).

"Heteropolar Ozonization of Aza-Aromatics and Their N-Oxides," E. J. Moriconi and F. A. Spano, J. Am. Chem. Soc., 86, 38 (1964).

"Pyrolysis and Photolysis of 1-Methyl-3-diazooxindole. Base Decomposition of Isatin 2-Tosylhydrazone," E. J. Moriconi and J. J. Murray, J. Org. Chem., 29, 3577 (1964).

"The Dimethyl Sulfoxide Oxidation of 2, 3-Bis(bromomethyl) quinoxaline," E. J. Moriconi and A. J. Fritsch, S.J., J. Org. Chem., 30, 1542 (1965).

"Organic and Biological Spectrochemical Studies XXII: The Infrared, Ultraviolet, and Nuclear Magnetic Resonance Spectra of Some Substituted 2-Indanones and Reference Compounds," E. J. Moriconi, J. P. St. George and W. F. Forbes, Can. J. Chem., 44, 759 (1966).

"Synthesis of *cis*- and *trans*-7-Azabicyclo[4.2.0]octanes," E. J. Moriconi and P. Mazzocci, J. Org. Chem., 31, 1372 (1966).

"N. M. R. Study of 2, 3-Quinoxalinedicarboxaldehyde and its Cyclic Monohydrate," E. J. Moriconi, J. W. Young, T. E. Brady and A. J. Fritsch, S.J., Can. J. Chem., 44 1596 (1966).

"β-Lactams Containing an Exocyclic Double Bond," E. J. Moriconi and J. F. Kelly, J. Am. Chem. Soc., 88, 3657 (1966).

"Ring Expansion of 2-Substituted-1-Indanones to 2-Hydroxyisocarbostyril Derivatives. Scope and Mechanism of Reaction. A Spectral Study of the Lactam-Lactim Tautomerism in Isocarbostyrils," E. J. Moriconi and F. J. Creegan, J. Org. Chem., 31, 2090 (1966).

"2-Hydroxy-3-methylisocarbostyril," E. J. Moriconi and F. J. Creegan, Org. Syntheses, 47, in press (1967).

"Synthesis and Reactions of Cyclic Amidines," E. J. Moriconi and A. A. Cevasco, to be submitted to J. Org. Chem.

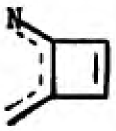
"Pyrolytic and Photolytic Extrusion of SO_2 from 2, 5-Diphenyl-2, 5-dihydroquinoxolino[2, 3-b]thiophene-1, 1-dioxide. A New Synthesis of benzo[b]phenazines," E. J. Moriconi and T. Brady, to be submitted to J. Am. Chem. Soc.

"Reaction of Chlorosulfonyl Isocyanate with Allenes," E. J. Moriconi and J. F. Kelly, to be submitted to J. Org. Chem.

"Small Ring Compounds," Final Report, AFOSR-66-2452.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The ultimate objective of this research was the synthesis of small ring compounds fused to an aromatic frame, such that the aza-atom was either exocyclic (1) or endocyclic (2) to the small ring.



(1)

(2)

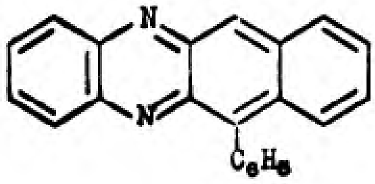
The following has been accomplished:

(A) 2-Substituted-1-indanones were ring expanded to 2-hydroxyisocarbostyrils (cyclic hydroxamic acids) via the intermediacy of isolable nitroso dimers.

(B) 1-Methyl-3-diazooxindole was prepared and both pyrolytically and photolytically decomposed in the presence of reagents which would react with the generated oxindolyl carbene in either or both singlet and triplet states. Thus the oxindolyl carbene reacted as a singlet in the formation of an olefin, azine, ether, spiro addition products with olefins cyclohexene and 1, 1-diphenylethylene, and 1-methylisatin via deoxygenation of pyridine N-oxide. Carbene displayed triplet properties in the ground state (esr spectrum), and in its reaction with oxygen to produce 1-methylisatin.

(C) The oxidation of 2, 3-bis(bromoethyl)quinoxaline with dimethyl sulfoxide (DMSO) produced in varying amounts 3-methyl, 3-bromomethyl, 3-dibromomethyl-2-quinoxalinecarboxaldehyde, in addition to 2, 3-bis(dibromomethyl)-quinoxaline and 2, 3-quinoxalinedecarboxaldehyde, isolated as its cyclic monohydrate. An nmr study of the structure and interconversion of 2, 3-quinoxalinedecarboxaldehyde and its cyclic monohydrate was also reported.

The new syntheses of benzo[b]phenazine derivatives (3), (4) were accomplished: (a) via pyrolytic extrusion of SO_2 from 2, 5-diphenyl-2, 5-dihydroquinoxalino[2, 3-b]thiophene-1, 1-dioxide, and (b) cyclization of 2-benzyl-3-benzoylquinoxaline in the presence of sulfuric acid.



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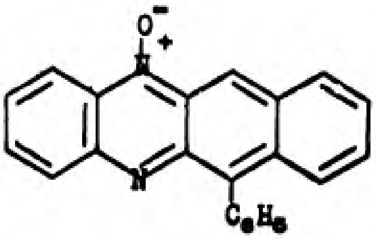


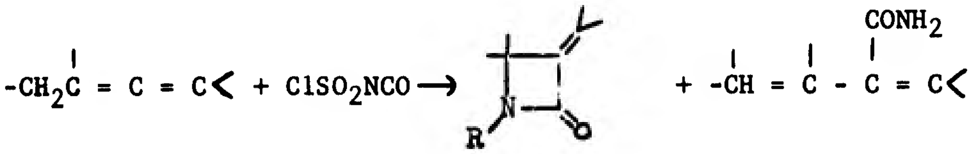
(4)

(D) The origin of the doublet (intensity ratio 40:1) in the carbonyl infrared region of 2-indanone and trans-hexahydro-2-indanone was examined. Infrared, ultraviolet and nmr spectral data suggested Fermi coupling.

(E) cis- and trans-7-azabicyclo[4.2.0]octane were prepared by conventional multistep syntheses. These are the first reported authentic members containing the 7-azabicyclo[4.2.0]octane framework.

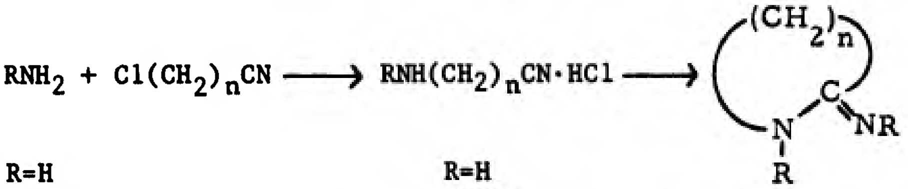
The azetidinone, 8-ketobenzo[d]-cis-7-azabicyclo[4.2.0] octane was prepared via cycloaddition of chlorosulfonyl isocyanate to 1, 2-dihydronaphthalene; its reduction led to benz[d]-cis-7-azabicyclo[4.2.0]octane.

(F) Four symmetrically and unsymmetrically substituted allenes reacted with chlorosulfonyl isocyanate to form N-chlorosulfonyl β-lactams (5) and 2-carboxamido-1, 2-butadiene derivatives. Reduction of (5) with benzenethiol and pyridine in acetone led to β-lactams (6).



(5) R = SO_2Cl
(6) R = H

(G) The sealed-tube reactions between ammonia/methylamine and 4-chlorobutyronitrile (n=3, 4) in ethanol produced cyclic amidines (7) (n-3, 4).



R=H
R=CH_3

R=H
R=CH_3

R = R' = H
R = CH_3; R' = H
R = R' = CH_3
R = H; R' = CH_3

(7)

Project Scientist: Dr. A. Matuszko

COMPLETED PROJECT SUMMARY

I. TITLE: Reactions of Metallic Ions

2. PRINCIPAL INVESTIGATOR: Dr. Joseph E. Earley

3. INCLUSIVE DATES: 2 October 1962 - 1 October 1966

4. GRANT NO: AF-AFOSR-133-63; AF-AFOSR-133-65

5. COST AND FY SOURCE: $21,310 FY63: $23,486 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. Roderich Cannon
Dr. Dusan Bustin

7. JUNIOR RESEARCH PERSONNEL: D. Petridis
W. Reed Whitten
F. Gomba
J. V. Prestia

8. PUBLICATIONS:

"On the Effect of trans Ligands on the Rate of Some Bridged Transfer Reactions," R. D. Cannon and J. E. Earley, J. Am. Chem. Soc., 87, 5264 (1965).

"The Aqueous Chemistry of Cr (III)," J. E. Earley and R. D. Cannon, Transition Metal Chemistry, Vol. 1, pp. 73-109, (1965) M. Dekker, New York.

"The Chromium (II) Reductions of Some Cobalt(III) Aquo-ammine Complexes," R. D. Cannon and J. E. Earley, J. Am.Chem.Soc.,88, 1872 (1966).

"Polarography of Tetraaquomonoxalato Chromium(III) Ion," D. Bustin, D. Petridis and J. E. Earley, in preparation.

"The Cr(II) Catalyzed Formation of Substituted Iminodiacetato Cr(III) Complexes," R. D. Cannon and J. E. Earley in preparation.

"Complexes of Chromium(III) with Some N-Substituted Ethylenediaminetriacetic Acids," Dusan I. Bustin and Joseph E. Earley, submitted to J. Am. Chem. Soc., November, 1966.

"Why Do Things Happen So Slowly," Joseph E. Earley, Georgetown University Research Bulletin, March, 1966, Vol. III, Number 2.

"Reactions of Metallic Ions," Final Report, AFOSR-66-2767.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project consisted of investigations on oxidation reactions, particularly the effect of non-bridging ligands on chromium (II) reductions, and on substitution reactions, especially those involving octahedral species in aqueous media.

Investigation of the kinetics and mechanisms of important reactions of inorganic species in aqueous solutions was carried out. A test of theoretical predictions of the effect of detailed stereochemistry of the oxidant on the rates of electron transfer reactions was completed. This publication has generated considerable reaction in the literature. Two papers dealing with this subject and extensively quoting the results have appeared.

Thermodynamics, rates and mechanisms of reductions of Cr(III) complexes of amino-acid ligands at the dropping mercury electrodes were completed. This work was submitted for publication.

The study of the polarographic properties of $[Cr(C_2O_4)(H_2O)_4]^+$ was completed. The study uncovered an interesting and potentially important effect. Heretofore, several mechanisms of electron transfer reactions had been elucidated at the dropping mercury electrode. The system studied provided a rare example of an occasion where the two sets of data could be correlated.

A major "state of the art" review on the chemistry of Cr(III) was completed and published. An automated computer-link system was assembled for the study of reactions of strongly reducing complex inorganic systems. A special feature of this system is the capability of analysis of strongly reducing species <u>in situ</u> by polarographic methods. This research will yield information relevant to the catalysis field.

Project Scientist:Mr.D.W.Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Gordon Research Conference on High Temperature Chemistry

2. PRINCIPAL INVESTIGATOR: Dr. LeRoy Eyring
Gordon Research Conferences, Inc.
University of Rhode Island
Kingston, Rhode Island

3. INCLUSIVE DATES: 1 March 1966 - 28 February 1967

4. GRANT NO: AF-AFOSR-1083-66

5. COSTS AND FY SOURCE: $3,000 FY66

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"1966 Gordon Research Conference on High Temperature Chemistry," Final Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

On July 25-29, 1966, the "Gordon Research Conference on High Temperature Chemistry" was held at Tilton School, Tilton, New Hampshire. This meeting was partially supported by the Directorate of Chemical Sciences, AFOSR.

The conference was devoted to selected formal presentations and informal discussions on basic scientific aspects of an area of obvious Air Force relevance. The organization of Gordon Conferences especially encourages the opportunities for informal exchanges of ideas and inquiries on specialized problems (in applications as well as in the interpretation of basic science). Improved understanding of the fundamental characteristics of materials and processes at high temperature is required for their still more effective exploitation in fulfilling practical needs.

The conference was attended by some 121 persons, each with an active interest in the field and the ability to contribute to the success of the meeting. Included were ten visitors from overseas.

Diverse subjects were emphasized in some twenty formal presentations; however, special emphasis was given to mass spectroscopy and Second and Third Law considerations (in the interpretation of high temperature materials and reactions). Other topics considered included phase equilibria, thermochemistry, and crystal structure.

Project Scientist: Dr. D. Ball

COMPLETED PROJECT SUMMARY

1. TITLE: Gordon Research Conference on Inorganic Chemistry

2. PRINCIPAL INVESTIGATOR: Dr. Edwin M. Larsen
Gordon Research Conferences, Inc.
University of Rhode Island
Kingston, Rhode Island

3. INCLUSIVE DATES: 15 March 1966 - 14 March 1967

4. GRANT NO: AF-AFOSR-1103-66

5. COSTS AND FY SOURCE: $3,500 FY 66

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"1966 Gordon Research Conference on Inorganic Chemistry," Final Report, AFOSR-66-1934.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The "1966 Gordon Conference on Inorganic Chemistry," supported in part by the Directorate of Chemical Sciences, AFOSR, was held on August 8-12, 1966, at the New Hampton School, New Hampton, New Hampshire.

The continuing support of the Inorganic Chemistry Conference is due to the relevance of this area of basic science to the development and technology of new and improved materials for the requirements of Air Force weapons systems. Inorganic chemistry contributes a major share of the basic knowledge required for new high temperature materials, new semiconductors and other solid state materials, and also new high energy oxidizers for propellants.

The conference was attended by one hundred and fifteen inorganic chemists of which about ten per cent were from foreign countries.

The first day of the conference was devoted to invited papers and discussions on the kinetics and mechanisms of oxidation reactions.

The next broad topic on the program was on hydrogen bonding in the solid state followed by a day and a half on inorganic synthesis. Of particular interest to the Air Force high temperature inorganic polymer program was a paper by Dr. M. F. Hawthorne on new compounds of the carborane series.

The final session of the program devoted to solvents and solutions included a review of recent progress on the structure of liquid water.

The conference was highlighted as usual by the discussion and interchange of new ideas by leaders in the field of inorganic chemistry.

Project Scientist: Dr. W. L. Ruigh
Review by: Mr. Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: "Rearrangement of Carbonium Ions and Free Radicals in the Bicyclo [3.1.0] hexyl System"

2. PRINCIPAL INVESTIGATOR: Dr. Peter K. Freeman
Department of Chemistry
University of Idaho
Moscow, Idaho 83843

3. INCLUSIVE DATES: 1 September 1962 - 30 September 1966

4. GRANT NO: AF-AFOSR-34-63; AF-AFOSR-875-65; AF-AFOSR-34-65

5. COSTS AND FY SOURCE: $18,174 FY63; $27,366 FY65

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL:
Marvin F. Grostic
Floyd A. Raymond
Donald G. Kuper
V. N. Mallikarjuna Rao
Dean M. Balls
Richard C. Johnson
Kenneth W. Pober

8. PUBLICATIONS:

"Synthesis of Bicyclo [3.2.1] octa-3,6-dien-2-one: An Unusual Valence Isomerization," P. K. Freeman and D. G. Kuper, Chem. and Ind. (London), 424 (1965).

"Reactive Intermediates in the Bicyclo [3.1.0] hexyl and Bicyclo [3.1.0]-hexylidene Systems. I. The Acid-Catalyzed Addition of Methanol and Acetic Acid to Bicyclo [3.1.0] hexene-2," P. K. Freeman, M. F. Grostic, and F. A. Raymond, J. Org. Chem., 30, 771 (1965).

"Reactive Intermediates in the Bicyclo [3.1.0] hexyl and Bicyclo [3.1.0] -hexylidene Systems. II. The Carbenoid Decomposition of the p-Toluenesulfonylhydrazones of 3-Bicyclo [3.1.0] hexanone and 2-Bicyclo [3.1.0] -hexanone," P. K. Freeman and D. G. Kuper, J. Org. Chem., 30, 1047 (1965).

"Photoisomerization of endo-and exo-Tricyclo $[3.2.1.0^{2,4}]$octene-6," P. K. Freeman, D. G. Kuper and V. N.M. Rao, Tetrahedron Letters, 37, 3301 (1965).

"Two Novel Tetracyclooctanes," P. K. Freeman, V. N. M. Rao and G. E. Bigam, Chem. Commun., 21, 511 (1965).

"Reactive Intermediates in the Bicyclo [3.1.0]hexyl and Bicyclo [3.1.0] hexylidene Systems. III. The Addition of Hydrogen Chloride and Deuterium Chloride to Bicyclo-[3.1.0]hexene-2," P. K. Freeman, F. A. Raymond, and M.F. Grostic, J. Org. Chem., 32, 24 (1967).

"The 8-Tetracyclo$[4.3.0.0^{2,4}.0^{3,7}]$nonyl Carbonium Ion," P. K. Freeman and D. M. Balls, Tetrahedron Letters, No.5, 437 (1967).

"Reactive Intermediates in the Bicyclo [3.1.0]hexyl and Bicyclo [3.1.0] hexylidene Systems. IV. The Free Radical Chlorination and Chloroformylation of Bicyclo [3.1.0] hexane," P. K. Freeman, F. A. Raymond, J. C. Sutton and W. R. Kindley, in preparation.

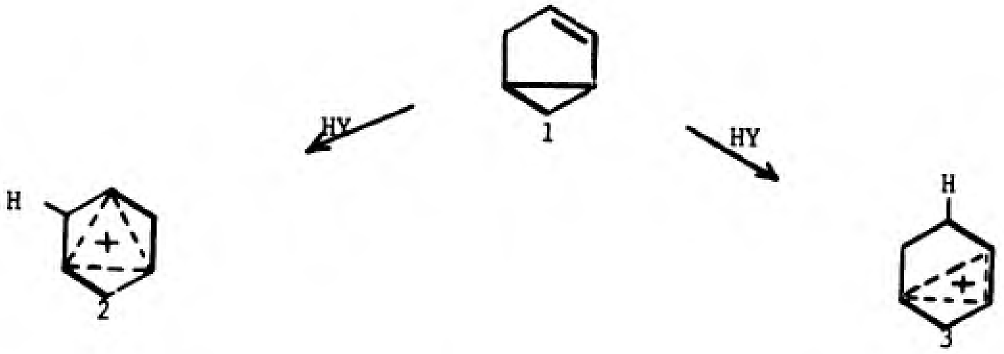
"Reactive Intermediates in the Bicyclo [3.1.0]hexyl and Bicyclo [3.1.0] hexylidene Systems. V. The Free Radical Addition of Methanethiol and Methanethiol-d to Bicyclo-[3.1.0]hexene-2," P. K. Freeman, M. F. Grostic and F. A. Raymond, in preparation.

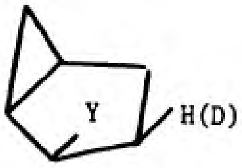
"Rearrangement of Carbonium Ions and Free Radicals in the Bicyclo [3.1.0]hexyl System," Final Report, AFOSR-67-1552.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was the characterization of carbonium ion and free radical intermediates in the bicyclo [3.1.0] hexyl system and carbene intermediates in the bicyclo [3.1.0] hexylidene system.

Electrophilic additions of hydrogen chloride and the conjugate acid of methanol to bicyclo [3.1.0]hexene-2 (1) demonstrate that the trishomocyclopropenyl carbonium ion (2) is not a detectable product determining intermediate and that the addition reactions proceed *via* a 2-bicyclo-[3.1.0]hexyl intermediate similar to 3, yielding 4 and 5 and small amounts of 6, under kinetically controlled conditions. The stereochemistry of the addition of deuterium chloride and the p-toluenesulfonic acid-d catalyzed addition of methanol-d to 1 were investigated. Deuterium chloride adds in a *cis* manner to both faces of the double bond to produce 4 and 5, with small amounts of 6. The stereochemistry of addition of methanol-d leading to 5 was determined to be completely cis.





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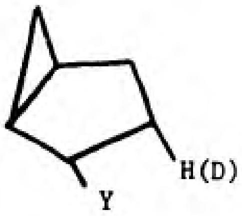

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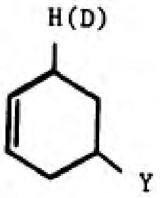

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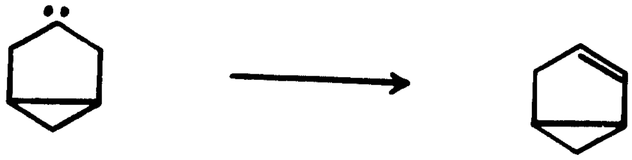
Bivalent intermediates 7 and 8 were generated by sodium methoxide induced decomposition of the p-toluenesulfonylhydrazones of 3-bicyclo-[3.1.0]hexanone and 2-bicyclo [3.1.0] hexanone. Intermediate 7 undergoes a simple 1,2-hydride shift, whereas bivalent intermediate 8 does exhibit transannular interaction of the cyclopropane ring with the electrophilic carbenoid carbon at C-2, producing ring fragmentation products 1,3-cyclohexadiene and 1-hexen-5-yne, as well as bicyclo-[3.1.0] hexene-2.



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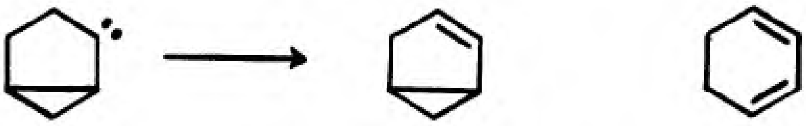

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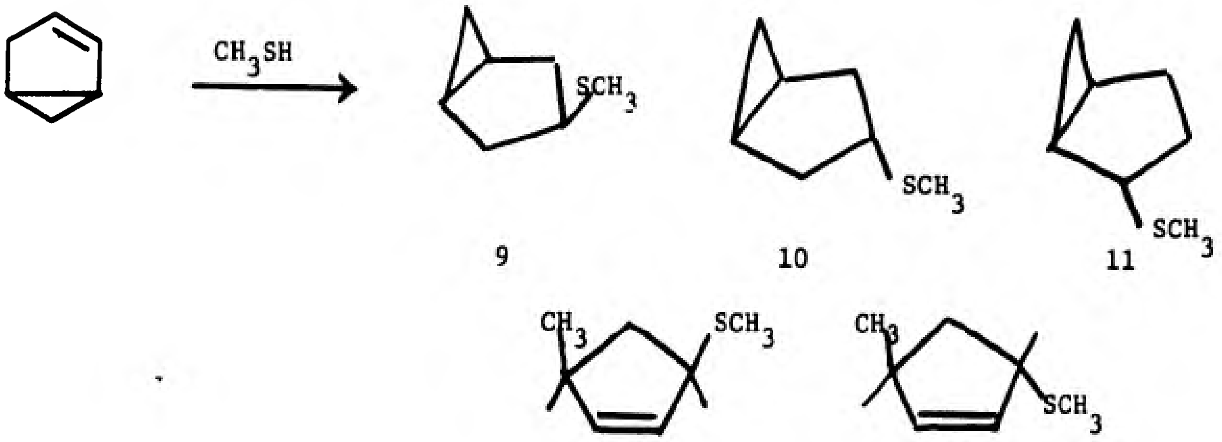
$CH_2=CH-CH_2CH_2C\equiv CH$

Free radical addition of methanethiol to bicyclo[3.1.0]hexene-2 yields thiomethoxybicyclohexanes (9-11) and thiomethoxymethylcyclopentenes (12 and 13). Thus, radical additions are similar to electrophilic additions; however, an additional rearrangement route, involving the C-1, C-6 bond, is open to radical intermediates in contrast to carbonium ion reactions where such a rearrangement appears to be unimportant. Experiments on the effect of the concentration of methanethiol upon the product ratios indicate that the 2-bicyclo[3.1.0]hexyl free radical is classical rather than a delocalized homoallylic intermediate.



9 10 11

12 13

Free radical chlorination, using t-butyl hypochlorite, and chloroformylation, using oxalyl chloride, generate exclusively 2- and 3-bicyclo [3.1.0]hexyl radical intermediates, which behave in a completely analogous fashion to the thiomethoxy radicals generated in methanethiol addition.

Project Scientist: Dr. A.J.Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: High Resolution Studies in the Far Infrared

2. PRINCIPAL INVESTIGATOR: Dr. D. W. Robinson
Department of Chemistry
The Johns Hopkins University
Baltimore, Maryland

3. INCLUSIVE DATES: 1 September 1962 - 28 February 1967

4. GRANT NO: AF-AFOSR-93-63; AF49(638)-1430

5. COSTS AND FY SOURCE: $65,378 FY63; $62,563 FY65

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: W. J. Lafferty
R. B. Reeves
C. J. Keffer
R. V. St. Louis
J. W. Russel
H. L. Strauss
P. Taimsalu
W. G. Von Holle
F. A. Mauer

8. PUBLICATIONS:

"The Far Infrared Spectra of Solid Methyl Halides," D. W. Robinson and W. J. Lafferty, J. Chem. Phys., 36, 82 (1962).

"Infrared Spectrum of Methylsilylacetylene," D. W. Robinson and R. B. Reeves, J. Chem. Phys., 37, 2625 (1962).

"The Electronic Emission Spectrum of BF," D. W. Robinson, J. Mol. Spectr., 11, 275 (1963).

"Spectra of Matrix-Isolated Water in the 'Pure Rotation' Region," D. W. Robinson, J. Chem. Phys., 39, 3430 (1963).

"The Infrared Spectra of $SiH_3C \equiv CH$ and $SiD_3C \equiv CH$," D. W. Robinson, R. B. Reeves and R. E. Wilde, J. Chem. Phys., 40, 125 (1964).

"Infrared Spectrum of Methylsilyl-d_3-acetylene," D. W. Robinson and R. B. Reeves, J. Chem. Phys., 41, 1699 (1964).

"Infrared Study of Some Oxalamidines," D. W. Robinson and V. Macovei, Applied Spectroscopy, 19, 48 (1965).

"Polymorphism in Hydrogen Iodide," D. W. Robinson, F. A. Mauer, C. J. Keffer and R. B. Reeves, J. Chem. Phys., 42, 1465 (1965).

"Far Infrared Spectrum of Tetrahydrofuran: Spectroscopic Evidence for Pseudorotation," D. W. Robinson, W. J. Lafferty, R. V. St. Louis, J. W. Russell, and H. L. Strauss, J. Chem. Phys., 42, 2915 (1965).

"The Far Infrared Spectra of Solid H_2S and D_2S at 5^oK and 77^oK," D. W. Robinson and P. Taimsalu, Spectrochimica Acta, 21, 1921 (1965).

"On the Nature of Valence-Shell Molecular Orbitals," D. W. Robinson, J. Phys. Chem., 69, 3357 (1965).

"Far-Infrared Spectra of Matrix-Isolated Hydrogen Fluoride," D. W. Robinson and W. G. Von Holle, J. Chem. Phys., 44, 410 (1966).

"Magnetic Rotation Spectrum of the $^2\Sigma \leftarrow {}^2\Pi_r$ Transition in NO," D. W. Robinson, J. Chem. Phys., in press.

"High Resolution Studies in the Far Infrared," Final Report, AFOSR-67-1607.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A molecule in the gaseous phase can fly in all directions as well as rotate about all axes. When the same molecule is "grounded" by cooling to the solid phase all such motions are frustrated by opposition from its neighbors. What was linear flight in the gas, becomes slight oscillation in the crystal; what was once free rotation in flight can, and usually does, become also oscillation. If, however, the molecule's neighbors do not forcefully hold it, or if the lattice position on which it finds itself looks symmetrical like the smooth inside of a little sphere, the molecule may still rotate essentially freely.

The strength and nature of forces between molecules in crystals has been studied by taking the spectra of these grounded molecules. The forces between molecules are always weak compared to those within one molecule, and the result of this is that motions of molecules which take place against these weak constraints have very low frequencies, about 1/100 as fast as the vibrations of the bonded atoms within each molecule. Thus the far infrared radiation must be used. Moreover, in order to condense volatile molecules, temperatures near the absolute zero are necessary.

It has been found that in the cases of some pure crystals like H_2S, HI, HCl, and HBr, rotation is completely prevented. In the spectra one can definitely see the vibrations that arise from the molecules' attempts to "takeoff," that is translational modes of vibration, as distinguished from the molecules' attempt to turn. By changing the mass of the molecule, substituting deuterium for hydrogen, the two types of new motions are readily distinguished. As expected the structure, or arrangement of molecules in the crystal, markedly affects these spectra. It is interesting that in the case of HI, warming from 5°K to 80°K encompasses five different structural arrangements of HI molecules in the crystal.

In order to produce an environment as nearly spherical as possible in a crystal, to test the rotation hypothesis, H_2O and HF were condensed together with the rare gases, neon, argon, krypton, and xenon with large excess of the latter. It was found that with both H_2O and HF, the little molecules actually do rotate almost as freely as in free gaseous flight. This was the first time this motion had been definitely and directly observed. The HF and DF, being the simplest type of molecule, have yielded extremely interesting results as functions of the different rare-gas hosts. As it turns out, the smallest rare gas, Ne, with the smallest cage to hold the HF, produces the least effect on the rotation of the HF molecule.

Because the long wavelengths are difficult to produce with high intensity, purify, and detect, a detector has been developed which operates at 1.5° above absolute zero in which the sensitive element changes resistance very steeply with temperature. So far this device, newly in operation, is a factor of 10 better than commercially available instruments. With this, studies of the type described above will be continued.

Infrared research is important to the Air Force which utilizes infrared techniques in reconnaissance and surveillance. Basic research in universities lead to improvements in technology as is here the case with far infrared detectors.

Project Scientist: Dr. W. L. Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Coincidence Measurements of Molecule-Ion Reactions

2. PRINCIPAL INVESTIGATORS: Dr. William H. Johnston
Mr. Marvin L. Vestal
William H. Johnston Laboratories, Inc.
Baltimore, Maryland

3. INCLUSIVE DATES: 1 February 1964 - 2 March 1967

4. CONTRACT NO: AF49(638)-1365

5. COSTS AND FY SOURCE: $49,653 FY64; $49,653 FY65; $49,653 FY66; $6,041 FY67

6. SENIOR RESEARCH PERSONNEL: Dr. G. Fergusson

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS: None

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of this research program were to make experimental and theoretical studies of the primary ionization and fragmentation processes which represent the initiation of radiation chemistry. Theoretical treatment of these processes is capable of predicting transition probabilities and fragmentation patterns as a function of excitation energy. These characteristics can also be experimentally measured by application of the coincidence principle to photoionization studies. Photons emerging from a vacuum UV monochromator may be used to ionize a particular molecule in a "coincidence mass spectrometer." The experimental results may then be compared directly with theoretical predictions and provide tests of the theories. Attempts may then be made to extend or modify the theories.

Unfortunately, the research as proposed was not completed. Untimely departure of the principal investigators from the Johnston Laboratories necessitated the closing of the contract eleven months short of its planned completion date. The majority of the expended contract time was used in designing the experiment and in the assembly, testing, calibration and modification of the equipment.

Project Scientist: Lt. Col. E. T. Walford

COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis and Chemistry of Acetals and Mercaptals of Formyl Halides

2. PRINCIPAL INVESTIGATOR: Dr. Richard N. McDonald
Department of Chemistry
Kansas State University
Manhattan, Kansas

3. INCLUSIVE DATES: 2 October 1962 - 1 October 1966

4. GRANT NO: AF-AFOSR 145-63; AF-AFOSR 145-65

5. COSTS AND FY SOURCE: $20,378 FY 63; $22,848 FY 65

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL:
R. A. Krueger
W. Stewart
C. E. Reineke
T. E. Tabor
M. H. Zakaria
P. A. Schwab
A. C. Kovelsky
R. Woodworth

8. PUBLICATIONS:

"The Synthesis and Thermal Decomposition of the Sodium Salts of Some N'-(P-tosyl) Hydrazimidocarboxylate Esters," R. N. McDonald and R. A. Krueger, Tetrahedron Letters, 857 (1965).

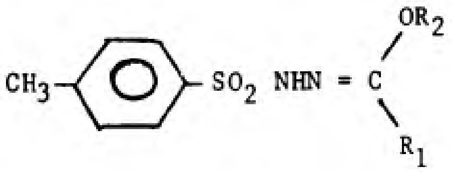
"The Reactions of Methyl and n-Butyllithium with Dichloromethyl Methyl Ether and Dichlorodiphenoxymethane," R. N. McDonald and R. A. Krueger, J. Org. Chem., <u>30</u>, 4372(1965).

"A Convenient Synthesis of Ester p-tosylhydrazones and Studies of the Thermal Decomposition of Some of Their Sodium Salts," R. N. McDonald and R.A.Krueger, J. Org. Chem., <u>31</u>, 488 (1966).

"Synthesis and Chemistry of Acetals and Mercaptals of Formyl Halides," Final Report, AFOSR-67-1068

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

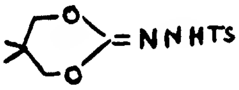
During this period we completed our analysis of the products from the reaction of sodium hydride and methyl formate p-tosylhydrazone (I, R_1 = H, R_2 = CH_3). These results [see publication, J. Org. Chem., <u>31</u>, 488 (1966)] along with those from thermal decompositions of the sodium salts of ethyl acetate p-tosylhydrazone (I, $R_1 = CH_3$, $R_2 = C_2H_5$) and methyl benzoate p-tosylhydrazone (I, $R_1 = C_6H_5$,

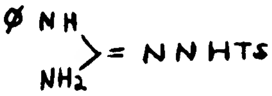


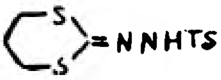
I

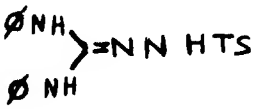
$R_2 = CH_3$) led us to conclude that reaction of I with sodium hydride followed two courses of reaction; (1) normal salt formation by abstraction of the acidic hydrogen, and (2) addition across the C=N, a process not at all expected.

We had previously been able to prepare what we thought to be the following p-tosylhydrazones. However, these were from single









attempts and on a very small scale. Attempts to duplicate these preparations and increase the scale have led to inconsistent results. When an interesting crude product is obtained, attempts to purify it lead to decomposition as evidenced by new infrared absorptions appearing in its spectra, melting points become more diffuse, and shifting of the n.m.r. spectral peaks. We had hoped that this series of compounds and studies of the thermal and photochemical decompositions of their salts might tell us much about the influence of an attached O, S, and N on a carbenoid center. After considerable time expended on this effort we regretfully have given up on this approach.

Project Scientist: Mr. D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Conference on Liquid Crystals

2. PRINCIPAL INVESTIGATOR: Dr. Glenn H. Brown
Dean of Research
Kent State University
Kent, Ohio

3. INCLUSIVE DATES: 15 July 1965 - 14 July 1966

4. GRANT NO: AF-AFOSR-971-65

5. COSTS AND FY SOURCE: $2,450 FY 65

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Proceedings of the International Liquid Crystal Conference - Part I," Molecular Crystals, 1, 201 (1966); Final Report, AFOSR 67-0972.

"Proceedings of the International Liquid Crystal Conference - Part II," Molecular Crystals, 1, 467 (1966); Final Report, AFOSR 67-0973.

"Proceedings of the International Liquid Crystal Conference - Part III,"Molecular Crystals, 2, 1 (1966); Final Report, AFOSR 67-0974.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The conference on liquid crystals was sponsored with Kent State University under the chairmanship of Dr. Glenn H. Brown. The conference was the first international meeting on this subject. The last major conference on liquid crystals was held in Britain in 1933. The objective of this conference was to furnish a point of departure for new research programs and open up new insights into the liquid crystalline state.

The liquid crystalline state has many unusual properties such as structure, response to external fields (electrical and magnetic), rotatory dispersion, thermal sensitivity and optical properties. Few applications of this phenomenon have been developed due primarily to lack of research on the structure and properties of this interesting state of matter. As of this date liquid crystals have found use in the areas of non-destructive testing, cancer detection and analysis, and as a new research tool.

Many interesting developments have taken place in the field of liquid crystals research in the past eight years. While the early work was primarily chemistry and physics, much recent work has been done by biologists and medical scientists. Dr. E.J. Ambrose, Royal Cancer Hospital, London, discussed the possibility that the structure of liquid crystals may contribute to the stability of living cells. A living cell requires stability combined with mobility for living processes to take place. Dr. H. Kelker, Farbwerke Hoechst, Frankfurt, reported on the behavior of crystalline liquids as stationary phases in gas-liquid chromatography. He found that certain liquid crystals were able to separate the meta-para substituted isomers of benzene homologs.

The examples of research noted above point out the interdisciplinary nature of the liquid crystal field. As research in this new area proceeds, more worthwhile applications will probably develop which cannot be foreseen at the present time. This conference may have provided the necessary impetus.

Project Scientist: LtCol E.T.Walford

COMPLETED PROJECT SUMMARY

1. TITLE: Studies in the Cyclobutane Series

2. PRINCIPAL INVESTIGATOR: Dr. Irving Lillien
Department of Pediatrics
School of Medicine
University of Miami
Miami, Florida

3. INCLUSIVE DATES: 2 October 1963 - 1 September 1966

4. GRANT NO: AF-AFOSR-123-63

5. COSTS AND FY SOURCE: $31,979 FY63

6. SENIOR RESEARCH PERSONNEL: Dr. K. Khaleeluddin

7. JUNIOR RESEARCH PERSONNEL: R. A. Doughty

8. PUBLICATIONS:

"Cyclopentane Conformations: Solvolysis of 3-Substituted Tosylates," I. Lillien and K. Khaleeluddin, Chem. & Ind. (London), <u>1028</u> (1964).

"Nonplanar Cyclobutane. I. The 3-Isopropylcyclobutyl System: NMR Spectra of Alcohols and Amines," I. Lillien and R. A. Doughty, J. Am. Chem. Soc., <u>89</u>, 155 (1967).

"Nonplanar Cyclobutane. II. The Methyl 3-Isopropylcyclobutanecarboxylate System," R. A. Doughty and I. Lillien, submitted to Tetrahedron.

"Nonplanar Cyclobutane. III. The Deamination of <u>cis</u> and <u>trans</u> 3-Isopropylcyclobutylamine," R. A. Doughty and I. Lillien, submitted to J. Am. Chem. Soc.

"Nonplanar Cyclobutane. IV. Solvolysis of <u>cis</u> and <u>trans</u> 3-Isopropylcyclobutyl Brosylate," R. A. Doughty and I. Lillien, in preparation.

"Studies in the Cyclobutane Series," Final Report, AFOSR-66-2002.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This work was undertaken in an effort to obtain chemical data supporting and amplifying the physical data-based conclusions re-

regarding the nonplanarity of cyclobutane and its derivatives, and providing a greater degree of insight into conformational conditions. The primary accomplishments in this work to date have been the synthesis and the study of derivatives of the 3-isopropylcyclobutane system. This has provided successful ingress to means for defining conformational consequences of nonplanarity. Cis and trans 3-isopropylcyclobutanecarboxylate esters have been equilibrated: cis and trans 3-isopropylcyclobutylamines and cis and trans 3-isopropylcyclobutanols have been synthesized and configurational assignments made by reference to equilibrated ester. NMR spectra of the above series of compounds and the equilibration data strongly support the conclusion that the isopropyl group is effective as a "holding" group in this system. The alcohols and amines appear to be conformationally homogeneous. Deamination of the cis and trans amines produces a mixture of the same five products but in significantly different ratios. Thus, there is little or no likelihood of a common intermediate, classical or non-classical, and results are interpreted in terms of concertion involving the conformational distinctions between equatorial and axial amino groups.

Project Scientist: Dr. A.J.Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Complex Formation, Ion Conjugation, and Unusal Valence States in Acetonitrile

2. PRINCIPAL INVESTIGATOR: Dr. I. M. Kolthoff
Department of Chemistry
University of Minnesota
Minneapolis, Minnesota

3. INCLUSIVE DATES: 1 November 1962 - 31 December 1966

4. GRANT NO: AF-AFOSR 28-63, AF-AFOSR 28-65

5. COSTS AND FY SOURCE: $24,806 FY 63; $27,528 FY 65

6. SENIOR RESEARCH PERSONNEL: Dr. M. K. Chantooni, Jr.

7. JUNIOR RESEARCH PERSONNEL: S. Bhowmik

8. PUBLICATIONS:

"Effect of Heteroconjugation on Acid Base Conductometric Titration Curves of 3-5 Dinitrobenzoic Acid in Acetonitrile," I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc., 85, 2195 (1963).

"Polarography in Acetonitrile of Titanium Tetrachloride and Tetraiodide in Various Supporting Electrolytes," I. M. Kolthoff and F. G. Thomas, J. Electrochem. Soc., III, 1065 (1964).

"Acid-Base Indicator Properties of Sulfonephthaleins and Benzeins in Acetonitrile," I. M. Kolthoff, Sadhana Bhowmik, and M. K. Chantooni, Jr., Proceedings of the National Academy of Sciences, 56, 1370 (1966).

"Acid-Base Properties of Mono- and Dinitrophenols in Acetonitrile," I. M. Kolthoff, M. K. Chantooni, Jr., and Sadhana Bhowmik, J. Am. Chem. Soc., 88, 5430 (1966).

"Acid-Base Indicator Constants in Acetonitrile," I. M. Kolthoff, M. K. Chantooni, Jr., and Sadhana Bhowmik, Analytical Chemistry, 39, 315 (1967).

"Hydration of Ions in Acetonitrile," M. K. Chantooni, Jr. and I. M. Kolthoff, J. Am. Chem. Soc., 89, 1582 (1967).

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"Hydration of Undissociated Salts in Acetonitrile," I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc., 89, June 1967.

"Complex Formation, Ion Conjugation, and Unusual Valence States in Acetonitrile," Final Reports, AFOSR 64-2201 and AFOSR 67-1268.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

In this research the dissociations and the optical properties of acid-base indicators in acetonitrile have been described. Knowing dissociation constants of the indicators and also of bases it is now possible to calculate the complete shape of the neutralization curves of bases or mixtures of bases with perchloric acid when titrated in acetonitrile.

Equations have been derived which permit the calculation of the hydration constants of ions from the solubility product of slightly soluble salts and the total ionic solubilities in the presence of varying concentrations of water. The hydration constants of lithium, sodium, potassium, and cesium ions and of the monovalent anions, perchlorate, periodate, methanesulfonate, nitrate 3,5-dinitrobenzoate, salicylate, picrate and 3,5 dinitrophenolate were determined in acetonitrile at 25°. In a further study the hydration constants of undissociated salts have been determined.

Project Scientist: Dr. A. Weissler
Reviewed By: LtCol E. T. Walford

COMPLETED PROJECT SUMMARY

1. TITLE: Mixed Heteropoly Acid Formation

2. PRINCIPAL INVESTIGATOR: Dr. John C. Guyon
Department of Chemistry
University of Missouri
Columbia, Missouri

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

4. GRANT NO: AF-AFOSR-205-63; AF-AFOSR-205-65

5. COSTS AND FY SOURCE: $23,770 FY63; $24,812 FY65

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: L. J. Cline
C. C. Clowers
R. L. Heller
B. L. Madison
J. Y. Marks
R. M. Matulis
N. L. Trautwein

8. PUBLICATIONS:

"Spectrophotometric Determination of Tantalum as Reduced 12-Molybdotantalic Acid," John C. Guyon, Anal. Chem. Acta, 30, 395 (1964).

"Spectrophotometric Determination of α-OH Carboxylic Acids: Application to Citric Acid," John C. Guyon and R. M. Matulis, Anal. Chem., 36, 118 (1964).

"Spectrophotometric Determination of Antimony Using the Molybdate Isopoly," John C. Guyon and R. M. Matulis, Anal. Chem., 37, 1391 (1965).

"Spectrophotometric Determination of Bismuth Using the Molybdate Isopoly," John C. Guyon and L. J. Cline, Anal. Chem., 37, 1778 (1965).

"Spectrophotometric Determination of Zirconium," J. C. Guyon and C. C. Clowers, Anal. Chem. Acta., 37, 401 (1967).

"Spectrophotometric Determination of Antimony," J. C. Guyon and R. M. Matulis, Chem. Analyst, 56, 22 (1967).

"Spectrophotometric Determination of Tungsten as Tungstate," John C. Guyon and Jerry Y. Marks, to be submitted to Anal. Chem.

"Spectrophotometric Determination of Copper(II)," John C. Guyon and Randall L. Heller, Jr., to be submitted to Anal. Chem.

"Spectrophotometric Determination of Thorium with Molybdophosphoric Acid," Bryan L. Madison and John C. Guyon, to be submitted to Anal. Chem.

"Spectrophotometric Determination of Hafnium," John C. Guyon and C. C. Clowers to be submitted to Anal. Chem.

"Mixed Heteropoly Acid Formation," Final Report, AFOSR-65-1126.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to study the concept of mixed heteropoly acid formation and to develop and improve analytical methods based on heteropoly acid formation.

As a result of this study it is possible to state that the group IVB and VB elements all form simple heteropoly acids. Furthermore, in the instances where mixed heteropoly acids had been postulated for these elements, a mixture of simple heteropoly acids was shown to exist.

A very interesting reaction between Sb, Bi, and the molybdate isopoly was discovered. It is currently postulated that this reaction is catalytic and related to the readily available multiple oxidation states of Sb and Bi. This premise is being further studied.

A very selective analytical method for α-OH acids has been developed and applied to citric acid. This method evolved out of an attempt to characterize the molybdate isopoly. This aspect of the work has been very well received.

Sensitive analytical methods for Ta, Sb, Bi, Zr, W, Cu, Th, and Hf have also been developed.

Project Scientist: Mr. D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Orientation and Reactivity in Free Radical Aromatic Substitution

2. PRINCIPAL INVESTIGATOR: Dr. Robert T. Morrison
Department of Chemistry
New York University
Washington Square, New York,
10003

3. INCLUSIVE DATES: 1 October 1961 - 30 September 1965

4. GRANT NO: AF-AFOSR-62-34; AF-AFOSR-519-64

5. COSTS AND FY SOURCE: $65,780 FY 62; $66,878 FY 64

6. SENIOR RESEARCH PERSONNEL: Dr. Sheldon Herbstman
Dr. Anthony Passannante
Dr. James Perel

7. JUNIOR RESEARCH PERSONNEL: Jack Cazes
David Davis
Robert Harvey
Faradoon Irani
Frank Litterio
Hope McLaren
John Olsen
Albert Rossi
Norman Samkoff
Margaret Toth
Su-chu Wang Tso
Gisela Witz

8. PUBLICATIONS:

"Validity of Rate Factors in Free Radical Aromatic Substitution," R. T. Morrison, J. Cazes, N. Samkoff and C. A. Howe, J. Am. Chem. Soc., 84, 4152 (1962).

"Orientation and Reactivity in Free Radical Substitution," Final Report, AFOSR-67-1059.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective was to study the factors controlling orientation and reactivity in free radical aromatic substitution by measuring isomer distribution and relative reactivity in the arylation of aromatic substrates by aroyl peroxides. It became necessary to establish the validity of rate factors derived from such data: that is, to show that product analysis reflects the relative rates of formation of the various intermediate arylcyclohexadienyl radicals (I), ArAr'H·.

A gas chromatographic method of analysis was worked out that gives rate factors about ten times as accurate as those previously measured. This method was applied to fourteen peroxide-substrate systems.

Although biaryl yields were found to increase as much as threefold when peroxides were decomposed in the presence of oxygen, rate factors remained unchanged, indicating that side-reactions of I are non-selective, and establishing the validity of rate factors based on product analysis.

The effects on rate factors of substituents in the substrate and in the radical showed that polar factors play a major role. Temperature studies showed that isomer distribution depends exclusively on differences in energy of activation; total reactivity does not, and hence is not simply the sum of the reactivities at the various positions, as would be the case if formation of I were rate-determining. It is suggested that total reactivity is controlled by pi-complex formation, orientation by subsequent fast sigma-complex formation (formation of I).

Gas chromatographic analysis showed that most "esters" formed in peroxide decomposition are not the simple substituted phenyl benzoates, ArCOOAr', they have been assumed to be. Such simple esters become the major product, however, when peroxides are decomposed in the presence of oxygen (at concentrations higher than the optimum for biaryl formation), or iodine, or both. Ester formation thus appears to proceed by free radical aromatic substitution and by a mechanism analogous to that established for aroyloxcyclohexadienyl radical (II), (ArCOO)Ar'H·. Intermediate II, unlike I, is evidently formed reversibly; most aroyloxy radicals, ArCOO·, formed in the peroxide decomposition attach themselves to the substrate to give II, but in the absence of an effective oxidizing agent most of the II undergoes side-reactions (dimerization, disproportionation) or regenerates the aroyloxy radicals, which ultimately lost carbon dioxide to form aryl radicals that can bring about arylation.

In arylation, substituent groups on the substrate ring cause only slight activation (and never, except by steric hindrance, deactivation), with isomer distribution typically chiefly <u>ortho</u>, and with meta about double para. In ester formation, in marked contrast, substituent groups can activate (or deactivate) strongly, and in the same general way as in electrophilic substitution. Orientation is exclusively ortho, para in anisole, and predominantly so in toluene and bromobenzene. Even under the most favorable conditions, nitrobenzene yields no detectable ester. These effects were actributed to the powerfully electrophilic nature of the aroyloxy radical, and suggest that, in contrast to arylation, the rate-determining step is formation of the sigma-complex, II.

Project Scientist: Mr. D. W. Elliott

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COMPLETED PROJECT SUMMARY

1. TITLE: Oxidation - Reduction Reactions of Organic Sulfur Compounds

2. PRINCIPAL INVESTIGATOR: Dr. John L. Kice
Department of Chemistry
Oregon State University
Corvallis, Oregon

3. INCLUSIVE DATES: 1 October 1962 - 30 November 1966

4. GRANT NO: AF-AFOSR-106-63; AF-AFOSR-106-65

5. COSTS AND FY SOURCE: $20,483 FY63; $28,118 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. Giancarlo Guaraldi
Dr. David C. Hampton

7. JUNIOR RESEARCH PERSONNEL: Nicolai Favstritsky
Leslie Heasley
George B. Large
Eva H. Morkved
Norman Pawlowski
Clifford G. Venier
James F. Barbour
J. Douglas Campbell
Alvin Fitzgerald
Bruce Toth

8. PUBLICATIONS:

"The Mechanism of the Disproportionation of Sulfinic Acids. The Thermal Decomposition of p-Toluenesulfinic Acid," J. L. Kice and N. E. Pawlowski, J. Org. Chem., 28, 1162 (1963).

"Mechanisms of Reactions of Sulfinic Acids. V. The Mechanism of the Alkyl Sulfide-Sulfinic Acid Reaction," J. L. Kice and E. H. Morkved, J. Am. Chem. Soc., 85, 3472 (1963).

"Mechanisms of Reactions of Sulfinic Acids. VI. The Mechanism of the Disulfide-Sulfinic Acid Reaction," J. L. Kice and E. H. Morkved, J. Am. Chem. Soc., 86, 2270 (1964).

"The Reaction of sec-Alkyl Sulfides with p-Toluenesulfinic Acid," J. L. Kice and E. H. Morkved, J. Org. Chem. 29, 1942 (1964).

"The Decomposition of Aromatic Sulfinyl Sulfones (Sulfinic Anhydrides). The Facile Homolysis of the Sulfur-Sulfur Bond," J. L. Kice and N. E. Pawlowski, J. Am. Chem. Soc., 86, 4898 (1964).

"Concomitant Electrophilic and Nucleophilic Catalysis of Sulfur-Sulfur Bond Cleavage in Aryl Thiolsulfinates," J. L. Kice and C. G. Venier, Tetrahedron Letters, 3629 (1964).

"The Effect of Structure on the Rate of Disproportionation of Aromatic Sulfinic Acids," J. L. Kice, D. C. Hampton and A. Fitzgerald, J. Org. Chem., 30, 882 (1965).

"Synthesis of Optically Active Phenyl Benzenethiolsulfinate by Asymmetric Oxidation of Phenyl Disulfide," J. L. Kice and G. B. Large, Tetrahedron Letters, 3537 (1965).

"Mechanisms of Substitution at Sulfinyl Sulfur. Concomitant Electrophilic and Nucleophilic Catalysis of the Hydrolysis of p-Toluenesulfinyl p-Tolyl Sulfone," J. L. Kice and G. Guaraldi, Tetrahedron Letters, 501 (1966).

"The Mechanism of the Alkyl Sulfide-Sulfinic Acid Reaction. The Direction of Cleavage of Unsymmetrical Sulfides," J. L. Kice, B. R. Toth, D. C. Hampton and J. F. Barbour, J. Org. Chem., 31, 848 (1966).

"The Mechanism of the Disproportionation of Sulfinic Acids. Rate and Equilibrium Constants for the Sulfinic Acid-Sulfinyl Sulfone (Sulfinic Anhydride) Equilibrium," J. L. Kice, G. Guaraldi and C. G. Venier, J. Org. Chem., 31, 3561 (1966).

"Mechanisms of Substitution Reactions at Sulfinyl Sulfur. Solvolysis of Aryl Sulfinyl Sulfones in Acetic Acid-Water," J. L. Kice and G. Guaraldi, J. Org. Chem., 31, 3568 (1966).

"Mechanisms of Substitution Reactions at Sulfinyl Sulfur. II. Concomitant Electrophilic and Nucleophilic Catalysis of the Solvolysis of Aryl Sulfinyl Sulfones in Acetic Acid-Water," J. L. Kice and G. Guaraldi, J. Am. Chem. Soc., 88, 5236 (1966).

"Mechanisms of Substitution at Sulfinyl Sulfur. III. The Relative Nucleophilicity of some Common Nucleophiles Toward Sulfinyl Sulfur," J. L. Kice and G. Guaraldi, Tetrahedron Letters, 6135 (1966).

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

"Mechanisms of Reactions of Thiolsulfinates (Sulfinic Anhydrides). I. The Thiolsulfinate-Sulfinic Acid Reaction," J. L. Kice, C. G. Venier, and L. Heasley, J. Am. Chem. Soc., 89, in press (1967).

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

"Mechanisms of Reactions of Thiolsulfinates (Sulfinic Anhydrides). II. Sulfide-Catalyzed Disproportionation and Racemization of Optically Active Phenyl Benzenethiolsulfinate," J. L. Kice, C. G. Venier, L. Heasley and G. B. Large, to be submitted to J. Am. Chem. Soc.

"Mechanisms of Substitution Reactions at Sulfinyl Sulfur. V. Halide and Acetate Ion Catalysis of the Solvolysis of Aryl Sulfones in Acetic Acid-Water," J. L. Kice and G. Guaraldi, submitted to J. Org. Chem.

"Mechanisms of Substitution Reactions at Sulfinyl Sulfur. VI. The Relative Nucleophilicity of Some Common Nucleophiles Toward Sulfinyl Sulfur," J. L. Kice and G. Guaraldi, to be submitted to J. Am. Chem. Soc.

"Oxidation-Reduction Reactions of Organic Sulfur Compounds," Final Report, AFOSR-67-0247.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The initial objective was to determine the detailed mechanisms of a variety of oxidation - reduction reactions involving organic sulfur compounds in the belief that studies of this type could lead to the discovery of fundamental mechanistic principles having applicability to broad areas of organosulfur chemistry. Such principles could then provide useful guidelines for suggesting previously overlooked potentialities in reactions of sulfur compounds. Along such lines the following results seem particularly noteworthy.

First, the scission of a considerable variety of sulfur-sulfur bonds in acid solution is subject to catalysis not only by acid, but also by a variety of nucleophilic additives. The amount of nucleophile required for such concomitant nucleophilic and electrophilic catalysis of the scission of an S-S bond is frequently amazingly low (10^{-5} - 10^{-6}M). Since the making and breaking of S-S bonds is involved in a wide variety of important reactions in organic sulfur chemistry, the existence and rather striking nature of this type of catalysis has profound implications, and should have many useful practical applications. By studying concomitant nucleophilic and electrophilic catalysis of the scission of the S-S bonds in sulfinyl sulfones, thiolsulfinates and disulfides, it has been possible not only to demonstrate the generality of this type of catalysis but also to elucidate the exact mechanism involved in each case.

The second important general finding of the research grew out of an investigation of the thermal decomposition of aryl sulfinyl sulfones. This research established that homolytic dissociation of the S-S bond in such a sulfinyl sulfone occurs extremely readily (half life = 30 min. at 50°). This rate of homolytic dissociation is at least 10^7 - 10^8 times faster than the rate of dissociation of the S-S bond in the analogous aryl disulfide. This means that changes in the oxidation state of the sulfur atoms paired in a sulfur-sulfur bond can lead to literally enormous changes in the ease of homolytic dissociation of that bond, a fact that had apparently not been realized before. Furthermore, since other work in this laboratory has shown that thiolsulfinates, the initial oxidation product of disulfides, also undergo very ready thermal dissociation, such variations in case of homolytic dissociation of sulfur-sulfur bonds may have important biological and biochemical implications.

A third area where the present research has been able to make a significant contribution involves substitution reactions occurring at sulfinyl sulfur. These have become of considerable interest lately because of the greatly increased interest in the chemistry of sulfoxides. The present work has involved study of the mechanism of hydrolysis of sulfinyl sulfones under a variety of reaction conditions. These studies have yielded the following significant findings: (1) the first example of substitution at sulfinyl sulfur occurring via an S_N1-type mechanism (i.e. no attack of a nucleophile on the sulfinyl sulfur either prior to or during the rate-determining step); (2) a scale of relative nucleophilicity toward sulfinyl sulfur for a range of common nucleophiles.

In addition to these findings the present research has led, in the course of the elucidation of the detailed mechanisms of various organosulfur reactions, to the discovery of several previously unreported and potentially useful reactions involving sulfinic acids, thiolsulfinates, and sulfinyl sulfones.

Project Scientist: Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Electronic Sturcture and Energy Levels of Many Electron Atoms

2. PRINCIPAL INVESTIGATOR: Dr. John Midtdal
Institute for Theoretical Physics
University of Oslo
Norway

3. INCLUSIVE DATES: 2 February 1966 - 28 February 1967

4. GRANT NO: AF-EOAR-64-32; AF-ECAR-66-33

5. COSTS AND FY SOURCE: $9,000 FY64; $9,020 FY66

6. SENIOR RESEARCH PERSONNEL: Dr. Erling Hølien

7. JUNIOR RESEARCH PERSONNEL: Mr. Kjell Aashamar
Mr. Gudmund Lyslo

8. PUBLICATIONS:

"New Investigation of the $^1S^e$ Autoionizing States of He and H^-," E. Holien and J. Midtdal, J. Chem. Phys., 45, 2209 (1966).

"Energy Calculation of the Metastable (1s2s2p) $^4P^o$ State of He^- and Li," E. Holien and J. Midtdal, Proc. Phys. Soc., 90, 883 (1967).

"Perturbation Theory Expansions Through 20th Order of Mass Polarization Correction, Relativistic Effects and Lamb Shift of the Two-Electron System $(1s)^2\ ^1S$," J. Midtdal and K. Aashamar, Physica Norvegica, 2, 99 (1967).

"On the Convergence Properties of the 1/Z Expansion as Furnished by the Variational Perturbation Theory Calculations," J. Midtdal, K. Aashamar and G. Lyslo, submitted to Proc. Phys. Soc.

"Perturbation Theory Expansions of Mass Polarization Correction, Relativistic Effects and Lamb Shift of the Two-Electron Systems $(1s)^2\ ^1S$ and $(2p)^2\ ^3P$," K. Aashamar, in preparation.

"Electronic Sturcture and Energy Levels of Many Electron Atoms," Final Report, AFOSR-67-0899.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main objectives of this research have been:

(1) to apply the variational perturbation procedure to still more two-electron systems. During the last ten years the search for bound states of negative ions, especially for H and He, has been intensified in order to explain experimentally observed phenomina from resonance scattering measurements. In the theoretical investigations published on this subject the major part of the numerical results have thus far been obtained by applying the Ritz variational method. However, the electron affinities are usually very small, and therefore the calculations have to be extended to a very high degree of accuracy if we want to answer the question whether a specific state is bound.

The variational perturbation procedure offers a somewhat different approach to the problem, and we were led to propose a modified definition of the concept of closed states of atomic systems. According to this definition an atomic state is said to be closed if the 1/Z expansion of its norm converges. The assumption is based on extensive numerical calculations for the states $(1s)^2\ ^1S$, $(2p)^2\ ^3P$, $1s2s\ ^{1,3}S$ and $1s2p\ ^{1,3}P$, using perturbation wave functions up to order 40, each containing up to 204 terms of the Hylleraas type.

(2) to compute numerically the perturbation expansion coefficients through 20th order of the mass polarization correction, the various relativistic effects, the Lamb shift and the expectation value of a number of additional operators for some two-electron systems. The calculations for the states $(1s)^2\ ^1S$ and $(2p)^2\ ^3P$ have been terminated.

(3) to investigate certain doubly excited, discrete states of two-electron systems. In this connection the convergence properties of some particular upper roots of the full Hamiltonian were studied. The detailed calculations using the scaling-variation orthogonalization procedure clearly demonstrated the stabilizing ability of particular upper roots in the second-step solution, which then could be associated with certain quasi discrete autoionizing states.

Note: This is an outgrowth of a project that was initiated by ARL, under Dr. S. J. Czyzak. In August 1963 the project was transferred to the Chemistry Directorate, AFOSR, at which time C. J. Czyzak and D. W. Elliott were designated as co-monitors. The project continued until February 1966. During the later part of this period Prof. Hylleraas passed away. The project was continued for an additional year with Dr. John Midtdal as the principal investigator under grant AF-EOAR-66-33.

Project Scientist: Mr. D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: "The Preparation and Properties of Nitronic Esters"

2. PRINCIPAL INVESTIGATOR: Dr. Nathan Kornblum
Department of Chemistry
Purdue University
West Lafayette, Indiana

3. INCLUSIVE DATES: 1 October 1962 - 30 September 1966

4. GRANT NOS: AF-AFOSR-122-63; AF-AFOSR-122-65

5. COSTS AND FY SOURCE: $27,300 FY 63: $27,516 FY 65

6. SENIOR RESEARCH PERSONNEL: Dr. R. Alan Brown

7. JUNIOR RESEARCH PERSONNEL:
Donald H. Hardies
Willard J. Jones
Michael T. Musser

8. PUBLICATIONS:

"The Synthesis and Characterization of Nitronic Esters," N. Kornblum and R. Alan Brown, J. Am. Chem. Soc., 86, 2681 (1964).

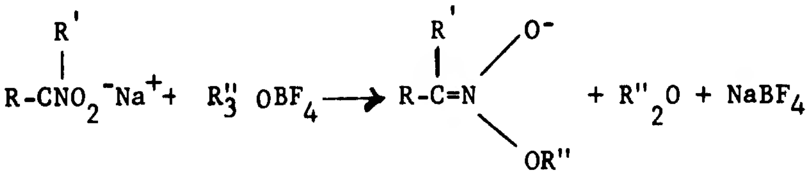
"The Action of Acids on Nitronic Esters and Nitroparaffin Salts, Concerning the Mechanisms of the Nef and the Hydroxamic Acid Forming Reactions of Nitroparaffins," N. Kornblum and R. Alan Brown, J. Am. Chem. Soc., 87, 1742 (1965).

"Stereochemistry and Mechanism in Reactions of Silver Salts with Alkyl Halides. The Reaction of Silver Nitrite with Alkyl Halides," N. Kornblum, W. J. Jones and D. H. Hardies, J. Am. Chem. Soc., 88, 1704 (1966).

"Concerning the Mechanism of Silver Salt Reactions: The Reaction of Silver Methanesulfonate with Allyl Chloride 1-C^{14}," N. Kornblum and M. T. Musser, J. Am. Chem. Soc., 90, 0000 (1968).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

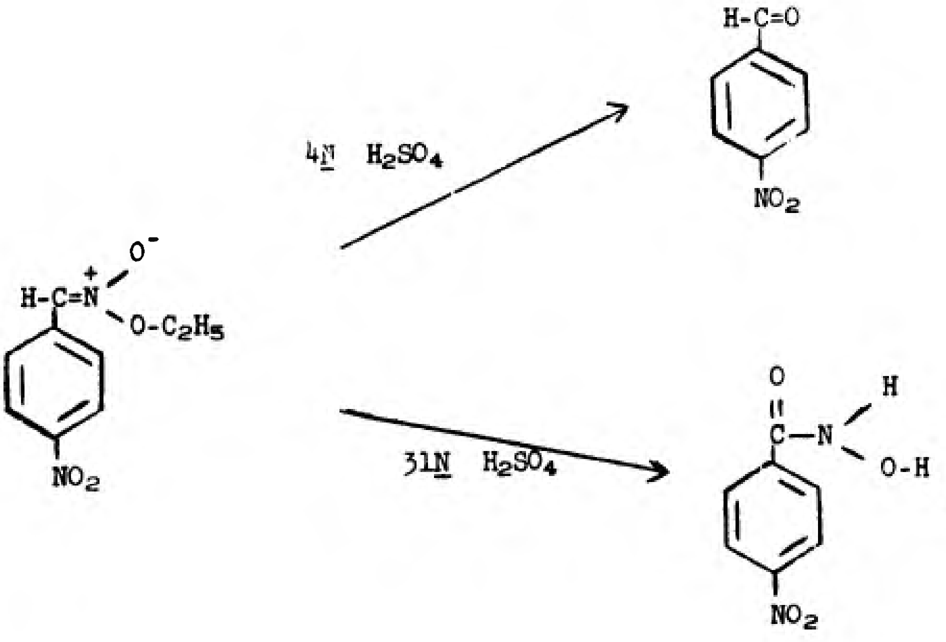
Our first objective was the preparation and characterization of nitronic esters (I) a little known group of compounds formally derived from aci-nitroparaffins. A new and general synthesis of nitronic esters was found. When the salts of nitroparaffins are treated with trialkyloxonium fluoroborates at 0° a rapid reaction ensues and a virtually quantitative yield of the nitronic ester (I) is produced:



$$R\text{-}\overset{R'}{\overset{|}{C}}NO_2^-Na^+ + R''_3OBF_4 \longrightarrow R\text{-}\overset{R'}{\overset{|}{C}}=N(O^-)(OR'') + R''_2O + NaBF_4$$

(I)

It was next found that nitronic esters are rapidly decomposed by acids and that the course which the reaction follows is strikingly dependent on the acid concentration. Thus, the ethyl nitronic ester of *p*-nitrophenylnitromethane (II) gives *p*-nitrobenzaldehyde in 80% yield on treatment with 4 N sulfuric acid while, in contrast, 31 N sulfuric acid converts it into *p*-nitrobenhydroxamic acid in 98% yeild.



80% yield

98% yield

The mechanism of the reactions of silver salts with alkyl halides was next studied. Reactions employing optically active 2-bromooctane (or 2-iodooctane) invariably proceed with inversion regardless of the solvent. In contrast, with optically active α-phenylethyl chloride, the steric course of the reactions is solvent dependent: in ethyl ether and in benzene, the nitrite (and nitrate) esters are formed with retention of configuration, whereas in acetonitrile, or in cyclohexane, the esters are produced with inversion. The mechanism of silver salt reactions was studied. The results can be raionalized in a simple way by regarding the reactions of silver salts with alkyl halides as concerted SN_1-SN_2 processes in which the relative importance of the electrophilic pull of the silver and the nucleophilic push of the anion in the transition state varies as a function of the alkyl halide, the silver salt, and the solvent.

Finally, a study employing allyl chloride labelled with carbon-14 has provided strong confirmation of the concerted pull-push mechanism proposed for the reactions of silver salts with alkyl halides. It was shown that the reaction with silver methanesulfonate occurs without any rearrangement at all, i.e.,

$$CH_2=\overset{14}{C}H_2Cl + CH_3SO_3^-Ag^+ \longrightarrow CH_2=CH-\overset{14}{C}H_2O-SO_2CH_3$$

Project Scientist: Dr. A. J. Matuszko
Review by: Dr. William L. Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Ultratrace Analysis by Coordination Chain Reactions

2. PRINCIPAL INVESTIGATOR: Professor Dale W. Margerum
Department of Chemistry
Purdue University

3. INCLUSIVE DATES: 1 November 1962 - 31 October 1966

4. GRANT NO: AF-AFOSR-134-63; AF-AFOSR-134-65

5. COSTS AND FY SOURCE: $21,808 FY63; $33,840 FY65

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: Ralph K. Steinhaus
Rudolph H. Stehl
Peter J. Menardi
Donald L. Janes
James Mieure
Jerry B. Pausch
John P. Jones
Gerald A. Nyssen
Michael L. Gelardi

8. PUBLICATIONS:

A. Completed under the present grant

"Ultratrace Determination of Metals Using Coordination Chain Reactions," D. W. Margerum and R. K. Steinhaus, Anal. Chem., 37, 222 (1965).

"Remote Ligand Substituents in Nickel(II) Complexes Affecting the Rate of Loss of Coordinated Water," D. W. Margerum and R. K. Steinhaus, J. Am. Chem. Soc., 87, 4643 (1965).

"Effect of Phenanthroline Substituents on the Rate of Replacement of Coordinated Water in Nickel(II) Complexes," R. K. Steinhaus and D. W. Margerum, J. Am. Chem. Soc., 88, 441 (1966).

"Multidentate Ligand Kinetics. X. Exchange Reactions of Metal(II)-Cyclohexylenediaminetetraacetate Complexes," D. W. Margerum, P. J. Menardi and D. L. Janes, Inorg. Chem., 6, 283 (1967).

"Determination of Trace Metals Using Coordination Chain Reactions with Masking Agents and with Automated Rate Measurement," R. H. Stehl, D. W. Margerum and J. J. Latterell, Anal. Chem., to be published, October, 1967.

"Trace Determination of Oxygen by Reaction with Pentacyanocobaltate(II) Coupled to Coordination Chain Detection," D. W. Margerum and R. H. Stehl, Anal. Chem., to be published, October, 1967.

"Multidentate Ligand Kinetics. Reactions of Copper(II) and Copperhydroxide with Nickel-polyamine Complexes," P. J. Menardi, D. W. Margerum and J. J. Latterell, Submitted for publication.

B. Published during the grant period but credited to AFOSR Grant AF 49(630)-60.

"Coordination Chain Reactions. Exchange between Ethylenediaminetetraacetatocuprate(II) and Triethylenetetraminenickel(II)," D. C. Olson and D. W. Margerum, J. Am. Chem. Soc., 85, 297 (1963).

"Multidentate Ligand Kinetics. III. The Formation and Dissociation of Triethylenetetraminenickel(II) and Tetraethylenepentaminenickel(II) and Their Exchange with Radionickel Ion," D. W. Margerum, D. B. Rorabacher and J. F. G. Clarke, Jr., Inorg. Chem., 2, 667 (1963).

"Multidentate Ligand Kinetics. IV. Copper(II) and N-Hydroxyethylethylenediaminetriacetatonickelate(II)," T. J. Bydalek and D. W. Margerum, Inorg. Chem., 2, 678 (1963).

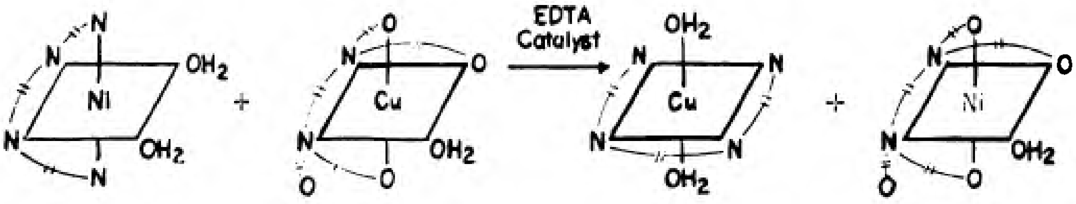
"Multidentate Ligand Kinetics. V. Copper(II) and Cyclohexylenediaminetetraacetatonickelate(II)," D. W. Margerum and T. J. Bydalek, Inorg. Chem., 2, 683 (1963).

"Exchange Reactions of Multidentate Ligand Complexes," Dale W. Margerum, Rec. of Chem. Progr., 24, 4 (1963).

"Multidentate Ligand Kinetics. VIII. The Effect of Hydroxide, Acetate and Azide Complexes of Copper(II) in Its Reaction with Ethylenediaminetetraacetate Complexes," D. W. Margerum, B. A. Zabin, and D. L. Janes, Inorg. Chem., 5, 250 (1966).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Coordination Chain reactions were discovered under a previous AFOSR grant (AF 49(638)-60) concerned with kinetic studies of multidentate ligand complexes. These complexes are formed between metal ions and organic molecules which can form multiple coordinate bonds to the metal. The exchange reactions between two such complexes are catalyzed by trace concentrations of multidentate ligands and inhibited by trace concentrations of metal ions. Thus, the exchange in eq. 1 between 10^{-3} $\underline{M}$ $\mathrm{Nitrien}^{2+}$ and CuEDTA^{2-} is catalyzed by as little as 10^{-9} $\underline{M}$ EDTA. The reaction proceeds by a chain mechanism similar to the mechanism of free



(1)

$\mathrm{Nitrien}^{2+}$ CuEDTA^{2-} $\mathrm{Cutrien}^{2+}$ NiEDTA^{2-}

radical reactions but in this case the chain centers are chemically stable free ligands rather than free radicals. As a result the concentration of chain centers can be carefully controlled and hence the reaction rate can be controlled. The chain-propagating steps for eq. 1 are

$$\mathrm{Nitrien}^{2+} + \mathrm{EDTA} \xrightarrow{k2} \mathrm{NiEDTA}^{2-} + \mathrm{trien} \qquad (2)$$

$$\mathrm{CuEDTA}^{2-} + \mathrm{trien} \xrightarrow{k3} \mathrm{Cutrien}^{2+} + \mathrm{EDTA} \qquad (3)$$

where EDTA and trien are the chain centers present in trace concentration compared to the reactants and products. A typical rate expression is

$$\mathrm{rate} = \frac{d\left[\mathrm{Cutrien}^{2+}\right]}{dt} = k\,[\mathrm{EDTA}]\,[\mathrm{Nitrien}^{2+}] \qquad (4)$$

so that the system responds to the addition of traces of EDTA or to the removal of traces of EDTA by metal ions. This kinetic response permits the analysis of ultratrace concentrations of metals.

The objective of the present work was to explore the analytical capabilities of this unique catalytic system including

(1) ultratrace determination of metal ions, (2) selective ultratrace analysis, (3) automation of the method and (4) coupling of the reaction system in order to detect other trace species. In addition fundamental studies of the factors affecting the exchange rate of ligands coordinated to metal ions was continued.

The application of this new kinetic method to ultratrace analysis was accomplished. As little as 10^{-8} M metal ions can be determined with 10% accuracy using manual techniques. Automatic measurement of the reaction rate constant permits analysis at the 0.01 ppm level within a few minutes. Stopped-flow mixing and an automated readout converts the transient photometric signal to a parameter which is a function of the trace metal present in the sample. The method is applicable to any metal capable of complexing EDTA. With pH control and the addition of masking agents the selective determination of metals is shown.

The presence of 10^{-8} moles of dissolved O_2 in water was detected by coupling reactions of O_2 to the coordination chain reaction system. The results show that oxidation-reduction reactions can be coupled to EDTA complexation and therefore permit application of the extremely sensitive coordination chain system to the detection of many trace species.

The automated rate instrument developed in this work is suitable for many other types of kinetic determinations.

Fundamental studies of coordination kinetics showed that remote substituents on coordinated ligands can affect the rate of replacement of coordinated water molecules in a complex. Electron-donating substituents cause accelerated replacement of water from the metal ion and the Hammett equation is applicable. The fact that the correlation exists is important to the theory of metal ion substitution mechanisms and it also is significant that the effect is small compared to the effect of varying the structure of the ligand.

The kinetics of exchange reactions of metal(II)-cyclohexylenediaminetetraacetate complexes show that one metal ion cannot participate in the replacement of another metal ion in these complexes. However, a proton can take part in the reaction because it is not sterically hindered. The results of this work suggest the possibility of differential kinetic analysis of the metallic elements using CyDTA. This opens an interesting new area of work and preliminary results indicate determinations of otherwise difficult mixtures such as the alkaline earths or rare earth ions to be possible.

Project Scientist: Dr. W. L. Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Solution Chemistry

2. PRINCIPAL INVESTIGATOR: Professor L. G. Sillén
Royal Institute of Stockholm
Stockholm, Sweden

3. INCLUSIVE DATES: 1 October 1962 - 15 March 1967

4. GRANT NOS: AF-EOAR-63-8; AF-EOAR-65-22

5. COSTS AND FY SOURCE: $43,500 FY63; $43,500 FY65

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL:
S. Johansson
R. Arnek
B. Wargviet
N. Ingri
P. Brauner
F. Brits
C. Patel
T. Sekine
I. Szilard
G. Neumann
L. Eriksson
R. Whiteker
D. Dyrssen
A. Vacca

8. PUBLICATIONS:

"Equilibrium Studies of Polyanions, Containing B(III), Si(IV), Ge(IV) and V(V)," Nils Ingri, Svensk. Kem. Tidskr., 75, 3 (1963).

"Studies on the Hydrolysis of Metal Ions 45. The Hydrolysis of Magnesium in Chloride Self-Medium," Derek Lewis, Acta. Chem. Scand., 17, 1891 (1963).

"Studies on the Hydrolysis of Metal Ions 44. Extraction Study of the Hydrolysis of Vanadium (V) at Very Low Concentration in Acid Perchlorate Media," David Dyrssen and Tatsuya Sekine, J. Inorg. Nucl. Chem., 26, 981 (1964).

"On the Hydrolysis of Niobates in 3 M K (Cl) Medium," Georg Neumann, Acta Chem. Scand., 18, 278 (1964).

"On the Hydrolysis of Fluoride Ion, F^-, in 3 M $Na^+(ClO_4^-)$ and 3 M $K^+(Cl^-, F^-)$ Media," Liberato Ciavatta, Arkiv Kemi, 21, 129 (1963).

"Potentiometric Purity Control of Salt Media for Equilibrium Studies, with an Appendix on the Analysis of Dilute Solutions of Strong Acids," Liberato Ciavatta, Arkiv Kemi, 20, 417 (1963).

"On the Determination of the Formation Constants of $GeO_2(OH)_2$ Using a Hydrogen Electrode. Measurements in 3M NaCl Medium," Nils Ingri and Gilbert Schorsch, Acta Chem. Scand., 17, 590 (1963).

"The Crystal Structure of $Na_4Ge_9O_{20}$," Nils Ingri and Georg Lundgren, Acta Chem. Scand., 17, 617 (1963).

"Studies on the Hydrolysis of Metal Ions 49. An emf Study of Lithium Hydroxide in 3 M ($NaClO_4$) Medium," Hitoshi Ohtaki, Acta Chem. Scand., 18, 521 (1964).

"Studies on the Hydrolysis of Metal Ions 50. The Yttrium(III) Ion Y^{3+}," Georg Biedermann and Liberato Ciavatta, Arkiv Kemi, 22, 253 (1964).

"Study on the Hydrolysis Equilibria of Cations by emf Methods," (Dissertation), Georg Biedermann, Sv. Kem. Tidskr., 76, 362 (1964).

"Techniques for Calorimetric Titrations in the Semimicro Range. Part I. Apparatus. A Sensitive, Automatically Recording Calorimeter," Stig Johansson, Arkiv Kemi, 24, 189 (1965).

"Are Aqueous Metavanadate Species Trinuclear, Tetranuclear or Both? Preliminary LETAGROP Recalculation of emf Data," Felipe Brito, Nils Ingri and Lars Gunnar Sillén, Acta Chem. Scand., 18, 1557 (1964).

"Studies on the Hydrolysis of Metal Ions 56. Solvent Extraction Study of the Hydrolysis of Zinc(II) in 3M $NaClO_4$ at Low Concentrations," Tatsuya Sekine, Acta Chem. Scand., 19, 1526 (1965).

"On Equilibria in Polymolybdate Solutions," Yukiyoshi Sasaki and Lars Gunnar Sillén, Acta Chem. Scand., 18, 1014 (1964).

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

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

"On the Structure of Some Hydroxosalts of Al^{3+}, Ga^{3+}, In^{3+}, and Tl^{3+}," Georg Johansson, Svensk. Kemisk. Tidskr., 75, 41 (1963).

"The Ion Activity Function--An Approach to the Study of Electrolyte Behavior in Concentration Solutions," Erik Högfeldt and Leslie Leifer, Acta Chem. Scand., 17, 338 (1963).

"The Ion Activity Function--An Approach to the Study of Electrolyte Behaviour in Concentrated Solutions," in "Electrochemistry," Leslie Leifer and Erik Högfeldt, Acta Chem. Scand., 17, 338 (1963).

"The Ion Activity Function--An Approach to the Study of Electrolyte Behaviour in Concentrated Solutions," in "Electrochemistry," Erik Högfeldt and Leslie Leifer, Proc, 1st Austral. Conf., Sydney 13-15th Febr. 1963, Pergamon Press 1964, p. 107.

"Estudios Sobre Equilibrios de Polianiones 13. Sobre la Polimerización de los Teluratos en NaCl 1 M y 25°C," Felipe Brito, Anales de Fís y Quím (Madrid), 62B, 197 (1966).

"Estudios Sobre Hidrolisis de Iones Metalicos. 55. Vanadio (III) en Medio KCl 3 M," Felipe Brito, Anales de Fís y Quím (Madrid), 62B, 193 (1966).

"Estudios Sobre Equilibrios de Polianiones 14. Vanadates en la Region de Inestabilidad, 40°C y NaCl 0.5 M," Felipe Brito, Anales de Fís y Quím (Madrid), 62B, 197 (1966).

"Vanadates in the 'Instability Range' at 40°C, " Felipe Brito, Acta Chem. Scand., to be printed.

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

"The Crystal Structure of $Zr_2(OH)_2(SO_4)_3(H_2O)_4$," Denis B. McWhan and Georg Lundgren, Inorg. Chem., 5, 284 (1966).

"Studies on the Chemistry of Ruthenium. 2. The Hydrolysis of Ruthenium (III, IV) in Sulfate Medium," Felipe Brito and Derek Lewis, Arkiv Kemi, in print.

"Studies on the Chemistry of Ruthenium 3. Reduction in 1 M Sulfate Media," Felipe Brito and Derek Lewis, Arkiv Kemi, in print.

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

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"Thermochemical Studies of Hydrolytic Reactions 4. Studies of Hydrolysed Cadmium Perchlorate Solutions," Robert Arnek and C. C. Patel, Acta Chem. Scand., in preparation.

"Thermochemical Studies of Hydrolytic Reactions 5. Studies on Hydrolysed Copper(II) Perchlorate Solutions," Robert Arnek and C. C. Patel, Acta Chem. Scand., in preparation.

"High-Speed Computers as a Supplement to Graphical Methods 5. HALTAFALL, a General Program for Calculating the Composition of Equilibrium Mixtures," Nils Ingri, Władisław Kakołowicz, Lars Gunnar Sillén and Björn Warnqvist, Acta Chem. Scand., in preparation.

"Thermochemical Studies of Hydrolytic Reactions 6. The Reaction of H^+ and CrO_4^{2-} in 3 M Na(ClO$_4$) Medium," Stig Johansson and Leif Eriksson, Acta Chem. Scand., in preparation.

"Equilibrium Studies of Polyanions. An emf Study of Polymolybdate Equilibria at 25°C in the Medium 3 M Na(ClO$_4$)," Yukiyoshi Sasaki and Lars Gunnar Sillén, Acta Chem. Scand., in preparation.

"Equilibrium Studies of Polyanions. A Recalculation of Some Literature Data on Polymolybdate Equilibria," Sirkka Hietanen, Yukiyoshi Sasaki and Lars Gunnar Sillén, Acta Chem. Scand., in preparation.

"Thermochemical Studies of Hydrolytic Reactions 7. The Reactions of H^+ and Molybdate Ions in 3 M Na(ClO$_4$)," Imre Szilard, Acta Chem. Scand., in preparation.

"High Speed Computers as a Supplement to Graphical Methods 8. Over-All Fitting of emf Titration Curves by Means of LETAGROP; Application to Phosphoric Acid," George Baldwin, Phyllis Brauner, Lars Gunnar Sillén, Björn Warnqvist and Roy Whiteker, Arkiv Kemi, in preparation.

"An emf Study of the Mixed Complex Function between Niobium(V), Fluoride and Hydroxide Ions in 3 M KCl Medium," Georg Neumann, Acta Chem. Scand., in preparation.

"Note on the Influence of Ionic Medium of the H and S of Functions of Chloromercury(II) Complexes," Georg Neumann, Acta Chem. Scand., in preparation.

"Solution Chemistry," Final Report, AFOSR-67-0952.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research effort was concerned with the solution chemistry of inorganic substances with special emphasis on: (a) the thermodynamics of formation of coordination compounds; (b) the formation of metalates in solution; and (c) x-ray diffraction studies of complexes in solutions and as crystals.

A potentiometric study of acidified solutions of normal ortho molybdate and tungsten ions ($[MoO_4]^{-2}$ and $[WO_4]^{-2}$, respectively) was performed at 25°C. In each system, excluding the highly acidified solutions, only one isopoly species was required to account for all experimental data. These two isopoly anions are paramolybdate, $[Mo_7O_{24}]^{-6}$, and paratungstate, $[HW_6O_{21}]^{-5}$. The formula for the paramolybdate anion, as deduced by Sillén's group, is in accord with that proposed earlier by Lindqvist in his x-ray study of ammonium paramolybdate. On the other hand, the formula proposed for the paratungstate anion while in agreement with the results of solution studies by many investigators is at odds with the formulas proposed by others who studied solids.

Very recently Aveston has proposed that the paratungstate anion is $[W_{12}O_{41}]^{-10}$ in solution; Lindqvist has proposed that this ion is $[W_{12}O_{46}]^{-20}$ in the solid he studied; and Lipscomb, who reevaluated Lindqvist's x-ray study proposed the formula $[H_2W_{12}O_{42}]^{-10}$ for the paratungstate anion, and he suggested a structure different from that proposed by Lindqvist.

Recently Rollins prepared and studied a new, reproducible, and well-defined ammonium sodium double-salt of the paratungstate anion. (See doctoral dissertation, University microfilm No 66-6065, Ann Arbor, Michigan). He studied both solutions and solids employing x-ray, potentiometric, and cryoscopic methods. His results show clearly and unambiguously that the paratungstate anion has the same degree of aggregation in both of these phases. His formulation, $[W_6O_{21+n}H_{1+2n}]^{-5}$, is the same as that proposed by Sasaki and Sillén with allowance for the possibility of constitutional water. Thus, a long-running controversy has finally been clarified.

The thermodynamic quantities H, S, and G were determined at 25°C for the reaction of Cl^- and Br^- with Hg^{+2} and for H^+ with hydrolyzed forms of Hg^{+2}, Cd^{+2}, Cu^{+2}, CrO_4^{-2}, and $[MoO_4]^{-2}$.

Vanadates were studied at high dilution by extraction methods, and at ordinary concentrations by emf methods. From these studies the various equilibria between the mononuclear and polynuclear (isopoly) vanadate species were deduced and the appropriate equilibrium constants were determined. A study was also made of vanadium(III) hydrolysis.

A study of the redox behavior of various ruthenium and ruthenate species in sulfate medium was made and a frequent occurrence of non-integer oxidation states was found.

A study of the borate, silicate, and germanate anions was made. The structure of the polynuclear germate complex in solution was elucidated as a result of this work.

The crystal structures of the basic sulfates and selenates of aluminum were determined. The two compounds are isostructural with each containing discrete $Al_{13}O_{40}$ aluminum-oxygen complexes. This complex is built up of 12 AlO_6 octahedra comprising four Al_3O_{13} groups which are joined by sharing edges. The arrangement gives a tetrahedron of oxygen atoms at its center. The thirteenth aluminum atom occupies the tetrahedral site. This overall structure is surprisingly similar to the classical Keggin structure, exemplified by the ion $[PW_{12}O_{40}]^{-3}$. In the Keggin structure the four W_3O_{13} groups (analogous to the Al_3O_{13} groups) are joined together by common corners, and the phosphorus atom occupies the central tetrahedron of oxygen atoms. Since hydrogen atoms are contained in the aluminum complex its true formula is $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7}$.

In work not supported by AFOSR, Simmons recently placed cobalt(III) in the center of a Keggin structure. This is the only example of tetrahedral coordination for this metal ion. The tetrahedral coordination for aluminum(III) discussed above is rare, and it is unexpected for this metal where oxygen is the ligand.

A crystal structure study of the solid potassium aluminate has shown, quite unexpectedly, that it is a dinuclear ion $[(OH)_3AlOAl(OH)_3]^{2-}$ instead of the classical $Al(OH)_4^-$.

Computer methods have been developed for calculating the composition of complex equilibrium mixtures, rather than making one special program for a special case. This general program, HALTAFALL, takes care of a practically unlimited number of reagents and products and is applicable to reactions in solution or in gas phase and with any number of solid phases present. It also covers equilibria of distribution between two solvents.

An investigation of charge carriers in liquid selenium was made, in which it was found that the conductivity of liquid selenium increases very much on addition of certain other elements, especially chlorine and bromine.

Project Scientist: Dr. W. L. Ruigh
Review by Dr. O. W. Rollins

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COMPLETED PROJECT SUMMARY

1. TITLE: Hydrogen Transfer Reactions in Catalytic Homogeneous Systems

2. PRINCIPAL INVESTIGATOR: Dr. Jack Kwiatek
Research Division
U. S. Industrial Chemical Company
National Distillers and Chemical Corp.
1275 Section Road
Cincinnati, Ohio 45237

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

4. CONTRACT NO: AF49(638)-1214

5. COST & FY SOURCE: $33,924 FY63; $37,420 FY64; $78,890 FY65

6. SENIOR RESEARCH PERSONNEL: J. K. Seyler

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Catalytic Hydrogenation by Pentacyanocobaltate(II)," J. Kwiatek and J. K. Seyler, in Proc. Intern. Conf. Coord. Chem., 8th, Vienna, 1964 (V. Gutmann,ed.), 308 (1964), Springer-Verlag, Vienna.

"Preparation of Organocyanocobaltate(III) Complexes," J. Kwiatek and J. K. Seyler, J. Organometal. Chem., 3, 421 (1965).

"Protonation of Organocyanocobaltate(III) Complexes: A New Synthesis of Nitriles," J. Kwiatek and J. K. Seyler, J. Organometal. Chem., 3, 433 (1965).

"Factors Involved in Catalytic Hydrogenation and Hydrogenolysis by Pentacyanocobaltate(II)," J. Kwiatek and J. K. Seyler, Advan. Chem. Ser., in press.

"Reactions Catalyzed by Pentacyanocobaltate(II) Anion," J. Kwiatek, Catalysis Reviews, in press.

"Hydrogen Transfer Reactions in Catalytic Homogeneous Systems," Final Report, AFOSR-67-1266.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main objectives of this research program were (1) the determination of mechanisms by which hydrogen transfer reactions take place in the pentacyanocobaltate(II) catalyst system, and (2) the investigation of "poisoning" and "reactivation" mechanisms in this system.

The detailed research accomplishments have been incorporated in a manuscript submitted for publication in Catalysis Reviews. The main features of these accomplishments are summarized as follows. The hydridocomplex $Co(CN)_5H^{3-}$ is the hydrogen-transferring agent in catalytic hydrogenations and hydrogenolyses of organic compounds, as well as reduction of inorganic compounds. Pentacyanocobaltate(III) complexes are inert to hydrogen, and are considered to be "poisoned" catalyst. "Reactivation" of hydroxo or allyl-pentacyanocobaltate(III) complexes may be effected by transfer of hydrogen from the hydridocomplex. Other reductions involve hydrogen transfers to organic radicals.

Two methods for the formation of organopentacyanocobaltate(III) complexes were found. These complexes are classified according to their response to protonation. The protonation reactions are useful in identifying organopentacyanocobaltate(III) complexes. One of the reactions constitutes a new nitrile synthesis.

Studies of the control of stereoselectivity by cyanide ion in the hydrogenation of conjugated dienes, and of deuteriogenations of other activated olefins provide data for comparison with that obtained with heterogeneous catalysts.

Project Scientist: Mr. D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: The Use of Mossbauer Effect in Chemistry

2. PRINCIPAL INVESTIGATOR: Dr. James F. Duncan
Department of Chemistry
Victoria University of Wellington
Wellington, New Zealand

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

4. GRANT NO: AF-AFOSR-27-63; AF-AFOSR-27-65

5. COSTS AND FY SOURCE: $25,900 FY63; $30,060 FY65

6. SENIOR RESEARCH PERSONNEL: Dr. A. Freeman
Dr. M. Bailey
Dr. R. E. Bailey

7. JUNIOR RESEARCH PERSONNEL: H. Whitfield
K. F. Mok
D. Stewart
K. McKenzie
H. Raethel
R. Christie
B. R. Frazier
R. Orwin
R. Smith
P. R. Brady
M. Jansen
M. Robins
M. Anderson
H. Percival

8. PUBLICATIONS:

"Nuclear Radiation Resonance," P. R. Brady, P. F. R. Wigley and J. F. Duncan, Aust. Rev. Pure Appl. Chem., 12, 165 (1962).

"Mossbauer Studies in Chemical Bonding," J. F. Duncan and R. M. Golding, Quart. Rev., 19, 36 (1965).

"Chemical Aspects of the Mossbauer Effect," P. R. Brady, J. F. Duncan and K. F. Mok, 287A, 343 (1965).

"Surface Adsorption of ^{57}Co-^{57}Fe on Iron(II) and Cobalt(II) Oxalates," P. R. Brady and J. F. Duncan, J. Chem. Soc., 130, 653 (1964).

"The Valence States of Iron Atoms in Complex Iron Cyanides," J. F. Duncan and P. F. R. Wigley, J. Chem. Soc., 2, 277 (1963).

"Magnetic Susceptibilities of High Spin Iron(II) Compounds," K. F. Mok, R. M. Golding and J. F. Duncan, Inorganic Chemistry, in press.

"Aliphatic Iron Complexes of Iron," J. F. Duncan, C. R. Kanekar and K. F. Mok, prepared.

"A Mossbauer Study of Iron(II) 1:10 Phenanthroline Complexes," J. F. Duncan and K. F. Mok, J. Chem. Soc., 1493 (1966).

"Infra-red Spectra of Some Iron(II) Pyridine Complexes," J. F. Duncan and K. F. Mok, Aust. J. Chem., 19, 701 (1966).

"A New Mossbauer Technique for Studying Metal Complexes," J. F. Duncan, R. M. Golding and K. F. Mok, J.I.N.C., in press.

"The Kinetics and Mechanism of Spinel Formation," J. F. Duncan and D. J. Stewart, prepared.

"The Kinetics and Mechanism of the High Temperature Reactions of Kaolinite Minerals," J. F. Duncan, K. J. D. McKenzie and P. K. Foster, Trans. Faraday Soc., in press.

"Applications of the Mossbauer Effect in Chemistry," Final Report, AFOSR-65-2530.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this project was to relate the observed chemical shifts and quadrupole splits of Mossbauer spectra with the bonding properties of molecules in different directions in space, expecially as the properties are changed by the introduction of different substituents into the molecule. The second objective was to use the effect for investigating the bonding properties of ligands in iron compounds.

Single crystal studies. Studies of single crystals of $K_2Fe(CN)_5NO$ and $K_3Fe(CN)_6$ have been completed. In each case the direction and magnitude of the magnetic field was determined and an estimate made of the asymmetry parameter. Conclusions from previously published work by others are wrong for $K_2Fe(CN)_5NO$.

Co-ordination chemistry. Numerous co-ordination compounds have been made and studied and used to develop theory. It has been shown that the fatty acid complexes are trimers with equivalent iron atoms, with unusual magnetic behavior.

Spinels. Several compounds of formula $A_xB_{1-x}Fe_2O_4$ have been made and their properties studied at liquid air and room temperature. Theoretical treatment has enabled predictions to be made as to when these compounds are magnetic or not.

The mechanism of formation of spinels. The reaction involved is

$$ZnO + Fe_2O_3 \longrightarrow ZnFe_2O_4$$

This reaction is important in allowing a detailed study of the role of cations in what appears to be a simple reaction. In fact conclusions emerge which are very significant to chemical theory. The techniques used and the results obtained at temperatures above 800° are as follows:

(i) *X-ray diffraction* - the reaction is diffusion controlled. The activation enthalpies and entropies have been evaluated.

(ii) *Mossbauer techniques* - the percentage $ZnFe_2O_4$ formed has been measured by observing the $ZnFe_2O_4$ split line and the six lines of Fe_2O_3. The reaction rate as measured by this technique is about half that of the X-ray technique indicating that the iron atoms do not occupy lattice sites at the same rate at which the oxygen atom spacing (measured by X-rays) becomes fixed.

(iii) *Adsorption of oxygen and zinc* - The rate and equilibria of adsorption of oxygen on ZnO and Fe_2O_3 have been determined. It has been shown that neither process is rate determining so far as the overall reaction is concerned. In addition, the rate of loss of zinc and oxygen from zinc oxide has been studied and a similar conclusion drawn.

(iv) *Theory* - By statistical mechanics, applied to the results obtained above, especially the activation entropy, it has been concluded that the reaction takes place as follows:

(1) Zinc oxide dissociates to give gaseous oxygen and zinc.
(2) The oxygen adsorbs on the Fe_2O_3.
(3) Iron atoms diffuse into this layer leaving defects in the remaining oxide.
(4) Zinc simultaneously deposits on the oxide surface layer.
(5) Zinc diffuses into the Fe_2O_3.

The two diffusion processes have very similar activation energies and are rate determining.

Mossbauer techniques. To obtain a clearer view of the role of impurity atoms in this system, the reactant was doped with ^{57}Co-^{57}Fe mixture and the change followed in Mossbauer spectrum. The impurity atoms were at first loosely held, but on heating to 650° (formation of spinel) crystalized, giving five distinct Mossbauer lines. These showed the presence of octahedral and tetrahedral sites, and a rather long relaxation time for the electrons. On heating to 900° or more this pattern was lost and did not become clearcut again until a time which was much longer than the reaction time as measured by X-ray. Two clearcut lines, corresponding to two sites were eventually obtained. Hence, once again the reaction is by no means complete when conventional techniques indicate it to be so.

Project Scientist: Mr. D. W. Elliott

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COMPLETED PROJECT SUMMARY

1. TITLE: Steric Effects in Conjugated Systems

2. PRINCIPAL INVESTIGATOR: Dr. Jerome A. Berson
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

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

4. GRANT NO: AF-AFOSR-389-63

5. COSTS AND FY SOURCE: $21,686 FY63

6. SENIOR RESEARCH PERSONNEL: Dr. M. Jones, Jr.
Dr. M. Pomerantz
Dr. R. A. Clark

7. JUNIOR RESEARCH PERSONNEL: G. Aspelin
R. S. Wood
E. Walsh

8. PUBLICATIONS:

"A Synthesis of Ketones by the Thermal Isomerization of 3-Hydroxy-1, 5-hexadienes. The Oxy-Cope Rearrangement," J. A. Berson and M. Jones, Jr., J. Am. Chem. Soc., 86, 5019 (1964).

"Stepwise Mechanisms in the Oxy-Cope Rearrangement," J.A. Berson and M. Jones, Jr., J. Am. Chem. Soc., 86,5017 (1964).

"On the Mechanism of the Indene-Maleic Anhydride Reaction," J. A. Berson and G. B. Aspelin, Tetrahedron, 20, 2697 (1964).

"Formation and Capture of a Reactive Intermediate Related to Dimethylpseudoindene," J. A. Berson and M. Pomerantz, J. Am. Chem. Soc., 86, 3896 (1964).

"On the Geometric Requirements for Thermolysis of Allylic Bonds. The 1,3-Sigmatropic Rearrangement of syn, cis-Bicyclo [3.2.0] hept-2-enyl 6-Acetate," J. A. Berson and R. S. Wood, J. Am. Chem. Soc., 89,1043 (1967).

"Skeletal Rearrangements of the Methyl 7,7-Dicyanonorcaradienes," J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, J. Am. Chem. Soc., 89,(1967).

"Steric Effects in Conjugated Systems," Final Report, AFOSR-67-1304.

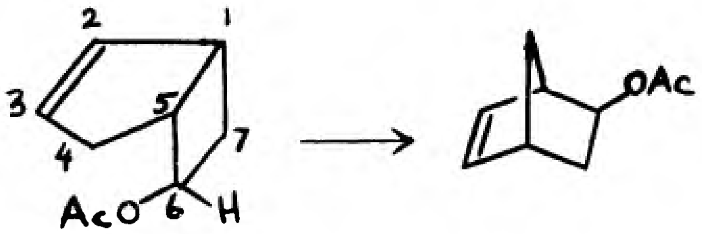
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This work is concerned with the development of a basic understanding of how covalent sigma bonds are broken in thermolysis reactions. The systems most easily studied are ones in which the bond or bonds in question are weakened by juxtaposition to a double bond.

The Cope rearrangement involves the junction of the 1 and 6 carbon atoms of a 1,5-hexadiene system and the cleavage of the 3, 4- bond. It is a homogeneous, unimolecular process:

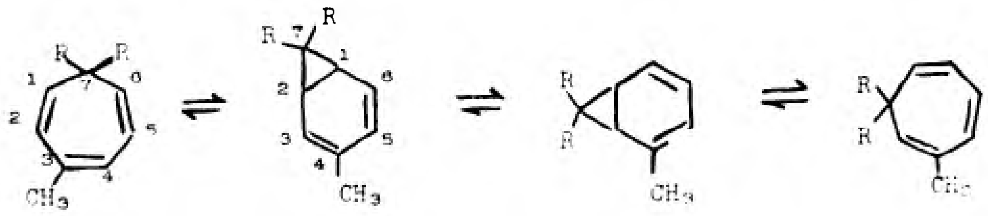
Dr. Berson and his research group found that when R is OH, the rearrangement also proceeds but the initial product, an enol, readily ketonizes. The overall change, which may be called the oxy-Cope rearrangement, is therefore one in which a 3-hydroxy-1, 5-diene is converted to an unsaturated carbonyl compound. Since the requisite dienes can be prepared readily by the action of vinyl organometallic compounds on β,γ-unsaturated ketones, the process suggests widespread application as a synthetic method for bishomologation of such ketones to δ, ϵ-unsaturated ketones. Beyond the synthetic applications, however, is the mechanistic insight provided when the simple Cope system is perturbed to the oxy-Cope one. The introduction of the hydroxy group has a pronounced bond-weakening effect and changes the mechanism from a concerted synchronous process to a step-wise one.

The thermolysis of an allylic bond also can be profoundly affected by its geometric relationship to the π-electron system. Berson has shown that thermal cleavage of the C-1:C-5 bond of the bicyclic acetate (I) is kinetically less favorable than cleavage of the C-1:C-7 bond by a factor of at least thirty. In one interpretation, the preference can be ascribed to steric inhibition of resonance in the transition state for forming the diradical by cleavage of the bond in the π-nodal plane. There is, however, the intriguing possibility that the rearrangement of (I) to exo-norbornenyl acetate (II) is controlled by orbital symmetry considerations of the kind embodied in the Woodward-Hoffmann rules. If so, the rearrangement requires inversion of configuration of the migrating group, a process that can occur if C-7 migrates but not if C-5 migrates. This is under investigation.



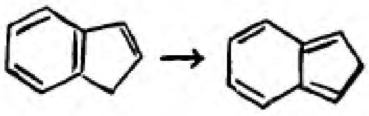
I II

A further study has been concerned with a 1,5-sigmatropic rearrangement, the skeletal reorganization of tropilidenes (III). In the proposed mechanism, a preliminary valency tautomerism, usually endothermic by 7-15 kcal/mole to a norcaradiene (IV) is followed by a circumambulatory rearrangement of C-7. It has been found that a change of the C-7 substituents from R is CH_3 to R is CN decreases the activation energy for the rearrangement by about 18 kcal/mole. This is strong confirmatory evidence for the mechanism, since the dicyano compounds, as Ciganek has shown, are norcaradienes rather than true tropilidenes. Elimination of the endothermic preparatory step thus has drastically diminished the energy requirements for the reaction. A further diminution is probably attributable to the bond-weakening effect of the cyano groups.



III IV

Dr. Berson and his research group have also studied the occurrence of the two valency tautomers isoindene (V) and pseudoindene (VI). These extremely reactive conjugated systems can be formed and trapped. Thus isoindene is formed by a hydrogen shift in indene. The reaction of benzyne with dimethylcyclopropene yields the 2,2-dimethyl derivative of pseudoindene.



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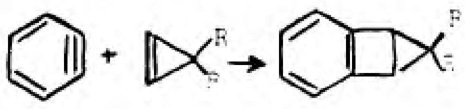

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Project Scientist: Dr. A. J. Matuszko

APPENDIX

DIRECTORATE OF CHEMICAL SCIENCES
AFOSR-OAR Arlington, Va. 22209
Area Code 202, OXford 45337

NOTE: To Proposers November 1967

The Directorate of Chemical Sciences of the Air Force Office of Scientific Research sponsors basic research in chemistry in areas of immediate or long-range interest to the Air Force. Funds are obtained by Congressional appropriations, via the Department of Defense and the Office of Aerospace Research.

Our support is provided in the form of grants or contracts to qualified 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 the Directorate of Chemical Sciences 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 true scholar has an urgent need to ponder his achievements and reflect on their portent. Only in this manner can his contributions be the most meaningful. This reflection, of course, requires a leisure and detachment which are difficult to achieve. Particularly with new investigators, the temptation is almost overhwelming to sacrifice long range quality for immediate quantity of effort. The tendency is commonplace to exploit familiar areas of research to the exclusion of more precarious but potentially more interesting and valuable ones. With the established investigator, creative energies are too often sapped by extraneous demands on time and thought.

To promote this scholarly atmosphere this office is prepared to shield the Principal Investigator as much as possible from such demands of sponsor origin. It is likewise prepared to offer reasonable patience with the beginner who is willing to shake off the harness of his mentor. To facilitate these research objectives our four year plan has evolved. The administrative 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.

Unofficial proposals of inquiry are entertained at any time. Official proposals should be submitted during November and December or in May and June. Starting dates generally may not include July, August and September. 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 of alloys; high strength and other special glasses; electrochemistry; the maximum conversion of chemical energy into electricity or in use in propulsion systems; non- conventional and advanced photographic systems; sensing and determining a few molecules at a distance. 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.

REPORT
ON THE
CHEMISTRY PROGRAM OF THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Prepared Under Grant No. AF-AFOSR-1302-67

BY THE

AD HOC ADVISORY COMMITTEE ON THE CHEMISTRY PROGRAM OF AFOSR

L. B. Rogers, Purdue University, Chairman
Jerome A. Berson, University of Wisconsin
Jacob Bigeleisen, Brookhaven National Laboratory
R. A. Bonham, Indiana University
N. Bruce Hannay, Bell Telephone Laboratories, Inc.
R. K. Iler, E. I. du Pont de Nemours & Company, Inc.

National Research Council
Division of Chemistry and Chemical Technology

Paul J. Flory, Stanford University, Chairman
Martin A. Paul, Executive Secretary

National Academy of Sciences
Washington, D. C.

October 1967

REPORT ON THE

CHEMISTRY PROGRAM OF AFOSR

Introduction

The Air Force Office of Scientific Research (AFOSR) was established in 1955, succeeding the former Office of Scientific Research. As a field agency in the Office of Aerospace Research, it is the primary Air Force agency for the support of extramural research. Its program is carried on through grants and contracts awarded mainly to universities, but also to other non-profit organizations and industrial laboratories, in response to unsolicited proposals. The program is evidence that the Air Force recognizes its dependence on basic science from which the technology of tomorrow will flow.

AFOSR is organized in seven directorates. The Directorate of Chemical Sciences, with a program of about $3.5 million (10% of the AFOSR budget), concerns us here. The mission of the Directorate of Chemical Sciences is "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 military exploitation of their military implications."[1] The Committee for the Survey of Chemistry of the National Academy of Sciences computed the total annual direct support of chemical research in Ph.D.- granting chemistry departments at universities alone in the United States as in excess of $60 million in fiscal 1964[2]. In view of the small fraction of this total contributed by AFOSR, the Director of Chemical Sciences, Dr. Amos G. Horney, has requested advice concerning the most effective way to utilize the funds at his disposal.

In a letter of 23 November 1966 to Professor Paul J. Flory, Chairman of the Division of Chemistry and Chemical Technology of the National Research Council, National Academy of Sciences, Dr. Horney put the question as follows: "In the light of the AFOSR Air Force mission and recognizing that the Directorate of Chemical Sciences AFOSR supports only a very small percent of the basic research in chemistry and therefore cannot meaningfully support all areas: What specific areas of chemistry should receive primary emphasis in the AFOSR sponsored research program, conversely what areas should be left to other resources?"

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[1] 12th Annual Chemistry Program Review, Air Force Office of Scientific Research, Publication AFOSR 66-1854, Arlington, Va., December 1966, p. 1.

[2] "Chemistry: Opportunities and Needs," NAS-NRC Publication 1962, National Academy of Sciences-National Research Council, Washington, D. C. November 1965, p. 170.

With the approval of the Governing Board of the Research Council, a representative committee of research chemists was convened to study the question and to try to formulate an answer. The membership, appointed with the approval of Dr. Frederick Seitz, President of the National Academy of Sciences, was as follows: Professor L. B. Rogers, Purdue University, (Chairman); Professor Jerome A. Berson, University of Wisconsin; Dr. Jacob Bigeleisen, Brookhaven National Laboratory; Professor R.A. Bonham, Indiana University; Dr. N. Bruce Hannay, Bell Telephone Laboratories, Inc.; Dr. R. K. Iler, E. I. du Pont de Nemours & Company, Inc. Professor Ervin R. Van Artsdalen, University of Virginia sat with the Committee in an ex officio capacity as Chairman of the Chemistry Research Evaluation Panel of AFOSR. Dr. Martin A. Paul, Executive Secretary of the Division of Chemistry and Chemical Technology, served as NRC staff representative. The Committee met for a full day on March 30, 1967 and again on June 7, 1967. Several members of the AFOSR staff attended part of these sessions by invitation. Informal discussions were held among members of the Committee at other times. This report presents a consensus of the Committee's deliberations and conclusions.

Characteristics of Basic Research

To understand the recommendations made later, it is important to recognize some of the characteristics of basic research and its discoveries. In a study by the Materials Advisory Board of the National Academy of Sciences - National Research Council[3] it was found that:

1) The time at which a "breakthrough" will occur, or even whether one will occur at all, cannot be predicted with any certainty. Such a characteristic merely reflects the incompleteness of our knowledge.

2) The basic discovery is often found to be valuable in areas only vaguely related to the problem under study at the time of the discovery.

3) There is a long period between the basic discovery and the time when it is widely appreciated and applied by scientists and engineers in developmental research. A period of five years appears to be minimal, while ten years is common, and periods of twenty to forty years are known.[4]

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[3] Report of the Ad Hoc Committee on Principles of Research-Engineering Interaction, Materials Advisory Board, Publication MAB-22-M, National Academy of Sciences-National Research Council, Washington, D. C. July 1966.

[4] Ibid.

These factors, especially the last one, pose great difficulties if one wishes to base the desirability of supporting a particular proposal for a basic study on its apparent relevance to a current pressing problem in developmental research or engineering. Even if basic research funds were concentrated in a current problem area, not only might the relevant important discoveries be slow in coming but more importantly, the pressing developmental problems of ten years from now might well be in some of the areas that were neglected. In contrast, increased efforts in developmental research, which systematically seek an optimum solution within narrower limits of knowledge, may be expected to yield useful results in a much shorter period of time, but only if a broad foundation of basic information is there to be tapped.

It is also important to realize that advances in basic research can be made in two different ways. One approach is to proceed from known principles, exploring their implications in a systematic way. The other approach is empirical, and is based on sketchy observations or incomplete reasoning that may even contradict existing concepts. The fact that many important discoveries have been initiated in the latter way, some by sheer accident as in the case of Pyroceram® brand glass-ceramics[5], argues in favor of supporting both types of research.

Chemistry and the Air Force

Chemistry involves the study of changes or reactions of materials at the atomic and molecular levels, and includes the characterization of products. Therefore, it is directly concerned with the synthesis of new materials and with the effects of chemical composition and structure on their physical and chemical properties.

There is no need to spell out in detail the heavy dependence of the Air Force upon chemistry. Clearly, the Air Force draws directly upon advances in chemistry for new materials (high-strength glasses and composite materials; high-temperature organic and inorganic polymers; heat-resistant and cold-resistant synthetic fabrics; special lubricants; chemical protective coatings; chemical ablatives; insulators, semiconductors, and magnetic and optical electronic devices; chemicals for control of fungi, insects, and disease) and new reactions as sources of power (explosives, propellants, jet and rocket fuels, fuel cells and batteries). Because of the tremendous breadth of the involvement of the Air Force with chemistry, it is virtually impossible to find an area of study within chemistry that is not of potential value to the Air Force and, hence, relevant to its needs.

It is important to note that significant discoveries in basic research of direct consequence to the Air Force have come from the program sponsored by

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[5] Ibid

the Directorate of Chemical Sciences AFOSR. Among such discoveries have been those of Professor W. F. Libby on the detection and measurement of low-level radioactivity, leading to development by the Air Force of the means of reconnaissance for detecting and analyzing the nature of distant nuclear explosions. Another discovery, the applications of which are still in their infancy, is the first truly chemical laser - a laser in which the radiation is derived from energy of a chemical reaction; this discovery by Professor George C. Pimentel in 1964 was an outcome of research on matrix isolation of transient molecules which he started eleven years earlier and which lead to his development of a rapid-scanning infrared spectrophotometer used in surveying chemical reactions for laser potentialities. Characteristically, the uses to which these discoveries could be put were not foreseen in the basic research programs originally conceived. Nevertheless, it is clear in retrospect that the discoveries themselves were dependent on a setting of basic research conducted by imaginative investigators.

Guidelines for Directing Support

The broad expanse of chemical areas that are of obvious interest to the Air Force and the wide applicability of many basic research findings together indicate that an equally broad, well-balanced program would best serve the mission of the Directorate of Chemical Sciences. Nevertheless, the Committee has explored different reasons for limiting the amount of Air Force support in certain areas or increasing it in others. Several important conclusions were reached.

First, it seems unwise for the Air Force to devote a major fraction of its budget to an area that falls within the primary mission of another agency and is well supported by that agency. For example, although the Air Force has an obvious interest in all aspects of health, the primary responsibility for major research efforts in that direction appears logically to rest with the National Institutes of Health.

On the other hand, the fact that the Air Force shares an interest in an area with one or more other agencies does not appear to be a valid reason for withholding support. To cite one example, new instruments and improved techniques for determining structure or composition of materials are of as much interest to the Air Force as to any other agency. Similarly, it seems appropriate for the Directorate of Chemical Sciences to stimulate research thinking in areas of chemistry that are of long-range interest to the Air Force but appear to be relatively neglected. Such stimulation might take place through sponsorship of informal discussions or formal conferences, with the goal of obtaining more and better proposals in that area over the long term. However, it is in the nature of basic research that easily recognizable contributions to the solution of current developmental problems will be small. Rather, a foundation will be laid for attacking developmental programs of the future.

The Committee made an effort to isolate those aspects of Air Force operations that were unusual and might, therefore, serve to distinguish its long-range needs from those of other agencies. Considering that Air Force operations encompass the globe and extend into outer space, it seems highly probable that continuing heavy demands will be made for new materials and new reactions that will perform satisfactorily over tremendous ranges of temperature, pressure, humidity, mechanical stress, and radiation. Furthermore, the materials must often withstand a rapid rate of change from one extreme to another. Thus, the discovery of new kinds of materials, the design of instruments and techniques for investigating their behavior under extreme conditions, the theory and experimental study of small-molecule chemistry and ionization phenomena, especially at low pressures, all promise to be enduring aspects of Air Force interest in Chemistry. These areas might, therefore, be considered as a broad definition of a chemical mission of the Air Force.

At one of its meetings, the Committee started to prepare a detailed list covering the theoretical and experimental aspects of topics of unusual interest to the Air Force, including such areas as: high-temperature polymers, systematic exploration of new inorganic ternary systems, spectroscopy related to energy-loss problems, surface chemistry, solid-state chemistry (defects, crystal growth), chemistry of glass, photographic chemistry, and improved methods of analysis. However, the Committee found themselves forced to make decisions about specific topics within those areas to emphasize the fact that certain aspects only, of those topics might deserve support. Because the acceptability of many of the specific topics depended on the state of information in the recent literature, the value of such a list would decrease rapidly with time. Moreover, it seems likely that such a list would soon become a check-list for determining the suitability of support and might lead to pressures to accept proposals that satisfied best such a superficial criterion. More important is the danger that even an up-to-date list would presuppose that the persons who made it up had all of the worthwhile ideas. It seems inevitable that the crucial components, program flexibility and timeliness of the study in relation to other basic studies, would rapidly decrease.

For those reasons, the Committee abandoned as undesirable the idea of preparing a list of specific research areas particularly worthy of AFOSR support. Instead, the Committee believes that a wiser course is to rely upon the collective judgment of members of the Chemistry Advisory Panel and the staff of the Directorate of Chemical Sciences to select, from among proposals freely submitted, those that represent the best chemistry in the broadly defined area of long-range interest to the Air Force.

Cost Sharing

The Directorate should explore ways of sharing direct costs as a means of increasing the effect of its program. The Committee first considered cost-sharing as a means of providing for the purchase of major items of research equipment which, though very expensive, are a necessity for modern chemical research. Sharing the costs with other agencies or with the institution appears to be especially attractive when more than one principal investigator would be able to use the apparatus. The concept of assisting one or more departments in an institution to acquire a vital instrument would make it possible for new staff members, as well as those with intermediate experience, to undertake improved research programs.

In principle, sharing of direct costs might be considered also for unusually large research programs aside from instruments. However, the danger must be recognized of rendering ineffective an otherwise sound program, if matching funds from other sources prove to be unavailable.

Another Aspect of the Funding Problem

The Committee believesthat their suggestions for restricting the scope of Air Force interests in basic chemistry and for stretching the funds through cost sharing will still leave a gap that will pose a difficult problem. At the Committee's request, Dr. Horney provided the information contained in the accompanying tables. According to Table I, both the number and the percentage of all new proposals received that could be supported in the Chemistry Program of AFOSR have decreased drastically since FY 1965. According to Table II, the percentage of new high-quality proposals that could be supported has dropped below 20%. Such a level of support is unrealistically low in relation to the number and variety of good ideas calling to be tested. The Committee predicts that, if the level of support continues to be so low, the competent investigators, on whom the success of a program depends, will be discouraged from submitting proposals. In order to ensure a continued flow of high-quality proposals, we believe that a substantial increase in funds for basic chemistry will be required.

Conclusions

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

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

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

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

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

Table I

Data Relating to All Proposals Received During the Specified Fiscal Year

	FY 65	FY 66	FY 67
New Proposals from Investigators Not Previously Supported:			
Number Received	238	287	298
Number Funded	55	18	6 (a)
Percent	23%	6%	2%
New Proposals from Investigators Previously Supported: (b)			
Number Received	33	35	29
Number Funded	3	13	7 (a)
Percent	9%	37%	24%
Total New Proposals:			
Number Received	271	322	327
Number Funded	58	31	13 (a)
Percent	21%	10%	4%
Renewal Proposals: (c)	24	48	53
Percentages of All Proposals Received:			
Funded	28%	21%	17%
Not Funded	72%	79%	74%
Awaiting Action	0	0	9%

a) On August 9, 1967, 33 new proposals (9% of all the proposals received) were awaiting action.

b) Most of the research support from the Directorate of Chemical Sciences is initiated as four-year efforts, so proposals for continuing or completing the four-year efforts are called renewals. If an investigator applies for another four-year effort, his proposal is classified as a new proposal, reviewed in competition with proposals from investigators not previously receiving support.

c) All the renewal proposals considered during the three fiscal years covered by the table were funded.

Table II

Data Relating to New Proposals

Judged to be of High Quality(a)

	FY 66	FY 67	FY 68
Number Received	110	100	75
Number Funded	37	13	12
Percent	34%	13%	16%
Dollars Requested	$3,061,000	$2,975,400	$2,667,000
Dollars Funded	$1,207,557	$ 580,669	$ 615,631
Percent	39%	20%	23%

a) Deemed to be worthy of support had funds been available. The numbers in this table refer to high-quality proposals on which action was taken during the specified fiscal year; some of these proposals were received during the previous year.

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13. ABSTRACT

The review provides a unified record of research in progress together with achievements resulting from the basic research program of the Directorate of Chemical Sciences, AFOSR (OAR). There are three main sections in the review. The first section is devoted to research high-lights under the headings of Aerospace Chemistry, Chemical Reactivity and Mechanisms, Boron, Glass, Electrochemistry, Inorganic Chemistry, and the Characterization of Liquids. The middle section contains geographic and other Program statistics, a list of scientific reports received during the year, and a list of active projects. In the final section a factual summary is provided for each project which was completed during fiscal year 1967.

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