

GEORGIA INSTITUTE OF TECHNOLOGY

OFFICE OF RESEARCH ADMINISTRATION

Date: 8 June 1966

RESEARCH PROJECT INITIATION

Project Title: Chemical Reactivity of Hydrogen, Nitrogen, and Oxygen Atoms at
Temperatures Below 100°K

Project No.: B-500

Project Director: Dr. J. A. Wright

Sponsor: National Aeronautics and Space Administration

Agreement Period: From 1 January 1966 until 31 December 1968

Type Agreement: Grant NSG-337, Supplement No. 1

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 (\$25,000 - 1 Jan 67 to 31 Dec 67)
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 15,858 - Total G.I.T. Contribution
 891,498 Total Stop Funded Budget, Three (3) Years.

Grant Administrator

Office of Grants and Research Contracts
Code SC
National Aeronautics and Space Administration
Washington, D. C. 20545

Reports Required

Status - Semiannually
Final - Upon completion of
 project

Assigned to: School of Chemical Engineering

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GEORGIA INSTITUTE OF TECHNOLOGY

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RESEARCH PROJECT TERMINATION

Date: 10 Aug 1971

Project Title : Chemical Reactivity of Hydrogen, Nitrogen, and Oxygen Atoms at
Temperatures Below 100°K.

Project No: B-19-602 (old B-509)

Principal Investigator: Dr. Henry A. McGee

Sponsor: NASA; Washington, D.C.

Effective Termination Date: 6-30-71

Clearance of Accounting Charges: by 7-31-71 (Final Fiscal Report due)

Grant/Contract Closeout Actions Remaining:

- Final Technical Report
- Final Fiscal Report
- Final Report of Inventions

Assigned to: School of Chemical Engineering

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GEORGIA INSTITUTE OF TECHNOLOGY
School of Chemical Engineering
Atlanta, Georgia

First Semi-Annual Report
Project B-509

CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN
ATOMS AT TEMPERATURES BELOW 100°K

by
James A. Knight, Jr.

NASA Grant Nsg-337 (Supplement No. 1)

Performed for
National Aeronautics and Space Administration
Washington, D.C.

September 1966

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Preface

This report covers work performed from January 1, 1966 to June 30, 1966 under NASA grant NsG-337 (supplement no. 1). A group of three excellent Ph.D. students finished their work during this period. Results of their investigations have been presented in several journal articles that are now in press, and several additional papers are now in preparation. A low graduate student enrollment during the past year has somewhat curtailed progress on this research, but we do expect to add from two to five new students at the beginning of the new academic year. Other than the principal investigator, people working on this project during this reporting period have included: Dr. H. A. McGee, Jr. as project scientist and three pre-doctoral students, Mr. R. J. Holt, Mr. P. H. Li and Mr. J. S. Taylor.

I. Introduction

This research program is concerned with the development of chemical information at cryogenic temperatures, particularly on systems that astronomers and astrophysicists feel are important in comets and in the atmospheric and surface chemistry of the Jovian planets. Each of these astronomical objects is very cold, and clearly insofar as chemistry plays a role in the behavior of these objects, this chemistry must be occurring at very low temperatures by terrestrial standards. This objective rather quickly resolves itself into studies of low molecular weight compounds of the four reactive elements of maximum cosmic abundance, namely hydrogen, carbon, nitrogen and oxygen.

The approach here is not one of free radical stabilization or of an attempt to isolate labile species in an inert matrix at very low temperatures. All evidence to date suggests that the activation energy for the reaction of low molecular weight free radicals is zero (or close to it), and hence it will be possible to prepare these species in "stable" forms only by diffusional inhibition techniques such as inert matrix isolation. The concentrations of such labile species that have been prepared are then limited to usually a few tenths of a per cent, and hence the importance of matrix isolated free radicals in cosmic chemistry would seem to be minimal. The matrix technique, particularly when combined with ir or epr, does, of course, provide a powerful means to study the physical and chemical properties of free radicals. By contrast, low molecular weight labile species which have singlet electronic ground states, i.e., species that are highly reactive but are not free radicals, are in an altogether different category. Typical species of this class are substances like cyclobutadiene, cyclopropanone, oxirene, diimide, ammonium ozonide, benzyne, tetrahydrofuran, and many others. This serves to indicate the kind of molecule that is being discussed. One would expect these species to exhibit an activation energy for reaction, but we would also expect this energy to be unusually small. If an activation energy exists, then substances such as these may be preparable as stable cryochemical reagents and a true chemistry at very low temperatures may be developed. Since the activation energies

involved in these systems is small, it will usually be necessary to maintain the compounds below some critical temperature if they are to be manipulated as stable, pure reagents. This means that manipulative techniques must be developed for use with unstable substances at cryogenic temperatures. Ideally, one would like to transpose all of the common or usual operations of bench scale chemistry to the point of convenient use at cryogenic temperatures. The most important operation in any chemical investigation is analysis. In past reports on this grant, the development of a cryogenically cooled reactor-inlet system attachment to a time-of-flight mass spectrometer has been described in detail. The cryogenic mass spectrometer continues to be the key to the approach to low temperature chemistry that is being pursued in this laboratory.

II. Equipment

As a result of an interview trip by a graduating Ph.D. student in this laboratory, the possible availability to this research program of a Model 14-107 Bendix time-of-flight mass spectrometer was discovered. This instrument had been purchased by the 3M Company for use on a government contract research project that was being conducted at their Central Research Laboratory in St. Paul, Minnesota. The project was completed and the instrument and certain accessories were about to be declared surplus.

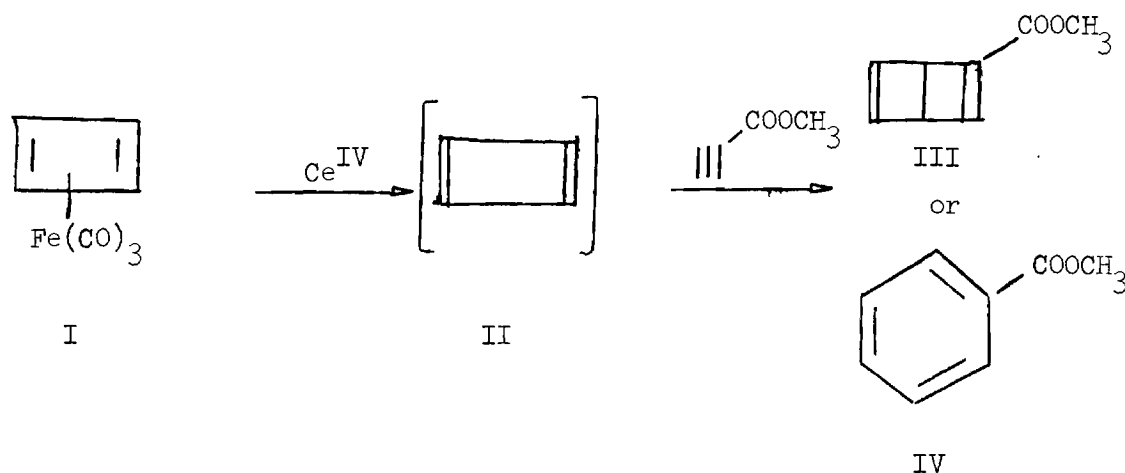
After much activity on the part of ourselves, NASA, 3M and the Defense Supply Agency, the basic instrument together with a rather rudimentary Knudsen cell accessory facility was transferred to this Institute on 11 April 1966. The total evaluation of all equipment received was \$67,309.

As was known throughout the long period of acquisition, the spectrometer was in very poor condition. In fact, three items of equipment, which are absolutely necessary before the instrument can function, were not even included in the shipment. These items were (1) a mechanical vacuum pump, (2) an oscilloscope and (3) an oscillograph. Thus it has been necessary to purchase about \$7,000 worth of equipment (not from these grant funds) before the instrument could be operated. In addition, there is a significant amount of electronic repair and maintenance, the total amount of which is still unknown. These data suggest that much time and money were and still are being expended in getting this "new" instrument up to a proficient operating level. However, the expanded instrumentation is certainly worth this effort, and this laboratory is very fortunate to have gotten the basic structure at essentially no cost. The availability of this instrument, which should be "on stream" within a month, will effectively double the rate of data acquisition in this laboratory.

III. Research

A. Cyclobutadiene

The synthesis of cyclobutadiene, C_4H_4 , has been of interest to organic chemists for a long time.¹ Pettit and his group have recently reported on the preparation of cyclobutadiene and have presented indirect evidence for its existence.² The reported synthesis involves the decomposition of cyclobutadieneiron tricarbonyl with ceric ion in an alcoholic solution. In all experiments reported by Pettit except one, the decomposition was carried out in the presence of an acetylenic compound. The reaction product isolated in these experiments was either the "Dewar" benzene or a benzene derivative. This sequence of operations may be indicated,

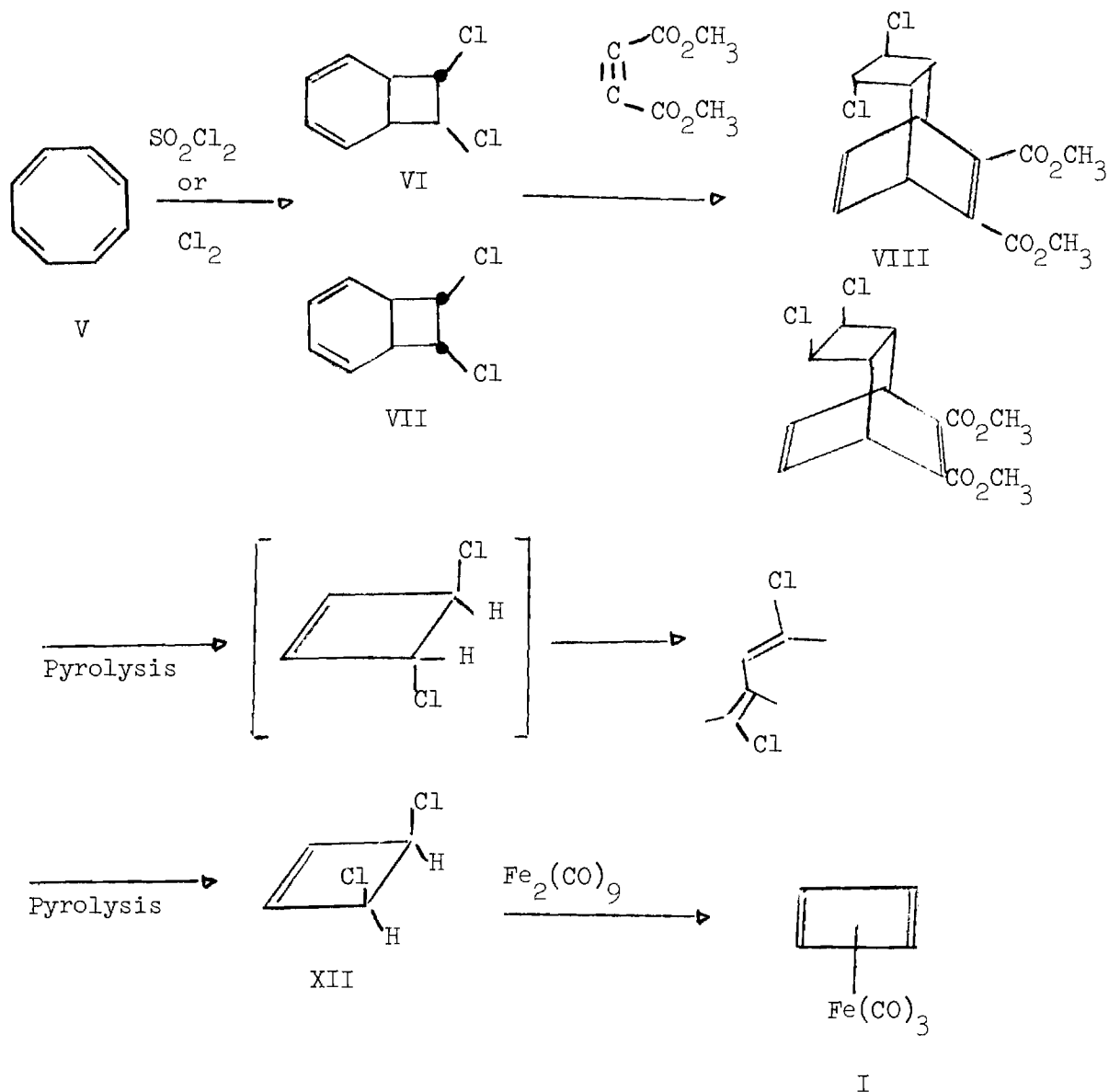


wherein the free cyclobutadiene (**II**) was never isolated or directly identified. In one experiment the gases evolved from the Ce^{IV} decomposition at 0° were passed through a short tube containing a plug of glass wool and condensed in a trap immersed in liquid nitrogen. Methyl propiolate was added to the condensed material in the flask. A small amount of methyl benzoate (**IV**) was detected by gas chromatography in the product, indicating that cyclobutadiene was present. This sort of evidence, while compelling, is not proof of the existence of cyclobutadiene as a free molecular species.

We are attempting to obtain and isolate free cyclobutadiene at low temperatures. Then, by taking advantage of the refrigerated mass spectrometer inlet apparatus developed in this laboratory, the mass spectrum of cyclobutadiene

will be determined. This would represent the first direct physical observation of this molecular species. The energetics of this compound are also of interest and will be investigated.

Cyclobutadieneiron tricarbonyl is itself a difficult substance to obtain and is prepared by the following sequence of reactions.



It has been reported that cyclooctatetraene can be chlorinated with either sulfuryl chloride or chlorine.^{1a} Our attempts to chlorinate with sulfuryl chloride were not successful, but chlorination with dry chlorine proceeded with little difficulty. The best technique for determining the correct amount of chlorine added to the cyclooctatetraene is to weigh the reaction mixture periodically during chlorination. The reaction mixture,

after treatment with potassium carbonate, was vacuum distilled. The infrared spectra of the product, mainly VI and VII, corresponded to the spectra reported by Cope and Burg³ for the same material.

The next step in the synthesis is the reaction of VI and VII with the dimethyl ester of acetylenic dicarboxylic acid to yield trans- and cis-3,4-dichloro-7,8-dicarbomethoxy-anti-tricyclo(4,2,2,0^{2,5})decadiene(7,9), (VIII and IX). This adduct when pyrolyzed at 60 torr and 130 - 210° (thermometer in liquid) yields a mixture of cis-3,4-dichlorocyclobutene-2 (XII) and trans, trans-1,4-dichlorobutadiene-1,3 (XI). The crude product, fractionally distilled at 60 torr, yielded the following fractions: (1) 64-70°; (2) 70-74°; (3) 74-75°. The infrared spectra of the third fraction, which consisted mainly of cis-3,4-dichlorocyclobutene-1, corresponded to the spectra reported by Avram^{1a} for the same compound.

Two successful preparations have been carried out in which relatively small amounts of cis-3,4-dichlorocyclobutene-1 were obtained. This cis-3,4-dichlorocyclobutene-1 was then reacted with Fe₂(CO)₉, but the amount of the chlorinated hydrocarbon that was used was not sufficient to give enough cyclobutadieneiron tricarbonyl (I) for crystallization or distillation. However, a mass spectrum of the tricarbonyl (I) was obtained, and it is clear that the long and difficult organic prep was successfully conducted.

We are now trying to bring up enough material to yield 10 to 20 cm³ of the purified tricarbonyl (I). This product will then be pyrolyzed in one of our fast flow mass spectrometric furnace arrangements⁴ in which the furnace effluent may be immediately analyzed prior to any further molecular collisions. This pyrolysis is to be conducted both in a clean pyrex tube and in a tube coated with solid Ce(NH₄)₂(NO₃)₆.

Pettit and his coworkers have already reported that Ce^{IV} will oxidize the tricarbonyl (I), but because this reaction was always conducted in solution, the thus liberated cyclobutadiene was largely lost before it could be evolved into the gas phase and quenched to low temperatures. The furnace pyrolysis in the presence of Ce^{IV} would appear to afford a much improved yield of cyclobutadiene.

If these pyrolysis experiments are successful, the next step will be pyrolysis followed by cryogenic quench and followed in turn by studies with the cryogenic mass spectrometer in the usual way.⁴

B. Oxirene

In a recent report⁴ a series of experiments were described in which atomic oxygen from a resonant rf discharge was contacted with acetylene in a reactor immersed in liquid oxygen (90°K). This low pressure gas phase reaction was accompanied by a blue-green chemiluminescent flame and yielded a yellow-red solid deposit on the cold walls of the reactor. The red color bleached on warming through -150° , and at the same time free acetylene was evolved. These observations were explained as arising from a low temperature charge transfer complex (the red solid) between acetylene and formic acid which decomposed near -150° . Only CO_2 , $(\text{CHO})_2$, O_2 , HCOOH and H_2O were observed during the warm-up of the composite solid product. A point of some note was the absence of ketene in the product mixture. Haller and Pimentel⁵ had earlier shown that ketene was formed at 20°K by the reaction of photolytically produced ^3P oxygen atoms (from N_2O) with C_2H_2 in a solid matrix of argon. The failure to observe ketene in our experiment must have been due to the inefficiency of the quenching process. This reaction would be exothermic by 127 kcal/mole.

One would expect oxirene to be formed by the addition of an excited ^1D oxygen atom across the triple bond of acetylene. Recent attempts to identify oxirene from room temperature experiments have failed,^{6,7} but with good quenching it should be possible to isolate this very interesting product molecule. Good quenching is even more crucial here than was true for ketene since the ^1D atom is 45 kcal above the ground state ^3P atom. Whereas the earlier experiments involved a quenched low pressure diffusion flame, the more severe quenching requirements have led to an apparatus which permits a mixture of $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ atoms to be bubbled through either liquid acetylene or through a solution of acetylene in any one of several cryo-solvents. Oxirene, or acetylene oxide, will be very unstable because of its highly strained three membered ring structure, and it is expected to be an active low temperature reagent.

C. Cyclopropanone

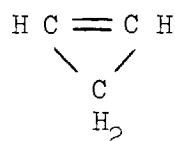
Cyclopropanone is a small ring compound that is expected to be very unstable due to its high strain. The species has often been postulated by organic chemists as a reaction intermediate, and substituted derivatives have actually been identified. However, the free, unsubstituted molecule has not been observed, and it is of some interest to inquire as to whether the new techniques of cryochemistry can successfully lead to its synthesis and isolation.

As discussed in an earlier report,⁴ the synthesis is being conducted at -145°C , by merely contacting liquid ketene and liquid diazomethane. These earlier exploratory studies employed a sample inlet system to the mass spectrometer which necessitated warming the sample to room temperature. In addition, the reactor could not be continuously monitored for identification of volatile compounds during the course of the reaction itself at -145°C . Both of these disadvantages have been designed around, and definitive data on the cycloproponone system should be forthcoming in the near future.

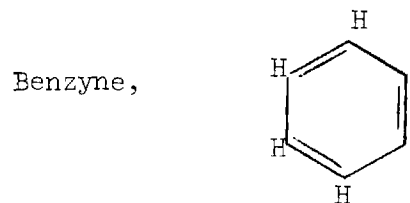
D. Other Species of Interest

Several other compounds are of immediate interest in this research program, but progress on the study of these substances does not warrant more than a passing notation at this time.

Cyclopropene,

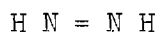


is an interesting molecule that is indefinitely stable at 77°K , but slowly polymerizes at dry ice temperature, -80°C . Experiments are just now getting underway to study several simple additional reactions of this species at cryogenic temperatures. Additions of singlet species such as excited O and CH_2 are of particular interest.



is another reaction intermediate that is often postulated by organic chemists, but that has never been directly observed. Cryochemical techniques offer the best probability of stabilizing and isolating this highly reactive hydrocarbon.

Diimide,



has been recently made in this laboratory from the reaction of atomic oxygen with ammonia in a quenched diffusion flame type of configuration.⁴ This material evidently reacts with itself near -113°C to yield N_2 and N_2H_4 . Efforts are underway to prepare this interesting substance in workable amounts, say 10 - 20 cm³, and to then investigate its low temperature reactivity with several simple substances. Diimide is evidently a very powerful reducing agent.

IV. Bibliography

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GEORGIA INSTITUTE OF TECHNOLOGY
School of Chemical Engineering
Atlanta, Georgia

Second Semi-Annual Report
Project B-509

CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN
ATOMS AT TEMPERATURES BELOW 100°K

by
James A. Knight, Jr.

NASA Grant NsG-337 (Supplement No. 1)

Performed for
National Aeronautics and Space Administration
Washington, D. C.

January 1967

Preface

This report covers work performed from July 1, 1966 to December 31, 1966 under NASA grant NsG-337 (Supplement No. 1). A low graduate student enrollment during the past year has somewhat curtailed progress on this research, but we do expect to add from two to five new students within the next few weeks. Other than the principal investigator, people working on this program during this reporting period have included: Dr. H. A. McGee, Jr. as project scientist, two predoctoral students, Mr. R. J. Holt and Mr. P. H. Li, and one masters student, Mr. M. A. Bell. This research constitutes the theses of these three students.

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I. INTRODUCTION

This research program is concerned with the development of chemical information at cryogenic temperatures, particularly on systems that astronomers and astrophysicists feel are important in comets and in the atmospheric and surface chemistry of the Jovian planets. Each of these astronomical objects is very cold, and clearly insofar as chemistry plays a role in the behavior of these objects, this chemistry must be occurring at very low temperatures by terrestrial standards. This objective rather quickly resolves itself into studies of low molecular weight compounds of the four reactive elements of maximum cosmic abundance, namely hydrogen, carbon, nitrogen and oxygen.

The approach here is not one of free radical stabilization or of an attempt to isolate labile species in an inert matrix at very low temperatures. All evidence to date suggests that the activation energy for the reaction of low molecular weight free radicals is zero (or close to it), and hence it will be possible to prepare these species in "stable" forms only by diffusional inhibition techniques such as inert matrix isolation. The concentrations of such labile species that have been prepared are then limited to usually a few tenths of a per cent, and hence the importance of matrix isolated free radicals in cosmic chemistry would seem to be minimal. The matrix technique, particularly when combined with ir or epr, does, of course, provide a powerful means to study the physical and chemical properties of free radicals. By contrast, low molecular weight labile species which have singlet electronic ground states, i.e., species that are highly reactive but are not free radicals, are in an altogether different category. Typical species of this class are substances like

cyclobutadiene, cyclopropanone, oxirene, diimide, ammonium ozonide, benzyne, tetrahydrofuran, and many others. This serves to indicate the kind of molecule that is being discussed. One would expect these species to exhibit an activation energy for reaction, but we would also expect this energy to be unusually small. If an activation energy exists, then substances such as these may be preparable as stable cryochemical reagents and a true chemistry at very low temperatures may be developed. Since the activation energies involved in these systems is small, it will usually be necessary to maintain the compounds below some critical temperature if they are to be manipulated as stable, pure reagents. This means that manipulative techniques must be developed for use with unstable substances at cryogenic temperatures. Ideally, one would like to transpose all of the common or usual operations of bench scale chemistry to the point of convenient use at cryogenic temperatures. The most important operation in any chemical investigation is analysis. In past reports on this grant and its precursor, NSG-337, the development of a cryogenically cooled reactor-inlet system attachment to a time-of-flight mass spectrometer has been described in detail. The cryogenic mass spectrometer continues to be the key analytical tool in the approach to low temperature chemistry that is being pursued in this laboratory.

II. EQUIPMENT

As a result of an interview trip by a graduating Ph.D. student in this laboratory, the possible availability to this research program of a Model 14-107 Bendix time-of-flight mass spectrometer was discovered. This instrument had been purchased by the 3M Company for use on a government contract research project that was being conducted at their Central Research Laboratory in St. Paul, Minnesota. The project was completed and the instrument and certain accessories were about to be declared surplus.

After much activity on the part of ourselves, NASA, 3M and the Defense Supply Agency, the basic instrument together with a rather rudimentary Knudsen cell accessory facility was transferred to this Institute on 11 April 1966. The total evaluation of all NASA owned equipment that was received was \$67,309.

After significant rebuilding, this instrument is now fully operative, and it equals or exceeds the manufacturer's specifications as regards sensitivity, resolution, etc. The expanded instrumentation was certainly worth the rebuilding effort, and this laboratory was very fortunate to have gotten the basic structure at essentially no cost.

III. RESEARCH

Some of the most interesting problems in astrochemistry, particularly as regards cometary phenomena, are concerned with the types of compounds and reactions that occur under environmental conditions that are very extreme by terrestrial standards. Spectral observations prove the presence of CN, C₃, NH₂, C₂, OH, NH and CH in comet heads. The parent compounds from which these species originate may be only conjectured, but in view of the very low temperature of the comet it seems clear that unusual and highly reactive parent species may well be present. Consequently, an important phase of this NASA program is the synthesis, reactivity, structure and energetics of principally C - H and N - H compounds that are of low molecular weight, are highly reactive, and which may exist only at very low temperatures. However, as long as these species are kept cold, they may be distilled, purified, reacted, etc. just as would any normal reagent at more ordinary temperatures.

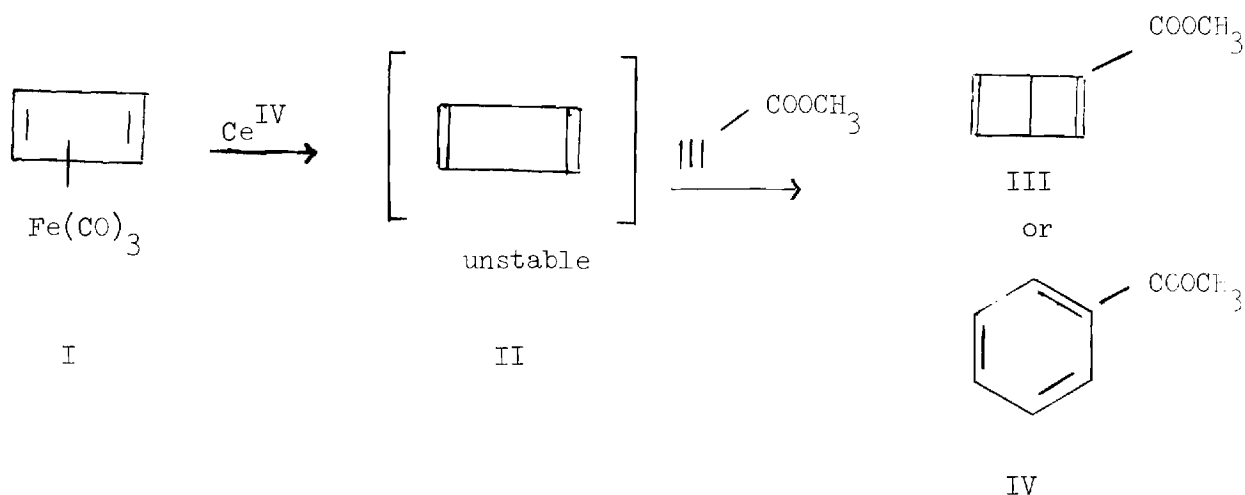
Several studies in this low temperature, preparative chemistry are being pursued, and the progress on each is categorized below with respect to the particular sought-for product molecule.

A. CYCLOBUTADIENE

1. Synthesis

The synthesis of cyclobutadiene, C₄H₄, has been of interest to organic chemists for a long time.¹ Pettit and his group at the University of Texas have recently reported on the preparation of cyclobutadiene and have presented indirect evidence for its existence.² The reported synthesis involves the decomposition of cyclobutadieneirontricarbonyl with ceric ion in an alcoholic solution. In all experiments reported by Pettit except one,

the decomposition was carried out in the presence of an acetylenic compound. The reaction product isolated in these experiments was either the "Dewar" benzene or a benzene derivative. This sequence of operations may be indicated,

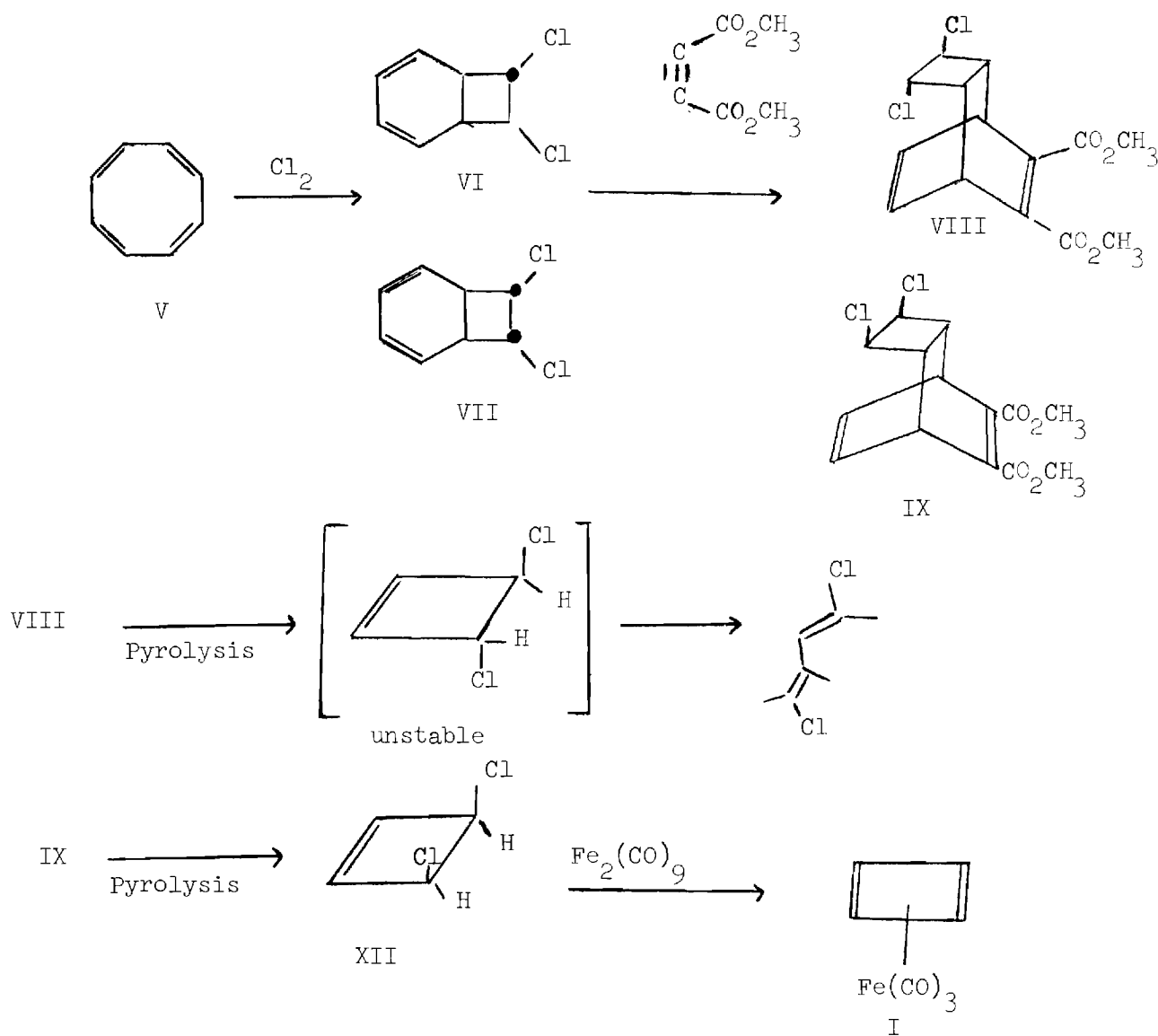


wherein the free cyclobutadiene(II) was never isolated or directly identified. In one experiment the gases evolved from the Ce^{IV} decomposition at 0° were passed through a short tube containing a plug of glass wool and condensed in a trap immersed in liquid nitrogen. After methyl propiolate was added to the condensed material in the flask, a small amount of methyl benzoate(IV) was detected by gas chromatography in the product, indicating that cyclobutadiene was present and that the vapor must have maintained its chemical integrity in its transfer from the reactor to the liquid nitrogen cooled condensor. This sort of evidence, while compelling, is not proof of the existence of cyclobutadiene as a free molecular species. Nor, of course, does it provide any insights into the physico-chemical behavior of this very interesting and theoretically significant molecule.

We are attempting to obtain and isolate free cyclobutadiene at low temperatures. Then, by taking advantage of the refrigerated mass spectrometer inlet apparatus developed in this laboratory, the mass spectrum

of the free cyclobutadiene will be determined. This would represent the first direct physical observation of this molecular species. The energetics of this compound are also of great interest and are being investigated by ionization efficiency techniques.

Cyclobutadieneirontricarbonyl is itself a difficult substance to obtain and is prepared by the following sequence of reactions starting with cyclooctatetraene (COT).



In the last report,¹ we indicated the successful preparation of cyclobutadieneirontricarbonyl from cyclooctatetraene through the above

synthesis procedure, and that the yield of product was poor. Since then, we have improved the yield dramatically by preventing the presence of acid and water during the chlorination of the cyclooctatetraene. About 8 grams of pure $C_4H_4Fe(CO)_3$ is obtained from 78 grams of COT, which is an adequate amount to enable us to do many of the further experiments with free cyclobutadiene. As discussed by Avram,³ the presence of water in the chlorine gas will cause the formation of hydrochloric acid which will convert cis-7,8-dichloro-1,3,5-cyclooctatetraene(VII) to the corresponding trans structure (VI). Consequently, the chlorine was first passed through a tube filled with potassium carbonate and calcium dichloride. After chlorination a large amount of potassium carbonate is added immediately and is stirred vigorously to neutralize any acid present in the reaction mixture. This mixture contains mainly cis-7,8-dichloro-1,3,5-cyclooctatetraene which yields cyclobutadieneirontricarbonyl after the indicated three additional synthesis steps.

Comparing the boiling point, infrared spectra and pale yellow color of the cyclobutadieneirontricarbonyl that we obtained with those properties reported by Pettit^{4,5}, it is evident that we have obtained the same compound.

The dominant peaks in the mass spectrum of cyclobutadieneirontricarbonyl reported by Pettit⁴ and by Watts⁵ are at m/e values of 192, 164, 136, 108, 52. The mass spectrum of cyclobutadieneirontricarbonyl was also determined in this laboratory and the relative abundances of the several ions are presented in Table I. In addition, a typical spectrum appears in Figure 1. The solid sample of cyclobutadieneirontricarbonyl is kept in a tube immersed in an ice bath, and a room temperature inlet line connects this reservoir to the ion source of the mass spectrometer. Immediately on introducing the sample into the mass spectrometer, the spectrum

showed only small amounts of impurity compounds. The sample in the tube was purified by continuous pumping as was apparent from the decreasing peaks of the impurity compounds in the mass spectrum. Following several hours of continuous pumping on the sample and after the small peaks of impurity compounds had disappeared, the mass spectrum of pure cyclobutadieneirontricarbonyl may be observed, and a typical trace is reported herein (see Table I and Figure 1).

The mass spectra of complex metal-organic compounds which have a sandwich type structure, diene-metal atom carbonyl complexes, and metal carbonyls have all been recently reported.^{6,7} Successive removal of CO is found in the mass spectra of $C_6H_8Fe(CO)_3$.⁷ Ions corresponding to $C_4H_4Fe(CO)_2^+$, $C_4H_4Fe(CO)^+$, $C_4H_4Fe^+$ which suggest the stepwise loss of CO from the parent molecule ion with increasing energy of the bombarding electrons are also detected in the mass spectrum of $C_4H_4Fe(CO)_3$. Iron dicarbonyl and iron monocarbonyl ions were found to have a low abundance in the $C_6H_8Fe(CO)_3$ mass spectrum and no $Fe(CO)_3^+$ was observed. Similarly, small peaks of $Fe(CO)_2^+$ and $Fe(CO)^+$ and no $Fe(CO)_3^+$ are also characteristic of the mass spectrum of $C_4H_4Fe(CO)_3$. No FeC^+ ion is found in the mass spectrum of $C_6H_8Fe(CO)_3$ but the mass spectrum of $C_5H_5Mn(CO)_2NO$, $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ ⁶ did yield peaks corresponding to MnC^+ , CoC^+ , and MnC^+ respectively. In the mass spectrum of $C_4H_4Fe(CO)_3$, the FeC^+ ion is found in low abundance.

The striking difference in our mass spectrum and the spectrum reported by Pettit lies in the presence of $FeC_2H_2^+$, Fe^+ , and $C_2H_2^+$ ions in our work. The peak heights at m/e 82, 81, 80, 79, 57, 56, 54, and 26 strongly suggest that these ions are $Fe^{56}C_2H_2^+$, $Fe^{56}C_2H^+$, $Fe^{54}C_2H_2^+$, $Fe^{54}C_2H^+$, Fe^{57+} , Fe^{56+} , Fe^{54+} and $C_2H_2^+$. Based on the absence of these

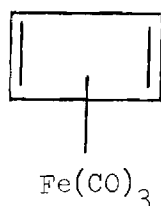
Table I. Relative abundances of the principal positive ions from cyclobutadieneiron tricarbonyl at 70 e.v.

m/e	Ion	Abundance
192	$C_4H_4Fe^{56}(CO)_3^+$	43.0
190	$C_4H_4Fe^{54}(CO)_3^+$	5.2
164	$C_4H_4Fe^{56}(CO)_2^+$	27.4
162	$C_4H_4Fe^{54}(CO)_2^+$	3.2
136	$C_4H_4Fe^{56}CO^+$	10.8
134	$C_4H_4Fe^{54}CO^+$	1.0
112	$Fe^{56}(CO)_2^+$	3.8
108	$C_4H_4Fe^{56+}$	100
106	$C_4H_4Fe^{54+}$	9.6
84	$Fe^{56}CO^+$	18.8
82	$Fe^{54}CO^+$	70.0
	$Fe^{56}C_2H_2^+$	
81	$Fe^{56}C_2H^+$	18.2
80	$Fe^{54}C_2H_2^+$	6.1
79	$Fe^{54}C_2H^+$	1.0
68	FeC^+	4.0
57	Fe^{57+}	3.4
56	Fe^{56+}	41.2
54	Fe^{54+}	5.6
52	$C_4H_4^+$	1.7

Table I (continued)

51	$C_4H_3^+$	1.7
50	$C_4H_2^+$	1.7
26	$C_2H_2^+$	2.1

peaks in his mass spectrum, Pettit favored the structure



over a conceivable bis(acetylene)-iron tricarbonyl formulation for his compound. In the mass spectrum of ferrocene, $(C_5H_5)_2Fe$, ions of $FeC_3H_3^+$, $FeC_3H_2^+$, FeC_2H^+ , $C_3H_3^+$ are found. Also in the mass spectrum of $C_5H_5Mo(CO)_2NO$, the ion $C_3H_3Mo^+$, is found. This strongly indicates the breakdown of the cyclopentadienyl bonds. Therefore the breakdown of cyclobutadiene bonding seems reasonable in $C_4H_4Fe(CO)_3$. No Fe^+ peak was reported by Pettit. From the mass spectra of complex compounds reported by Denning⁶ and by Winters⁷, the metal ion is present in the spectrum of each compound. Analogous to and in correlation with this we conclude that ions of $FeC_2H_2^+$, Fe^+ , and $C_2H_2^+$ are also present in the mass spectrum of $C_4H_4Fe(CO)_3$. The mass spectrum of $C_4H_4Fe(CO)_3$ reported by Pettit⁴ is therefore questionable, but it may be that they just neglected to report ions of lower abundance.

The variation of ion intensity as a function of ionizing energy is being studied, and initial ionization efficiency curves have been obtained. Experimental difficulties have prevented an accurate determination of the appearance potentials of the dominant ions, but these difficulties

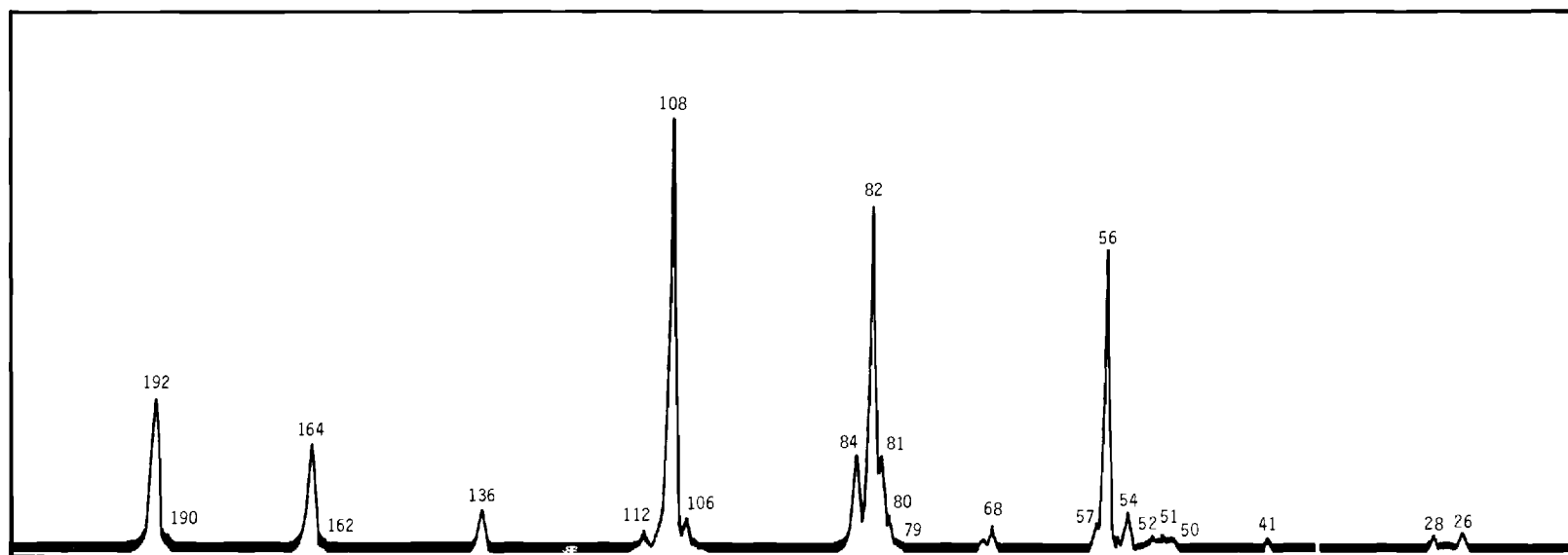


Figure 1. Mass Spectrum of Cyclobutadieneirontricarbonyl Using 70 e.v. Electrons.

are being resolved and accurate data will soon be available. The ionization potential of $C_4H_4Fe(CO)_3$, and the appearance potentials of Fe^+ and $C_4H_4^+$ are receiving most attention at the present time. Approximate data indicate that the ionization potential of $C_4H_4Fe(CO)_3$ lies between 11 and 12 e.v. The appearance potential of Fe^+ is around 19 e.v. and $A(C_4H_4^+)$ is around 20 e.v.

Upon completion of the energetic measurements on the product molecule itself, it will then be pyrolyzed in one of our fast flow mass spectrometric furnace arrangements⁸ in which the furnace effluent may be immediately analyzed prior to any further molecular collisions. This pyrolysis is to be conducted both in a clean pyrex tube and in a tube coated with solid $Ce(NH_4)_2(NO_3)_6$. Pettit and his coworkers have already reported that Ce^{IV} will oxidize the tricarbonyl(I), but because this reaction was always conducted in solution, the thus liberated cyclobutadiene was largely lost before it could be evolved into the gas phase and quenched to low temperatures. The furnace pyrolysis in the presence of Ce^{IV} would appear to afford a much improved yield of cyclobutadiene.

If these pyrolysis experiments are successful, the next step will be pyrolysis followed by cryogenic quench and followed in turn by studies with the cryogenic mass spectrometer in the usual way.⁸

2. Metal Atom Spectra in Comets

Sodium is observed in comet head spectra at about 1 A.U. and iron and nickel appear at about 0.01 A.U. Both iron and nickel form volatile carbonyl compounds as well as hydrocarbon carbonyl complexes of the sort discussed in the preceding section of this report. The possible existence at very low temperatures of sodium in a state very different from its usual metallic state has been investigated in these laboratories, and related systems have been studied in other laboratories. It seems not too

unreasonable to suggest that the source of the metal atoms, which give rise to their corresponding spectra in comets, may be from such highly reactive molecules and molecular complexes. These may perhaps be only stable at very low temperatures. Hence, although we are presently studying cyclobutadieneirontricarbonyl largely as a convenient precursor of cyclobutadiene, the information developed on the iron complex itself may bear some relevancy to cometary phenomena. A paper, now in preparation, will summarize some of the energetics and decomposition behavior of this as well as several other known diene-iron complexes.

3. Low Temperature Charge Transfer Complexes as a Source of Color of Planetary Disks

In a recent report from this laboratory,⁹ the results from a series of observations on the quenched acetylene-atomic oxygen flame were presented and discussed. Mass spectrometric techniques failed to identify a red solid which bleached on warming through -135° to -115°C with the simultaneous evolution of free acetylene. However, arguments were presented to suggest that the red solid was a charge transfer complex of acetylene and formic acid which was stable only below -135°C . Benzene behaved similarly and red charge transfer complexes of this molecule are well known.

The presence of unstable low temperature charge transfer complexes in equilibrium with its constituent molecules could be the source of, e.g., the colors on Jupiter. The equilibrium, and hence the degree of color, would shift with temperature and pressure as these meteorological variables changed with time of day, season of year, etc.

B. OXIRENE

We are attempting to prepare the unsaturated, hetero, three membered

ring compound, oxirene,



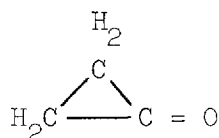
The status of this synthesis is about as described earlier wherein a series of experiments were conducted in which atomic oxygen from a resonant rf discharge was contacted with acetylene in a reactor immersed in liquid oxygen (90°K). This low pressure gas phase reaction was accompanied by a blue-green chemiluminescent flame, yielded a yellow-red solid deposit on the cold walls of the reactor, and underwent both color change and effervescent behavior on warm-up. Only CO_2 , $(\text{CHO})_2$, O_2 , HCOOH and H_2O were observed during the warm-up of the composite solid product. A point of some note was the absence of ketene in the product mixture. Haller and Pimentel¹⁰ had earlier shown that ketene was formed at 20°K by the reaction of photolytically produced ground state ^3P oxygen atoms (from N_2O) with C_2H_2 in a solid matrix of argon. The failure to observe ketene in our experiment must have been due to the inefficiency of the quenching process. This reaction would be exothermic by 127 kcal/mole.

One would expect oxirene to be formed by the addition of an excited ^1D oxygen atom across the triple bond of acetylene. Recent attempts to identify oxirene from room temperature experiments have failed,^{11,12} but with good quenching it should be possible to isolate this very interesting product molecule. Good quenching is even more crucial here than was true for ketene since the ^1D atom is 45 kcal above the ground state ^3P atom. Whereas the earlier experiments involved a quenched low pressure diffusion flame, the more severe quenching requirements have led to an apparatus which permits a mixture of $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ atoms to be bubbled through either liquid acetylene or through a solution of acetylene in any one of several

cryo-solvents. Oxirene, or acetylene oxide, will be very unstable because of its highly strained three membered ring structure, and it is expected to be an active low temperature reagent.

C. CYCLOPROPANONE

As discussed in an earlier report,⁸ this laboratory is endeavoring to synthesize and isolate the free, unsubstituted, highly strained, small ring compound cyclopropanone,



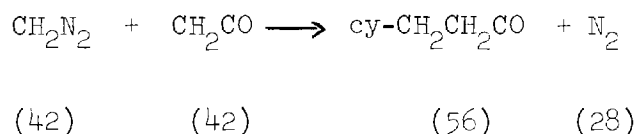
by the reaction of liquid ketene (CH_2CO) and liquid diazomethane (CH_2N_2) at -145°C . Several modifications to earlier procedures have been made. The previous preparation of ketene had yielded a crude product of about 80% ethylene and only 20% ketene. This synthesis involves essentially the pyrolysis of acetone on a heated filament, followed by trapping and bulb-to-bulb distillation of the crude product. To increase yields: (1) a more rapid sweep of gaseous nitrogen carrying the acetone is used for shorter filament contact times; and (2) it was suspected that the first trap for the condensation of unreacted acetone which was maintained at -100°C was also condensing a large amount of the ketene. Therefore this trap was raised to a temperature of -50°C .

Diazomethane was previously separated from its reaction mixture (a thin slurry) by vaporization, but poor and impure yields have resulted. A much quicker and more cleancut method was found. First, the reaction was allowed to take place for 20 minutes at 30°C . Then, after cooling to 0°C , carefully throttled gaseous nitrogen was used to blow the explosive

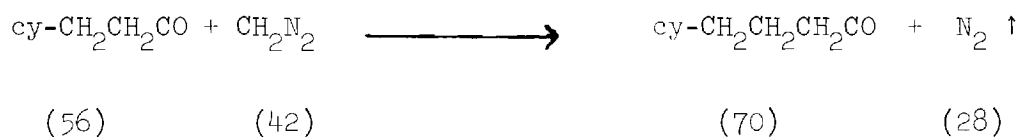
diazomethane out of its reaction mixture and carry it into a receiving flask.

Both of these reagents were purified by distilling from a trap whose temperature could be varied from -145° to room temperature into another trap which was held at -196° . By continual monitoring of the distillation with the mass spectrometer, any desired fraction could be obtained by a simple switching of receiving traps. This could be repeated as necessary.

The reaction of liquid ketene and liquid diazomethane at -145° has been performed with continuous mass spectrometric monitoring of the gaseous products. An increase of $m/e = 28$ during the reaction indicates the reaction,



is occurring. Analysis of the liquid product shows a $m/e = 70$ near -50°C with two separate maxima at $m/e = 56$ at -130°C and -35°C . Neither ketene nor diazomethane had $m/e = 70$ or 56 in their spectrum; thus it is concluded that 70 and 56 are arising from reaction products. Consider the reaction:



wherein it is clear that the very stable compound, cyclobutanone, ($m/e = 70$) is a likely byproduct formed by the mere insertion of a second CH_2 group into the three-membered cyclopropanone ring.

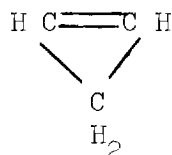
Both from the literature¹³ and from calibration experiments in this laboratory, it is clear that $m/e = 56$ is not present in the spectrum of cyclobutanone. Other plausible reaction products of $m/e = 70$ and 56

(as well as additional characteristic peaks) must be eliminated by either, or all, vapor pressure, spectra, and energy measurements before the positive identification of cyclopropanone can be justified. The spectra of this system is particularly difficult to study and interpret because of the many overlapping ions: ketene (42,14), diazomethane (42,14,28), cyclobutanone (70,42,28), and cyclopropanone (56,42,28). The resolution of the mass spectrometers used here (Bendix time-of-flight) is not adequate to distinguish between ions such as $\text{H}_2\text{C} = \text{C} = \text{O}^+$ and $\text{H}_2\text{C} = \text{N} = \text{N}^+$.

D. OTHER SPECIES OF INTEREST

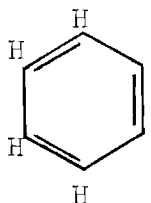
Several other compounds are of immediate interest in this research program, but progress on the study of these substances does not warrant more than a passing notation at this time.

Cyclopropene,



is an interesting molecule that is indefinitely stable at 77°K, but slowly polymerizes at dry ice temperature, -80°C.¹⁴ Experiments are just now getting underway to study several simple additional reactions of this species at cryogenic temperatures. Additions of singlet species such as excited O and CH_2 are of particular interest.

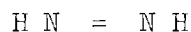
Benzyne,



is another reaction intermediate that is often postulated by organic

chemists, but that has never been directly observed. Cryochemical techniques offer the best probability of stabilizing and isolating this highly reactive hydrocarbon.

Diimide,



has been recently made in this laboratory from the reaction of atomic oxygen with ammonia in a quenched diffusion flame type of configuration.⁸ This material evidently reacts with itself near -113°C to yield N_2 and N_2H_4 . Efforts are underway to prepare this interesting substance in workable amounts, say 10 - 20 cm³, and to then investigate its low temperature reactivity with several simple substances. Diimide is evidently a very powerful reducing agent.

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Third Semi-Annual Report
Project B-509

CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN
ATOMS AT TEMPERATURES BELOW 100°K

by
Henry A. McGee, Jr.

NASA Grant NsG-337 (Supplement No. 1)

Performed for
National Aeronautics and Space Administration
Washington, D. C.

July 1967

Preface

This report covers work performed from January 1, 1967 to June 30, 1967 under NASA grant NsG-337 (Supplement No. 1). A low graduate student enrollment during the past year has somewhat curtailed progress on this research, but we have recently added a number of new students such that there are now eleven predoctoral and postdoctoral students involved in the various activities of the Cryochemistry Laboratory. With several of these additional students being phased into the work of this grant, we anticipate reporting on progress in several other areas in our next Semi-Annual Report. Other than the principal investigator, people working on this program during this reporting period have included: two predoctoral students, Mr. R. J. Holt and Mr. P. H. Li, and one masters student, Mr. M. A. Bell. The work of each of these students, which has been fully supported by this grant, will also function in its entirety as fulfilling the research requirements for their respective degrees.

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I. INTRODUCTION

This research program is concerned with the development of chemical information at cryogenic temperatures, particularly on systems that astronomers and astrophysicists feel are important in comets and in the atmospheric and surface chemistry of the Jovian planets. Each of these astronomical objects is very cold, and clearly insofar as chemistry plays a role in the behavior of these objects, this chemistry must be occurring at very low temperatures by terrestrial standards. This objective rather quickly resolves itself into studies of low molecular weight compounds of the four reactive elements of maximum cosmic abundance, namely hydrogen, carbon, nitrogen and oxygen.

The approach here is not one of free radical stabilization or of an attempt to isolate labile species in an inert matrix at very low temperatures. All evidence to date suggests that the activation energy for the reaction of low molecular weight free radicals is zero (or close to it), and hence it will be possible to prepare these species in "stable" forms only by diffusional inhibition techniques such as inert matrix isolation. The concentrations of such labile species that have been prepared are then limited to usually a few tenths of a per cent, and hence the importance of matrix isolated free radicals in cosmic chemistry would seem to be minimal. The matrix technique, particularly when combined with ir or epr, does, of course, provide a powerful means to study the physical and chemical properties of free radicals. By contrast, low molecular weight labile species which have singlet electronic ground states, i.e., species that are highly reactive but are not free radicals, are in an altogether different category. Typical species of this class are substances like

cyclobutadiene, cyclopropanone, oxirene, diimide, ammonium ozonide, benzyne, tetrahydrofuran, and many others. This serves to indicate the kind of molecule that is being discussed. One would expect these species to exhibit an activation energy for reaction, but we would also expect this energy to be unusually small. If an activation energy exists, then substances such as these may be preparable as stable cryochemical reagents and a true chemistry at very low temperatures may be developed. Since the activation energies involved in these systems is small, it will usually be necessary to maintain the compounds below some critical temperature if they are to be manipulated as stable, pure reagents. This means that manipulative techniques must be developed for use with unstable substances at cryogenic temperatures. Ideally, one would like to transpose all of the common or usual operations of bench scale chemistry to the point of convenient use at cryogenic temperatures. The most important operation in any chemical investigation is analysis. In past reports on this grant and its precursor, NSG-337, the development of a cryogenically cooled reactor-inlet system attachment to a time-of-flight mass spectrometer has been described in detail. The cryogenic mass spectrometer continues to be the key analytical tool in the approach to low temperature chemistry that is being pursued in this laboratory.

II. EQUIPMENT

We continue to put reliance upon the Bendix time-of-flight mass spectrometer as our primary analytical tool for the investigation of very low temperature chemical systems. Three of these instruments are now operative in the Cryochemistry Laboratory. A significantly redesigned cryogenic reactor-inlet system is now under construction but at no cost to the grant. The new system draws heavily upon our experience with existing reactor-inlet arrangements, but it promises to be a rather more versatile system. Its design and operation will be described in a forthcoming paper, preprints of which will be forwarded to NASA as soon as they are available.

The NASA owned Model 14-107 Bendix mass spectrometer is not sufficiently instrumented to allow ionization efficiency measurements to be performed. Yet such measurements are a necessary part of our identification procedures that have been rather highly developed for use with unstable chemical systems at very low temperatures. In addition, the ionization efficiency measurements permit one to develop the molecular energetics of these cryochemicals. Rather than merely duplicating the existing ionization efficiency instrumentation on one of the other spectrometers, it has seemed advisable to reevaluate the equipment and technique with a view toward their possible improvement. Several points are being explored:

1. The fact that the Bendix spectrometer is pulsed (10 kc) provides a ready-made, ideal possible application for phase sensitive detection using a lock-in amplifier. This would greatly increase the signal to noise ratio and hence make possible (1) energetic measurements at much lower temperatures, and (2) more accurate energetic measurement at all temperatures. We insist upon a minimum precision of ± 0.1 e.v. in these data.

2. It is important to be able to perform an energetic measurement rapidly during the course of an experiment. Present techniques, both in this laboratory and elsewhere, require that the raw data be taken in a 1/2 to 1 hour operation followed by manipulation of these data requiring 1 to 2 additional hours before a final appearance potential is obtained. It appears that a plot of the ionization efficiency data using an X-Y plotter could reduce this entire operation to a required time of 1/4 to 1/2 hour.

3. It is well known that the effective life of the dynode and field strips of the Bendix magnetic electron multiplier can be greatly lengthened if electrons corresponding to undesired or uninteresting ions are prevented from entering the multiplier. This problem has been extensively investigated at Argonne National Laboratory, and a rather simple circuitry has been developed which permits only the ions of interest to enter the multiplier. Complete descriptions of the apparatus have been kindly furnished by ANL. The linearity of the multiplier may also be enhanced by use of the Argonne filter apparatus, and the linearity is particularly important in ionization efficiency measurements.

III. RESEARCH

Some of the most interesting problems in astrochemistry, particularly as regards cometary phenomena, are concerned with the types of compounds and reactions that occur under environmental conditions that are very extreme by terrestrial standards. Spectral observations prove the presence of CN, C₃, NH₂, C₂, OH, NH, and CH in comet heads. The parent compounds from which these species originate may be only conjectured, but in view of the very low temperature of the comet it seems clear that unusual and highly reactive parent species may well be present. Consequently, an important phase of this NASA program is the synthesis, reactivity, structure and energetics of principally C - H and N - H compounds that are of low molecular weight, are highly reactive, and which may exist only at very low temperatures. However, as long as these species are kept cold, they may be distilled, purified, reacted, etc. just as would any normal reagent at more ordinary temperatures.

Several studies in this low temperature, preparative chemistry are being pursued, and the progress on each is categorized below with respect to the particular sought-for product molecule.

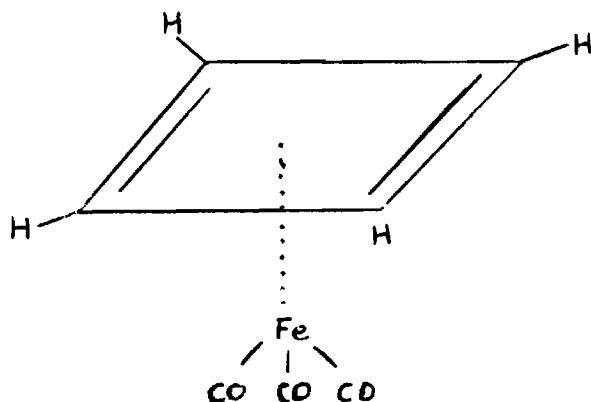
A. CYCLOBUTADIENE

Cyclobutadiene is a cyclic and highly reactive dimer of acetylene. It has never been isolated, although it has been frequently discussed by organic chemists for many years. Acetylene is a postulated cometary constituent, and if this be true, then it seems entirely reasonable that the dimer, C_4H_4 , might also be present in icy cometary nuclei. Cyclobutadiene seems sure to exhibit interesting chemistry, the relevancy of which to cometary phenomena could be significant. Thus, it has seemed reasonable to explore (1) the synthesis, (2) proof of existence, (3) isolation, (4) energetics and (5) the most simple reactivity of cyclobutadiene using the techniques of cryochemistry. It has further turned out, perhaps fortuitously, but nonetheless interestingly, that the only promising route to cyclobutadiene involves a newly synthesized parent substance in which the hydrocarbon is complexed with iron tricarbonyl. Now iron is also apparent in comet spectra at approximately 0.01 AU, and it is conceivable that this iron is present in the icy cometary nuclei as a complex with some highly reactive, unstable hydrocarbon such as cyclobutadiene. Nickel also forms similar highly reactive and volatile hydrocarbon and carbonyl complexes. It appears then, that both the parent molecule as well as the free hydrocarbon ligand could be of interest in cometary chemistry considerations. Molecules of cyclobutadiene with iron as well as the other transition metals may exist at low temperatures in configurations analogous to dibenzyl iron or ferrocene.

In 1956, Longuet-Higgins and Orgel¹ predicted the stability of complexes of cyclobutadiene with certain transition metal carbonyls. In 1965, Pettit and

¹H. C. Longuet-Higgins and L. E. Orgel, J. Chem. Soc., 1969 (1956).

co-workers at the University of Texas reported the first stable cyclobutadiene complex, cyclobutadieneiron-tricarbonyl, CIT.² The geometry of this complex is still unknown, but the geometry of the four proton system has recently been determined from nmr studies.³ It is clear that the proton geometry is, within experimental error, square, i.e., the ratio of adjacent sides of the "rectangle" were found to be 0.9977 ± 0.0045 . This deduction was based on the observation of the nematic pmr spectrum of CIT at 76° which appeared as a symmetric eight-line multiplet. As usual TMS was employed as an internal reference. Thus, this observation of the square configuration of the four protons, together with the earlier indirect indication of a square configuration of the carbon skeleton⁴, suggest that the structure of CIT should best be visualized as,



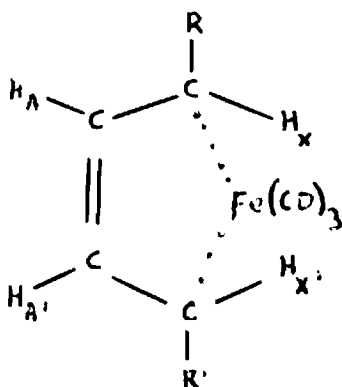
where the carbons and the protons are co-planar.

² G. F. Emerson, L. Watts and R. Pettit, J. Am. Chem. Soc., 87, 131 (1965).

³ C. S. Yannoni, G. P. Ceasar and B. P. Dailey, J. Am. Chem. Soc., 89, 2833 (1967).

⁴ J. D. Fitzpatrick, L. Watts, G. F. Emerson and R. Pettit, J. Am. Chem. Soc., 87, 3254 (1965).

It is perhaps interesting to compare the above situation with that of the addition of the iron atom across the similar 1,4 diene system to yield complexes like,



Here, the four carbon atoms that were the 1,4 diene before complex formation are coplanar. But Fe is below, H_X and $H_{X'}$ are above and H_A and $H_{A'}$ are somewhat below the plane of the carbon skeleton. These observations are also deduced from nmr data.⁵

In earlier reports we have reported the successful duplication of the Texas synthesis of CIT first reported in 1965. We have compared the boiling

⁵ H. S. Gutowsky and J. Jonas, Inorg. Chem., 4, 430 (1965).

point, infrared spectra and pale yellow color of the CIT that we synthesized with those properties reported by Pettitt^{2,6}, and it was evident that we have obtained the same compound. We also have, more recently, determined the low resolution nmr spectrum of CIT which consists of a single sharp absorption at $\tau 6.09$ relative to TMS which also confirms Pettit's result².

The ionization potential of CIT was measured as 8.5 ± 0.1 e. v. This ionization potential was determined by the semi-log and linear intercept methods with the energy scale calibrated immediately before and after each energy measurement using argon. It is interesting to compare this result with the ionization potential of $C_6H_8Fe(CO)_3$ of 8.0 ± 0.4 e.v. which was determined by Winters⁷. This suggests that in such complexes, the electron is removed from an iron orbital in the ionization process. Further confirmation of this idea is apparent in the similarity of the ionization potentials of a number of hydrocarbon metal carbonyls as well as metal carbonyls themselves. Table I contains a summary of such data.

⁶ L. Watts, "Cyclobutadieneirontricarbonyl," Ph.D. Thesis, Univ. of Texas, 1966.

⁷ R. E. Winters, Ph.D. Thesis, Kansas State University, 1965.

TABLE I
IONIZATION POTENTIALS OF CARBONYLS

<u>Carbonyl</u>	<u>Ionization Potentials</u>		<u>Reference</u>
	<u>Carbonyl</u>	<u>Metal</u>	
$\text{Co}_2(\text{CO})_8$	8.12	7.81	8
$\text{Mn}_2(\text{CO})_{10}$	8.55	7.43	8,9
$\text{Re}_2(\text{CO})_{10}$	8.27	7.87	9
$\text{ReMn}(\text{CO})_{10}$	8.15	7.43, 7.87	9
$\text{C}_6\text{H}_8\text{Fe}(\text{CO})_3$	8.0	7.83	7,10
$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{NO})$	8.1	7.35	10
$\text{Fe}(\text{CO})_5$	8.53	7.83	11 a
$\text{Mo}(\text{CO})_6$	8.23	7.35	11 b

Since the ionization potential of CO is about 14 e.v., it seems clear that ionization involves the removal of a valence electron from the metal atom.

CIT was readily sublimed into the source, and there was no evidence of its thermal decomposition. The isotopic abundancies were as expected and in keeping with accepted values.

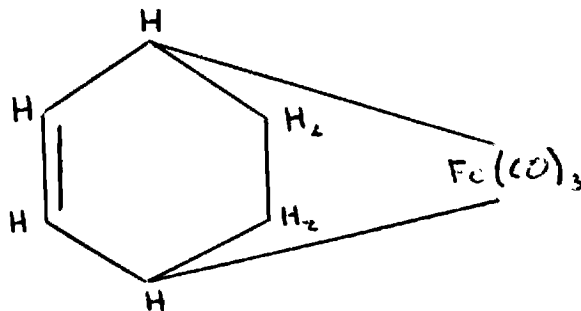
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- ⁸ R. E. Winters and R. W. Kiser, J. Phys. Chem., 69, 1618 (1965).
⁹ H. J. Svec and G. A. Junk, J. Am. Chem. Soc., 89, 2836 (1967).
¹⁰ R. E. Winters and R. W. Kiser, J. Phys. Chem., 69, 3198 (1965).
^{11a} R. E. Winters and R. W. Kiser, Inorg. Chem. 3, 699 (1964); ^{11b} Inorg. Chem. 4, 157 (1965).

Some comparisons between the spectrum of CIT and other hydrocarbon metal carbonyls and related compounds is of interest.

TABLE II
TRANSITION METAL CARBONYLS STUDIED BY MASS SPECTROMETRIC TECHNIQUES

Compound	Reference
I $C_5H_5Mo(CO)_2NO$	10
II $C_6H_8Fe(CO)_3$	10
III $C_6F_8Fe(CO)_3$	12
IV $C_4H_4Fe(CO)_3$	This work

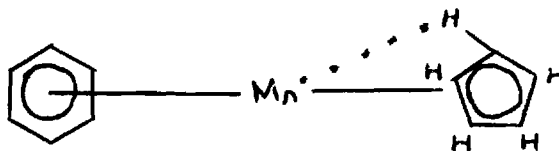
The mass spectra of each of the compounds in Table II show ions formed by the successive, removal of the carbonyl (or nitrosyl) entity. $FeCO^+$ and $Fe(CO)_2^+$ ions are present in II and IV, but II loses H_2 to form $C_6H_6Fe^+$ rather than $C_6H_8Fe^+$, in fact, this latter ion is completely absent from the spectrum of II. The $C_6H_6Fe^+$ ion is present to 57.8% of the most prevalent ion, and it is the second most dominant ion in the spectrum of II, while the corresponding $C_4H_4Fe^+$ is the most prevalent ion in the spectrum of IV. This preferential loss of H_2 in II may be pictured in terms of a postulated structure,



¹² H. H. Hoehn, L. Pratt, K. F. Watterson and G. Wilkinson, J. Chem. Soc., 2738 (1961).

whose resemblance to that of non-cyclic iron-dienes is apparent. It seems reasonable that such a structure would be less strained and more stable by the formation of the symmetric diene structure. A second point of interest is the low abundance of $\text{Fe}(\text{CO})_x^+$ ions in the spectrum of both II and IV, whereas these ions are the most abundant in the spectrum of III. This suggests that the hydrocarbon-iron bond in II and IV is greater than that in the corresponding perfluoro derivative such as III.

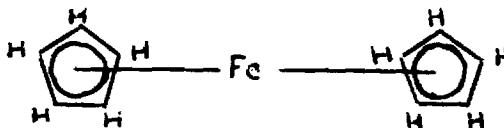
A third point of interest is the presence of metal-hydrocarbon ions containing smaller hydrocarbon fragments than the original ligand. For example, $\text{C}_3\text{H}_3\text{Mo}^+$ is 95% of the dominant ion, $\text{C}_5\text{H}_5\text{Mo}^+$, in I, and $\text{C}_2\text{H}_2\text{Fe}^+$ is 80% of the dominant ion, $\text{C}_4\text{H}_4\text{Fe}^+$, in the mass spectrum of IV. The presence of such fragmented hydrocarbon-metal ions is also noted in ferrocene $\text{Cp}_2\text{Fe}^{13}$, BzCpMn^{14} and $\text{Bz}_2\text{Cr}^{14}$. (Here Cp = cyclopentadienyl and Bz = benzene). Bimolecular reactions in the source leading to the fragmented hydrocarbon are unlikely due to the low source pressure, for if, e.g., MnBz^+ existed long enough to undergo such a bimolecular reaction, it would have assuredly appeared in the mass spectrum; but it did not. This has led to the postulate of a concerted decomposition mechanism,¹⁴



¹³ F. W. McLafferty, Anal. Chem., 28, 306 (1956).

¹⁴ R. G. Denning and R. A. D. Wentworth, J. Am. Chem. Soc., 88, 4619 (1966).

in which the hydrogen atom attaches itself to the metal atom as the C_5H_4 fragment is leaving. Similar ion decomposition mechanisms have been invoked in discussing the fragmentation pattern of substituted ferrocenes,¹⁵ but ferrocene itself,



shows no evidence of a similar mechanism being operative, i.e., $C_5H_5 - FeH^+$ does not appear in its spectrum.

Production of Free C_4H_4 from CIT

Studies of the pyrolysis of CIT have been conducted in a coaxial furnace inlet system in which the furnace exhaust is only 1/8 in. from the ionizing electron beam of the mass spectrometer.¹⁶ Both 1/8 and 3/16 in. O.D. pyrex glass furnaces have been used. In both furnaces, the maximum intensity of m/e 52 (i.e., free cyclobutadiene) was observed at 380°. The dominant peaks of the pyrolysis products using 70 e.v. electrons and their assignments are summarized in Table III.

¹⁵ A. Mandelbaum and M. Cais, Tetrahedron Letters, 3847 (1964).

¹⁶ H. A. McGee, Jr., Final Report on NASA grant NsG-337, July, 1966.

TABLE III

MASS SPECTRUM OF THE PRODUCTS FROM THE PYROLYSIS
OF CYCLOBUTADIENEIRONTRICARBONYL AT 380°C

<u>m/e</u>	<u>Assignment</u>
104	$C_8H_8^+$
78	$C_6H_6^+$
56	Fe^+
52	$C_4H_4^+$
51	$C_4H_3^+$
50	$C_4H_2^+$
44	$C_3H_8^+$
39	$C_3H_3^+$
28	CO^+
27	$C_2H_3^+$
26	$C_2H_2^+$
16	O^+
12	C^+
2	H_2^+

Since the mass spectrum of cyclooctatetraene (C_8H_8) does not have a peak at m/e 52, but benzene (C_6H_6) does have such a peak, one might well question whether the 52 peak is a fragment of benzene, free cyclobutadiene or

free vinyl acetylene ($\text{H}_2\text{C} = \text{CH} - \text{C} \equiv \text{CH}$). The intensity of m/e 52 from C_6H_6 at 70 e.v. is only 20% of the intensity of C_6H_6^+ . In our spectra the intensity of m/e 52 is 40% of m/e 78 and hence the remainder must be due either to free cyclobutadiene or to vinyl acetylene. A calibration experiment with vinyl acetylene will resolve this uncertainty, as will a measurement of the appearance potential of m/e 52. Both of these tasks are now underway.

From the photolysis of CIT, Gunning et al.¹⁷, in very recent work, (May 1967) have tentatively observed free cyclobutadiene. This constitutes the nearest to unequivocal observation of cyclobutadiene that has yet been reported. Dominant peaks of the photolysis products in the mass spectrometer were m/e = 26 (C_2H_2^+), 52 (C_4H_4^+), 78 (C_6H_6^+), 104 (C_8H_8^+), 140 ($\text{Fe}(\text{CO})_3^+$) and Fe^+ , CO^+ . We failed to observe m/e 140 ($\text{Fe}(\text{CO})_3^+$) which is evidently due to the decomposition of $\text{Fe}(\text{CO})_3$ at 380°C . Supporting evidence that the C_4H_4 species contained an unbranched carbon chain have been shown by Gunning¹⁷ in the formation of furan in an experiment in which CIT was photolyzed in the presence of oxygen.

The appearance potential of C_4H_4^+ from C_6H_6 is $15.6 \sim 15.9$ e.v.,¹⁸ and the ionization potential of vinyl acetylene is 9.9 ± 0.09 e.v.¹⁸. The appearance potential of C_4H_4^+ in our mass spectrum has not been measured accurately. But this is underway, and clearly the difference in the value of $I(\text{C}_4\text{H}_4^+)$ from $A(\text{C}_4\text{H}_4^+)$ from C_6H_6 and $I(\text{C}_4\text{H}_4^+)$ from vinyl acetylene, will further support the hypothesis that free cyclobutadiene is obtained from our pyrolysis experiments with CIT. The measurement of $A(\text{C}_2\text{H}_2^+)$ from CIT will also permit one to deduce the heat of formation of this molecule.

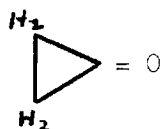
¹⁷ H. E. Gunning, et al., Chem. Comm., No. 10, 497 (1967).

¹⁸ F. H. Field and J. L. Franklin, "Electron Impact Phenomena", Academic Press, New York, N. Y., 1957.

The reaction of CIT with ceric ammonium nitrate in ether solution has also been carried out. This is the same reaction that was used by Pettit in his original studies that led to the first indirect data suggesting that free cyclobutadiene may be producible.⁴ CIT in ether was added to aqueous ceric ammonium nitrate solution at 0°C. The gas evolved was passed through a tube kept at 0° and was quenched at -197° in our cryogenic inlet system attached to the mass spectrometer.¹⁶ Mass spectra were observed during a slow warm-up period. We failed to detect m/e 52 but m/e 104 appeared at -100°. Experimental difficulties caused the temperature of the inlet system to increase to -160° before the mass spectra could be observed. Hence, if free cyclobutadiene was evolved, it very likely was pumped away. Whether this m/e 104 is the cyclobutadiene dimer or cyclooctatetraene also requires further investigation.

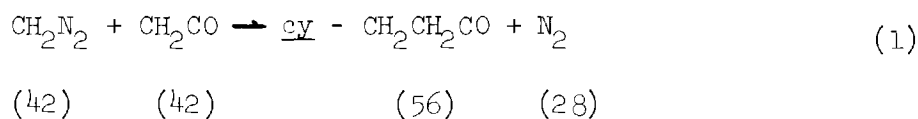
B. CYCLOPROPANONE

Recent evidence obtained in this laboratory strongly suggests that we have synthesized cyclopropanone,

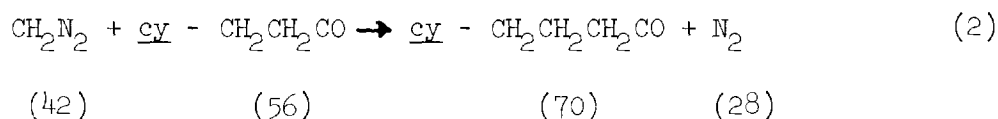


as a free, stable cryochemical which will remain unreactive up to temperatures approaching that of dry ice (-78°). In view of the presence of the carbonyl carbon, one would expect the three-membered ring of cyclopropanone to be highly strained. Due to its theoretical importance as a proposed organic reaction intermediate, the synthesis of cyclopropanone has been the subject of much research activity which has however proved unsuccessful until the past year.^{19,20}

The reaction of diazomethane with ketene affords a direct approach to the synthesis of cyclopropanone:



Room temperature attempts of this synthesis have always yielded the butanone which was viewed as resulting from further reaction of diazomethane with cyclopropanone:



¹⁹ N. J. Turro and W. B. Hammond, J. Am. Chem. Soc. **88**, 3672 (1966).

²⁰ S. E. Schaafsma, H. Steinberg, Th. J. De Boer, Rec. Trav. Chim. **85**, 1170 (1966).

Our interest has been to determine whether the techniques of cryochemistry permit the synthesis and isolation of cyclopropanone by the above reaction and the observation of its stability, mass spectrum, energetics and reactivity.

As discussed in an earlier report,²¹ explosive diazomethane and toxic ketene are prepared, purified and finally analyzed using the T.O.F. mass spectrometer. The mass spectrometric data confirm the presence of the desired reagents and the absence of $m/e = 56$ and $m/e = 70$. The reaction of diazomethane and ketene was carried out in a cooled, evacuated trap by arranging, at liquid nitrogen temperature (77°K), a ring of diazomethane above a ring of ketene (in great excess) and then plunging the trap into a dewar held at -150° whereupon the solid yellow diazomethane became a viscous liquid which slowly ran down into and reacted with the now also liquid ketene producing a white solid and a volatile gas. The solid product (which should have a higher reaction energy of activation than the gas or liquid) combined with the low temperatures should deter any further reaction of the initial products.

The product gas proved to be uncondensable at 77°K and exhibited a two line mass spectrum at $m/e = 28$ and $m/e = 14$ in proportions nearly that of nitrogen indicating that the product gas was nitrogen and that reactions (1) and/or (2) were probably occurring. After the excess reactants (which was proved to consist entirely of ketene) was removed by warming and pumping on the reactor, the solid product was transferred to the cryogenic inlet system,¹⁶ where it was warmed until it exerted a sufficiently high vapor pressure ($10^{-5} \sim 10^{-3}$ torr) to be analyzed in the mass spectrometer. Product peaks corresponding to $m/e = 56$ and $m/e = 70$ were observed and studied at -90° and -75° respectively.

²¹ J. A. Knight, Jr. Second Semi-Annual Report on Grant NsG-337 (Supplement No. 1) January 1967.

The volatilities of the two species allowed them to be separated sufficiently to obtain their mass spectra (see Figures 1 and 2). The vapor pressure, mass spectra, and energetic values of the heavier sample (maximum m/e 70) of our product were very similar to the same data obtained in this laboratory from a sample of pure cyclobutanone (purchased from K & K Laboratories, Plainview, New York, #3906, and used without further purification). In interpreting the experimental traces shown in Figures 2 and 3, the following facts were taken into consideration: a large air leak produced peaks at $m/e = 32, 16, 28, 14$ and 29; background water causes peaks at $m/e = 18$ and 17; the calibrating gas argon has peaks at $m/e = 40$ and 20; impurity acetone and product cyclopropanone exhibit peaks at 58, 43 and 15; and 56, 42, 41, 28, 27, and 26 respectively. A comparison of the heavier product (maximum $m/e = 70$) and pure cyclobutanone is made in Table IV. The mass spectra of the lighter sample (maximum $m/e = 56$) exhibited the same major ions as those reported by Schaafsma²⁰ for cyclopropanone. (See Table IV).

TABLE IV
MASS SPECTRA OF CYCLIC KETONES

Source	Percent of Peak of Maximum Intensity															
	m/e 70	56	42	41	40	39	38	37	36	29	28	27	26	25	24	14
Cyclobutanone ²²	30	0	100	9	2	9				7	8	6				6
Cyclobutanone (this work)	22	0	100	12	?	14	5	4	2	?	?	12	8			?
Product $m/e = 70$ (this work)	20	0	100	14	?	16	5	5	2	?	?	12	8			?
Cyclopropanone ²⁰		18	14								100	38	38			
Product $m/e = 56$ (this work)		15	15	5	?	4	4	4	3	?	100	35	34	4	1	?

²² H. J. Hofman, Tetrahedron Letters No. 34, 2329 (1964).

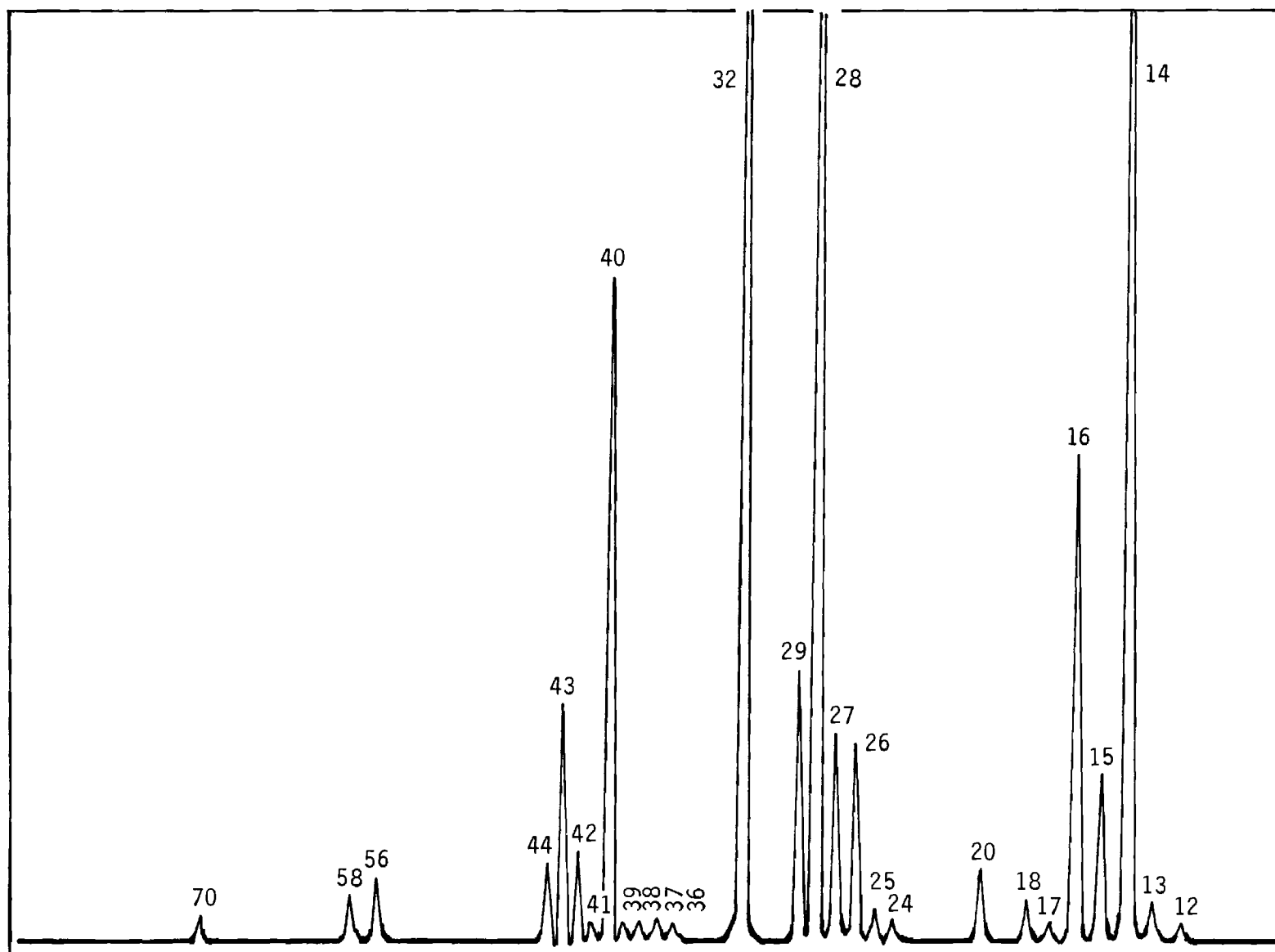


Figure 1. Mass spectrum of light product (maximum m/e 56) from ketene-diazomethane reaction. Spectrum obtained with cryogenic inlet system at -90° and using 70 e.v. electrons.

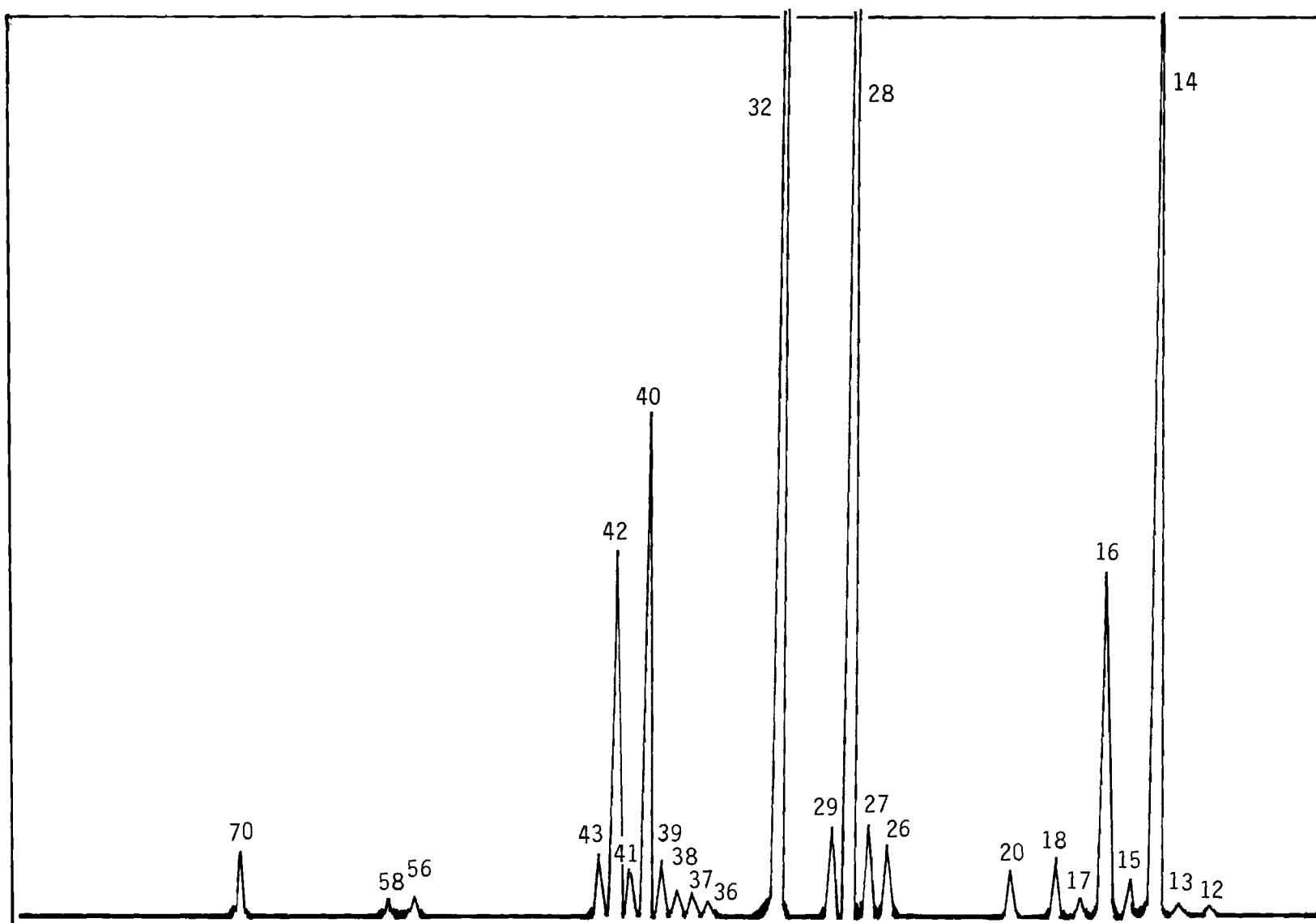


Figure 2. Mass spectrum of heavy product (maximum m/e 70) from ketene-diazomethane reaction. Spectrum obtained with cryogenic inlet system at -75° and using 70 e.v. electrons.

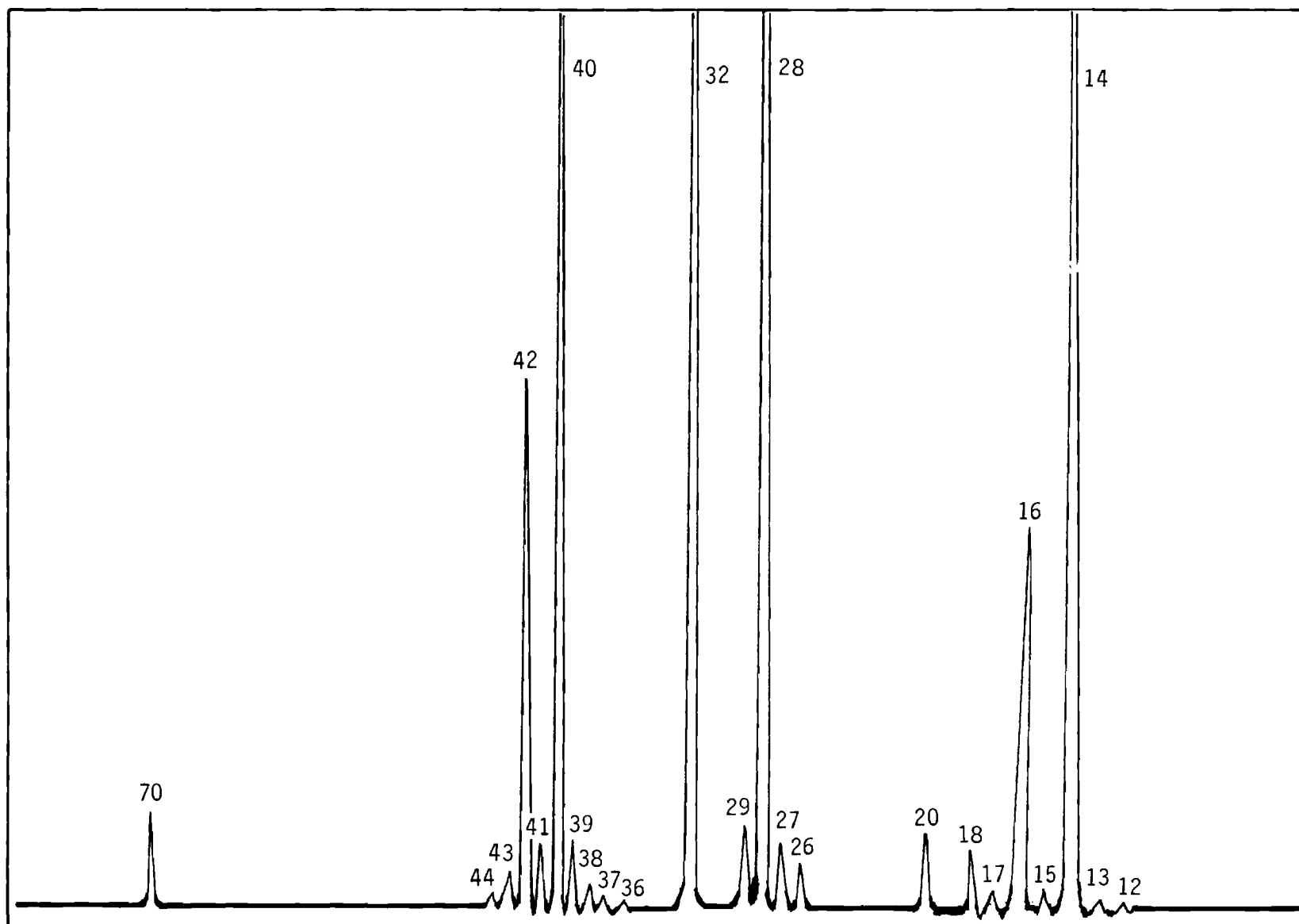


Figure 3. Mass spectrum of cyclobutanone with cryogenic inlet system at -75° and using 70 e.v. electrons.

Although $m/e = 28$ could not be determined accurately (air leak), the relative intensities of $m/e = 56, 42, 27$ and 26 agree well with the data of Schaafsma. This leads one to conclude that our heavy sample corresponds to cyclobutanone and resulted from further reaction of the lighter product, cyclopropanone. Cyclopropanone and cyclobutanone yield the same ions upon electron bombardment revealing their similar structure.

We have studied the effect of temperature on the stability of the lighter and heavy species by soaking isolated samples of each at various temperatures, following this by a quench and subsequent warmup and analysis. Cyclopropanone appears to be stable indefinitely at temperatures from -196° to -145° probably because it is a solid with a negligible vapor pressure. Some, if not all, of the cyclopropanone retained its identity after a one hour, -90° soaking. Although a one hour room temperature soaking revealed that cyclopropanone had been destroyed, no volatile reaction products were observed. A non-volatile, white, waxy substance soluble in acetone remained in the soaking trap which is in agreement with evidence^{19,20} that cyclopropanone reacts with itself to form a polymer. In view of these results, it is evident that cyclopropanone does not decompose, that, in fact, its ring may remain intact, but which, as a gas, is very reactive. Monel metal or glass surfaces did not effect the above results. Cyclobutanone retained its identity throughout all stability experiments.

Some preliminary ionization efficiency data are reported in Table V, and an example of the type of data obtained is shown in Figure 4 wherein the ionization potential of cyclopropanone appears to be 0.4 e. v. lower than that of cyclobutanone.

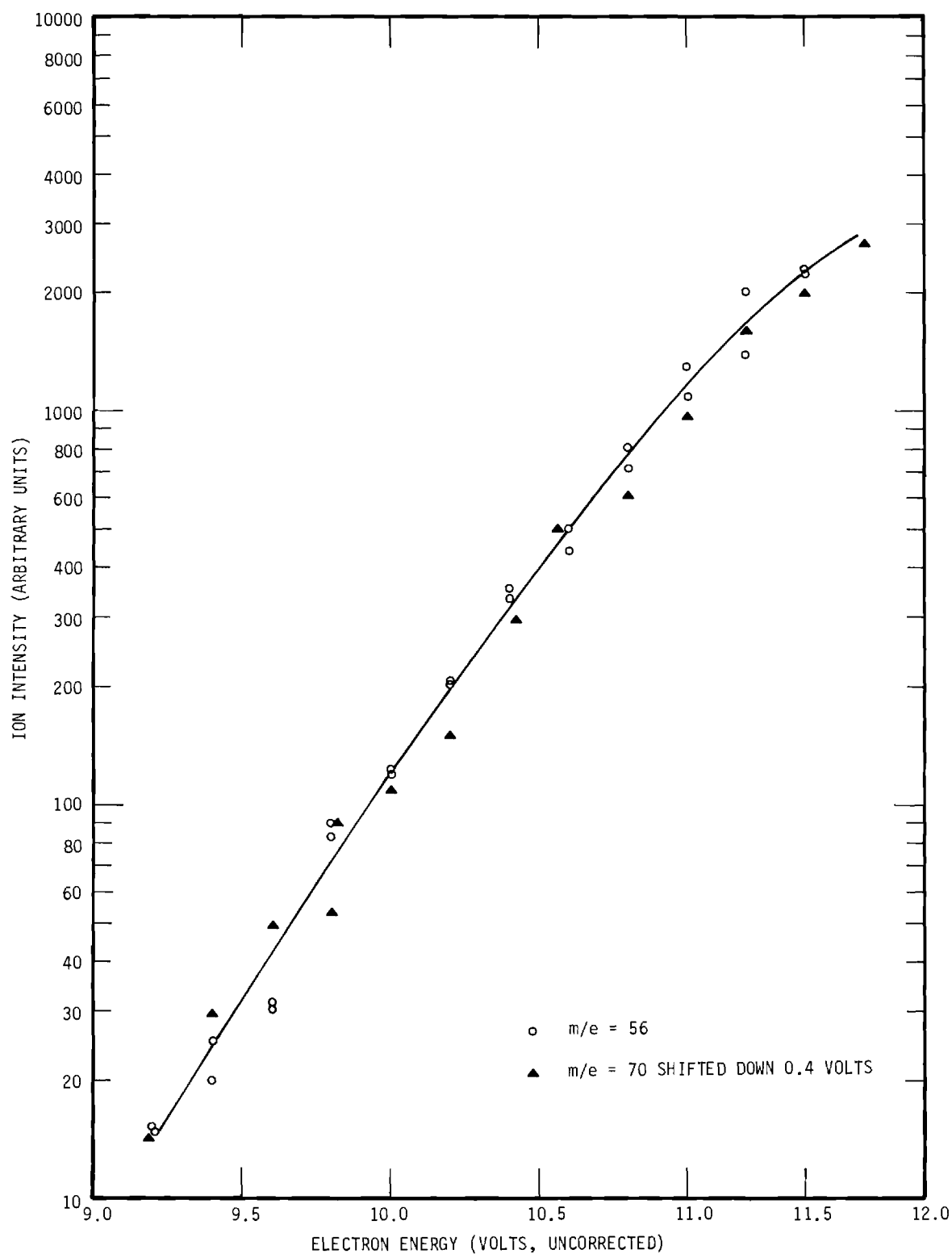


Figure 4. Semi-log plot of ionization efficiency data for ions m/e 56 and m/e 70. The data for m/e 70 have been shifted 0.4 e.v. indicating that the ionization energy of cyclopropanone is 0.4 e.v. less than the ionization energy of cyclobutanone.

TABLE V

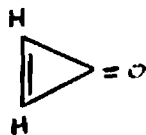
IONIZATION AND APPEARANCE POTENTIALS FROM
CRYOCHEMICAL SYNTHESIS EXPERIMENTS

Parent Compound	Fragment Ion Appearance Potentials (e.v.)			
	m/e 70	56	42	28
Cyclobutanone	9.7		11.0	
Product m/e = 70	9.6		11.2	10.2
Product m/e = 56		9.3	10.5	9.9

The incomplete separability by volatility of $m/e = 56$ and $m/e = 70$ proved troublesome in obtaining energetic data because even low ion intensities of the same m/e may be significant. In addition, both cyclopropanone and cyclobutanone exhibit observable peaks at $m/e = 40$, 32 , and 28 which interfere with three commonly used calibrating gases (argon, oxygen, and nitrogen). These experimental difficulties are being resolved. The energetics of cyclopropanone and cyclobutanone should prove to be challenging due to the added feature of the simultaneous cleavage of two bonds during fragmentation of the ring structure.

C. CYCLOPROPENONE

Cyclopropenone,



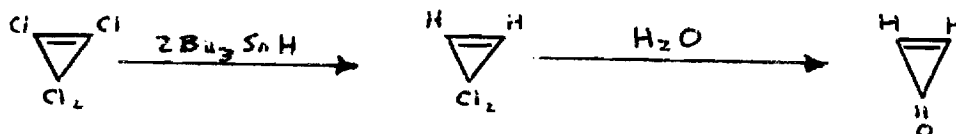
is a highly strained, small ring system that appears to possess considerable conjugative stabilization. Studies with the substituted molecule date from 1959, and compelling, but not absolutely conclusive, evidence for the synthesis of the parent ketone has appeared within the past few weeks.²³ The synthesis yields the ketone in aqueous solution, but attempts to isolate the substance, whether by removal of the solvent by distillation, or by vapor phase chromatography under a variety of conditions have so far failed. Cyclopropenone is lost by polymerization just as is true of the hydrogenated analog, cyclopropenone. However, the olefin appears to be more stable than the saturated compound.

Both of these ketones are interesting cryochemical systems. The cyclopropene is particularly interesting in view of the failure of standard techniques in attempts to isolate the substance. The cryochemical equipment and procedures that have been developed in this laboratory will be applied to the isolation, energetics, and reactivity questions that represent fundamental gaps in our understanding of this brand-new and exciting molecule. This comment and stated objective is in no way to diminish the creativity and originality of Dr. Breslow's work, but it is rather to suggest that the techniques of cryochemistry may well be the only way to effectively study this most interesting molecule.

²³ R. Breslow and G. Ryan, J. Am. Chem. Soc. 88, 3073 (1967).

It has seemed appropriate to briefly recapitulate the synthesis of cyclopropenone at this point.

Reaction of tetrachlorocyclopropene with two equivalents of tri-n-butyltin hydride at room temperature in paraffin oil produced a volatile mixture of mono-, di-, and tri-chlorocyclopropenes, one of which is 3,3-dichlorocyclopropene. This mixture of chlorinated isomers may, upon distillation, be separated and the desired 3,3 isomer may be absorbed in CCl_4 . Upon hydrolysis of this solution with cold water, the aqueous phase yields a single nmr signal at $\delta = 9.0$ (relative to tetramethylsilane) which may be assigned to the protons of cyclopropenone. This sequence of reactions may be represented schematically as follows:



The required tetrachlorocyclopropene may be easily synthesized from readily available materials in the following way:

A.²⁴ Trichloroethylene (2500 ml) and trichlorosodium acetate (1600 gm) may be mixed and stirred under reflux until dry. Then 750 ml of dry 1,2-dimethoxyethane are added to the flask whereon CO_2 evolution is immediate and the solution darkens. Reflux, accompanied by CO_2 evolution and darkening, continued at 80° for 2.5 days. Approximately 500 ml of a dark brown oil was then obtained from the crude reactant solution. The oil was distilled and the fraction boiling at 75° at 20 torr was a colorless, minty smelling oil, which was pure pentachlorocyclopropane. The above quantities yielded 390 gr. of product, or about 22% yield based on tri-chlorosodium acetate.

²⁴ S. W. Tobey and R. West, J. Am. Chem. Soc. 88, 2478 (1966).

B.²⁵ The pentachlorocyclopropane now needs only to be dehydrohalogenated (-HCl) to yield the desired tetrachlorocyclopropene. The cyclopropane derivative (50 gm) was added to 0.6 moles of KOH in 40 ml of water, and the reaction mixture was kept at 85-95° for 30 min. Upon cooling and acidification with HCl, the emulsion broke and about 25 ml of an oily layer was separated off. Simple distillation of this oil under nitrogen at 129-133° provided about 33 gms of clear, colorless tetrachlorocyclopropene.

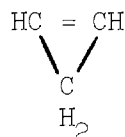
The above syntheses, A and B, have been taken directly from references (24) and (25). The amounts of reagents used in typical runs are also taken from references (24) and (25) and are included to give an idea of the scale of these chemical operations and the yields of product.

²⁵ S. W. Tobey and R. West, ibid. 88, 2481 (1966).

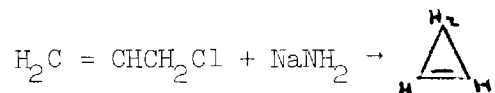
D. OTHER SPECIES OF INTEREST

Several other compounds are of immediate interest in this research program, but progress on the study of these substances does not warrant more than a passing notation of this time.

1. Cyclopropene



This compound is indefinitely stable at 77°K but it slowly polymerizes at dry ice temperature (-78°).²⁶ We have synthesized this molecule by the reaction of allyl chloride with sodium amide,



under conditions where the unstable cyclopropene can readily escape from the reaction mixture and be immediately trapped at 77°K.²⁷ The apparatus consisted of a three-neck flask heated by a water bath and equipped with a magnetic stirrer. The flask was fitted with an addition funnel, a nitrogen purge-gas inlet capillary, and a jacketed condenser filled with glass helixes and cooled by circulating ice water. The product coming through the column was washed in 2 N sulphuric acid and trapped at 77°K. A pump was connected to this final trap through a drying tube, and in operation the entire system was operated at about 5 in. Hg vacuum. The flask was charged with 12 gm of NaNH₂ in 20 ml of mineral oil and was heated to 75°. To this stirred suspension was added dropwise 23 gm of

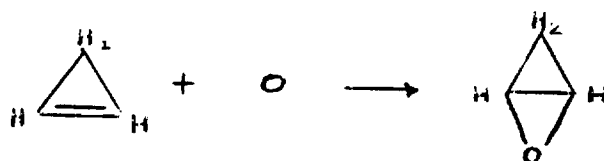
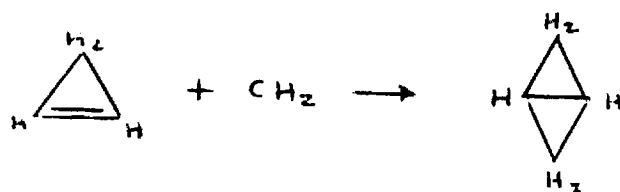
²⁶ K. B. Wiberg and W. J. Bartley, J. Am. Chem. Soc. **82**, 6375 (1960).

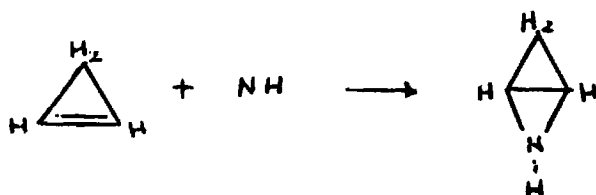
²⁷ G. L. Closs and K. D. Krantz, J. Org. Chem. **31**, 638 (1966).

allyl chloride diluted with 15 ml of mineral oil. The gaseous product was evolved from the reaction mixture, but persistent frothing was a problem. The entrapment of the product in this froth will delay its transport to the 77°K trap to such an extent that the highly reactive product may be lost by polymerization before it ever leaves the reaction flask. The froth was minimized by directing a stream of cold air over the top of the flask not immersed in the hot water bath. The addition of the allyl chloride took 2 to 4 hours and the reaction flask was maintained at 75° for an additional 2 hours while a slow nitrogen gas purge was passed through the entire apparatus. The final product may be purified by simple distillation.

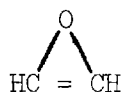
The energetics of cyclopropene are being developed for correlation and comparison with that of cyclopropenone and cyclopropanone.

Addition reactions at low temperatures could lead to interesting products, e.g.,





2. Oxirene



The status of this synthesis is about as described earlier¹⁶ wherein a series of experiments were conducted in which atomic oxygen from a resonant rf discharge was contacted with acetylene in a reactor immersed in liquid oxygen (90°K). This low pressure gas phase reaction was accompanied by a blue-green chemiluminescent flame, yielded a yellow-red solid deposit on the cold walls of the reactor, and underwent both color change and effervescent behavior on warm-up. Only CO_2 , $(\text{CHO})_2$, O_2 , HCOOH and H_2O were observed during the warm-up of the composite solid product. A point of some note was the absence of ketene in the product mixture, for ketene was formed at 20°K by the reaction of photo-lytically produced ground state ^3P oxygen atoms (from N_2O) with C_2H_2 in a solid matrix of argon.²⁸ The failure to observe ketene in our experiment must have been due to the inefficiency of the quenching process. This reaction would be exothermic by 127 kcal/mole.

²⁸ I. Haller and G. C. Pimentel, J. Am. Chem. Soc. 84, 2855 (1962).

One would expect oxirene to be formed by the addition of an excited ^1D oxygen atom across the triple bond of acetylene. Recent attempts to identify oxirene from room temperature experiments have failed,^{29,30} but with good quenching it should be possible to isolate this very interesting product molecule. Good quenching is even more crucial here than was true for ketene since the ^1D atom is 45 kcal above the ground state ^3P atom. Whereas the earlier experiments involved a quenched low pressure diffusion flame, the more severe quenching requirements have led to an apparatus which permits a mixture of $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ atoms to be bubbled through either liquid acetylene or through a solution of acetylene in any one of several cryosolvents.

3. Vinyl Alcohol



This compound has never been observed, although it is frequently postulated as a reaction intermediate.³¹ This molecule apparently undergoes a facile rearrangement to acetaldehyde. We are studying the synthesis of this compound by the reaction of excited atomic oxygen (^1D) with ethylene wherein we expect the oxygen atom to merely insert in the C-H bond. The ground state atom is expected to abstract a hydrogen atom giving the two radicals OH and C_2H_3 , both of which would be expected to react further in a complex manner.

²⁹ R. N. McDonald and P. A. Schwab, J. Am. Chem. Soc. **86**, 4866 (1964).

³⁰ J. K. Stille and D. S. Whitehurst, J. Am. Chem. Soc. **86**, 4871 (1964).

³¹ J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry", Benjamin, Inc., New York, N. Y., 1965.

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Fourth Semi-Annual Report
Project B-509

CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN
ATOMS AT TEMPERATURES BELOW 100°K

by
Henry A. McGee, Jr.

NASA Grant NsG-337 (Supplement No. 1)

Performed for
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PREFACE

This report covers work performed from July 1, 1967 to December 31, 1967 under NASA grant NsG-337 (Supplement No. 1). Other than the principal investigator, people working on this program during this reporting period have included: two predoctoral students, Mr. R. J. Holt and Mr. P. H. Li, and one masters student, Mr. M. A. Bell. The work of each of these students, which has been fully supported by this grant, will also function in its entirety as fulfilling the research requirements for their respective degrees. Mr. Bell has completed his degree requirements, and copies of his thesis will be forwarded to NASA within the very near future.

The total cryochemistry research program presently involves more predoctoral and postdoctoral research students than are working in the remainder of our Department combined. Our graduates with backgrounds in physical chemistry, chemical engineering and research in cryochemistry continue to receive salary offers in the national upper 10 percent for all new Ph.D.'s in science and engineering.

I. INTRODUCTION

This research program is concerned with the development of chemical information at cryogenic temperatures, particularly on systems that astronomers and astrophysicists feel are important in comets and in the atmospheric and surface chemistry of the Jovian planets. Each of these astronomical objects is very cold, and clearly insofar as chemistry plays a role in the phenomenology of these objects, this chemistry must be occurring at very low temperatures by terrestrial standards. This objective rather quickly resolves itself into studies of low molecular weight compounds of the four reactive elements of maximum cosmic abundance, namely hydrogen, carbon, nitrogen and oxygen.

The approach here is not one of free radical stabilization or of an attempt to isolate labile species in an inert matrix at very low temperatures. All evidence to date suggests that the activation energy for the reaction of low molecular weight free radicals is zero (or close to it), and hence it will be possible to prepare these species in "stable" forms only by diffusional inhibition techniques such as inert matrix isolation. The concentrations of such labile species that have been prepared are then limited to usually a few tenths of a percent, and hence the importance of matrix isolated free radicals in cosmic chemistry would seem to be minimal. The matrix technique, particularly when combined with ir or epr, does, of course, provide a powerful means to study the physical and chemical properties of free radicals. By contrast, low molecular weight labile species which have singlet electronic ground states, i.e., species that are highly reactive but are not free radicals, are in an altogether different category. Typical species of this class are substances like cyclobutadiene, cyclopropanone, oxirene, diimide, ammonium ozonide, benzyne, tetrahydro, and many others. This serves to indicate the kind of molecule that is being discussed. One would expect these species to exhibit an activation energy for reaction, but we would also expect this energy to be unusually small. If an activation energy exists, then substances such as these may be preparable as stable cryochemical reagents and a true chemistry at very low temperatures may be developed. Since the activation energies involved in these systems is small, it will usually be necessary to maintain the compounds below some critical temperature if they are to be manipulated as stable, pure reagents. This means that manipulative techniques must be developed for use

with unstable substances at cryogenic temperatures. Ideally, one would like to transpose all of the common or usual operations of bench scale chemistry to the point of convenient use at cryogenic temperatures. The most important operation in any chemical investigation is analysis. In past reports on this grant and its precursor, NsG-337, the development of a cryogenically cooled reactor-inlet system attachment to a time-of-flight mass spectrometer has been described in detail. The cryogenic mass spectrometer continues to be the key analytical tool in our approach to low temperature chemistry, and there are presently three such instruments in use in this laboratory.

II. APPARATUS AND TECHNIQUE

A. Blanking Circuit

To increase the time interval between necessary cleanings of the electron multiplier assembly of the Bendix spectrometers, a circuit designed by Mr. J. Haumman* for Dr. Martin Studier of Argonne National Laboratory has been built and added to one of our machines. This device, known as a predynode gating circuit, allows all but a small part of the ion beam to be blanked out before it reaches the electron multiplier plates in the analyzer. This in effect decreases the number of electrons passing through the multiplier and thus increases the time interval between cleanings.

In the analyzer assembly of the spectrometer, the ion beam impinges on cathode 1 causing the emission of electrons which are attracted to cathode 2 at a more positive voltage bias and then to the Z-plate and into the multiplier section. The circuit designed by Haumman holds cathode 2 and the Z-plate at the same negative potential except for a short interval of time during which cathode 2 is pulsed about 300 V more negative than the Z-plate. While the two are at the same potential, no electrons pass into the multiplier. The pulse width is variable from 1 microsecond up to a time greater than that required for a full mass scan of 10 microseconds. This pulse circuit is triggered by the gate pulse from one of the analyzers in the spectrometer, and can be

*We acknowledge the kindness of Mr. Haumman in supplying us with circuit diagrams and comments which permitted us to construct this very useful device.

positioned to look at any segment of the mass scan by varying the location of this gate pulse.

This circuit will obviously not isolate single mass peaks which are of 50 nanosecond duration or less, but it is useful where a great variety of ions are produced which would quickly lead to contamination of the electron multiplier. Ion peaks may also be foreshortened by a large preceding peak due to the depletion of electrons on the multiplier glasses by large electron currents. The ability to blank out these large peaks now obviates this difficulty.

B. Automatic Ionization Efficiency Measurements

Ionization efficiency data, as they have been collected in this laboratory in the past, involve a rather tedious process usually taking one half hour or more to complete one set of measurements. To reduce the time involved in making these measurements, a circuit has been added to one of our spectrometers which can vary the electron energy bias automatically over either of three voltage ranges. The ion current is used to drive one axis of an X-Y recorder and the electron energy bias drives the other, yielding a direct and reasonably rapid plot of the ionization efficiency curve. These on-line or real-time evaluations of appearance potentials permit the utilization of the energy measurement as a control during the course of an experiment. This then is a highly useful development.

The power supply for this circuit consists of a 6.3 V filament transformer with full wave rectification and capacitor filtering. The three voltage ranges are obtained by using three zener diodes, which in operation have voltage drops of 2.4, 3.9 and 6.0 volts across them. The voltage across the selected zener is placed across a 38 step precision voltage divider. The voltage divider is tapped by a unidirectional stepping relay, which may be stepped manually or automatically by a microswitch driven by a cam on a variable speed motor. The motor allows the entire voltage range to be swept in times ranging from 40 seconds to 4 minutes. The voltage that appears on the output of the stepping relay can be added to or subtracted from the electron energy bias, thus allowing the electron energy to be increased or decreased in 38 equal steps spanning the voltage range chosen.

The ion current is taken directly from the Bendix analyzer and fed into the Y-axis of a Moseley Model 700LAR X-Y recorder. The X-axis is driven by either the short voltage range produced from the above circuit or by the total electron energy bias, depending on which is the most convenient. Thus it is possible to automatically measure the ion current as a function of electron energy in an interval of time less than 5 minutes.

One complication that arises concerns the manipulation of the control grid bias to maintain a constant electron beam current during an entire sweep. Due to the manner in which the stepped voltage is introduced into the circuitry, it has become necessary to manually control the grid bias while a sweep is being made. This does not slow down the rate at which an ionization efficiency curve can be recorded, however, and this device now aids considerably in the collection of ionization efficiency data.

C. Derivatives of Ionization Efficiency Curves

In many of the studies done on ion production by electron impact, it has been experimentally determined that near the threshold energy the density of ions produced for a constant electron flux obeys a very simple rule. It appears that the number of ions produced is directly proportional to the excess electron energy above some critical onset level. In cases where this rule holds, the first derivative of the ion beam as a function of the electron energy would exhibit a step at the onset potential, and be zero below this and a constant value above. The second derivative would display a sharp infinitely high peak at the onset potential. Since real systems are involved, and the energy of the electron beam exhibits approximately a Maxwellian spread with a half width in the vicinity of 0.5 eV unless care has been taken to narrow it, the curve representing the ion current as a function of electron energy is not a sharp breaking curve consisting of two straight segments, and consequently the curves representing the derivatives are not as well defined as mentioned above. However, in many cases the first derivative does exhibit what is nearly a step function, and a peak corresponding to the inverse of the electron beam energy distribution appears at the threshold energy.

This threshold law does not hold rigidly for all cases, and is complicated by many factors even where it does seem to dominate, but it does provide another way to look at ionization efficiency data which may be useful in many cases.

Based on the above general background an attempt was made to experimentally obtain the curves representing the first and second derivatives of the ion current with respect to the ionizing electron energy. The attempt was based on an apparatus used by Morrison,¹ and depends on the fine structure triode characteristics that were discussed by Van Der Pol and Weijers.²

According to studies made on triodes, when a low level sinusoidal voltage is placed on the grid, the response in the anode current is not strictly sinusoidal. The current that does appear at the anode carries harmonics of the grid frequency, and in the limit of a very low amplitude applied to the grid, the harmonics approach the derivatives of the anode current with respect to the level of the D.C. grid bias. The second harmonic corresponds to the second derivative and the first corresponds to the first derivative. If one assumes that the electron source in a mass spectrometer is roughly analogous to a triode and that no complications occur in the ionization process, varying the voltage on the grid that controls the electron energy with a small sinusoidal voltage should produce variations in the ion current produced by the electron beam, and monitoring the fundamental frequency of the sinusoidal input should yield an amplitude proportional to the first derivative of the ion current with respect to the ionizing energy while the amplitude of the second harmonic should yield the second derivative.

To do this experiment an audio frequency generator was used to produce the sinusoidal voltage used to vary the electron energy, and the output from the ion current analyzer was used to drive a Princeton Applied Research Company model JB-5 lock-in amplifier. To detect the second harmonic the fundamental sine wave was passed through a full-wave rectifier and the resulting wave form was filtered by the lock-in amplifier to provide the necessary second harmonic reference signal. The output from the lock-in amplifier was used to drive the Y-axis of a Moseley 7001AR X-Y recorder, and the D.C. bias on the electron energy grid drove the X-axis.

The results obtained using this apparatus in conjunction with the Bendix Model 14 TOF instrument were not satisfactory. The system for producing an

1. J. D. Morrison, J. Chem. Phys. 21, 2090 (1953)

2. B. Van Der Pol and T. J. Weijers, Physica 1, 481 (1933-34)

electron beam in the Bendix instrument is evidently not analogous to a triode, both because of geometry and because of the method by which the beam is pulsed during normal operation. When looking for the first derivative a signal was observed that very crudely resembled a step function. However, the step took place over 3-4 eV in the neighborhood of the threshold. When looking for the second derivative only noise was observed, and this increased in amplitude as the threshold was passed, but was probably due to noise generated in the electron multiplier-electrometer circuitry.

It is thus apparent that the Bendix machine is not going to lend itself readily to measurements of this type. The reason that anything was observed when looking for the first derivative seems easy to explain. In applying a sinusoidal voltage to the electron energy bias one creates approximately sinusoidal fluctuations in the ion current, especially in the limit of a very low amplitude for the applied voltage. The amplitude of the ion current fluctuations can be called ΔI for the constant peak-to-peak voltage difference ΔE . Varying the D.C. bias on the electron energy, and monitoring the amplitude of the first harmonic will yield ΔI , and since ΔE is constant $\Delta I/\Delta E$ is proportional to ΔI . In the limit of small amplitudes $\Delta I/\Delta E$ approaches the derivative dI/dE . This rather simple approach does not predict a second derivative proportional to the second harmonic.

There is a slight possibility that this approach would work if the electron beam were run continuously and the electron energy controlled by the control grid bias. This could be accomplished by raising the electron energy bias to ground or nearly ground and running the control grid above ground. The electron optics of such a system would be in question, as well as the difficulties involving a continuous electron beam in a pulsed system. To attempt this experiment would require some rather extensive modifications of the Bendix circuits, and to date no attempt has been made to do this.

D. Application of Second Derivative Technique

Notwithstanding the above described lack of success with instrumentation designed to automatically plot the second derivative of the ionization efficiency curve, we have successfully used the method in more manual graphical manipulations with raw ion intensity vs. electron energy data.

Let us recall the essential ingredients of Morrison's second derivative method. Over the whole range of ionizing electron energies, the ionization probability $p(E)$ for normal transitions to a single level is some function of energy such that its second differential has a low value except at the ionization potential V_c where it gives a sharp peak. The maximum at V_c will not be infinitely sharp, but will possess a natural width, and the area under it can be shown to be proportional to transition probability for the process involved. An actual ionization efficiency curve is made up by the linear superposition of the ionization probabilities for each energy state of the ion. If the further assumption is now made that the separate values of $p(E)$ for transitions to all possible states are additive, the presence of each of these processes will obviously be shown by peaks in the second derivative ionization efficiency curve.

The second derivative ionization efficiency curve has been readily obtained in this laboratory using an analog computer. The measured ionization efficiency curve was regenerated by a function generator and the second derivative of the function was then obtained by an analog computation technique.

The ionization efficiency curve for BH_3^+ from BH_3 obtained in this laboratory³ has been reinterpreted by Morrison's method. The second derivative of the ionization efficiency curve for BH_3^+ from BH_3 and the corresponding curve for argon are shown in Figures 1 and 2. The large peak in Figure 1 at $E = 12.125$ eV (uncorrected) can be interpreted as corresponding to the vertical ionization potential of BH_3 and the smaller peak at $E = 11.83$ eV (uncorrected) as corresponding to the adiabatic ionization potential of BH_3 . The energy scale has been corrected by using the second derivative ionization efficiency curve for argon, Figure 2, which gives a large peak at $E = 16.26$ eV (uncorrected) corresponding to the appearance potential of Ar^+ . Therefore, we may argue that the correct value of the vertical ionization potential of BH_3 is $I(BH_3) = 12.125 - (16.26 - 15.76) = 11.625$ eV and that of the adiabatic ionization potential is $I(BH_3) = 11.83 - (16.26 - 15.76) = 11.33$ eV. The peak in Figure 1 at $E = 12.32 - (16.26 - 15.76) = 11.82$ eV very probably corresponds to the formation of BH_3^+ in its first vibrationally excited level.

3. J. H. Wilson and H. A. McGee, Jr., J. Chem. Phys. 46, 1444 (1967)

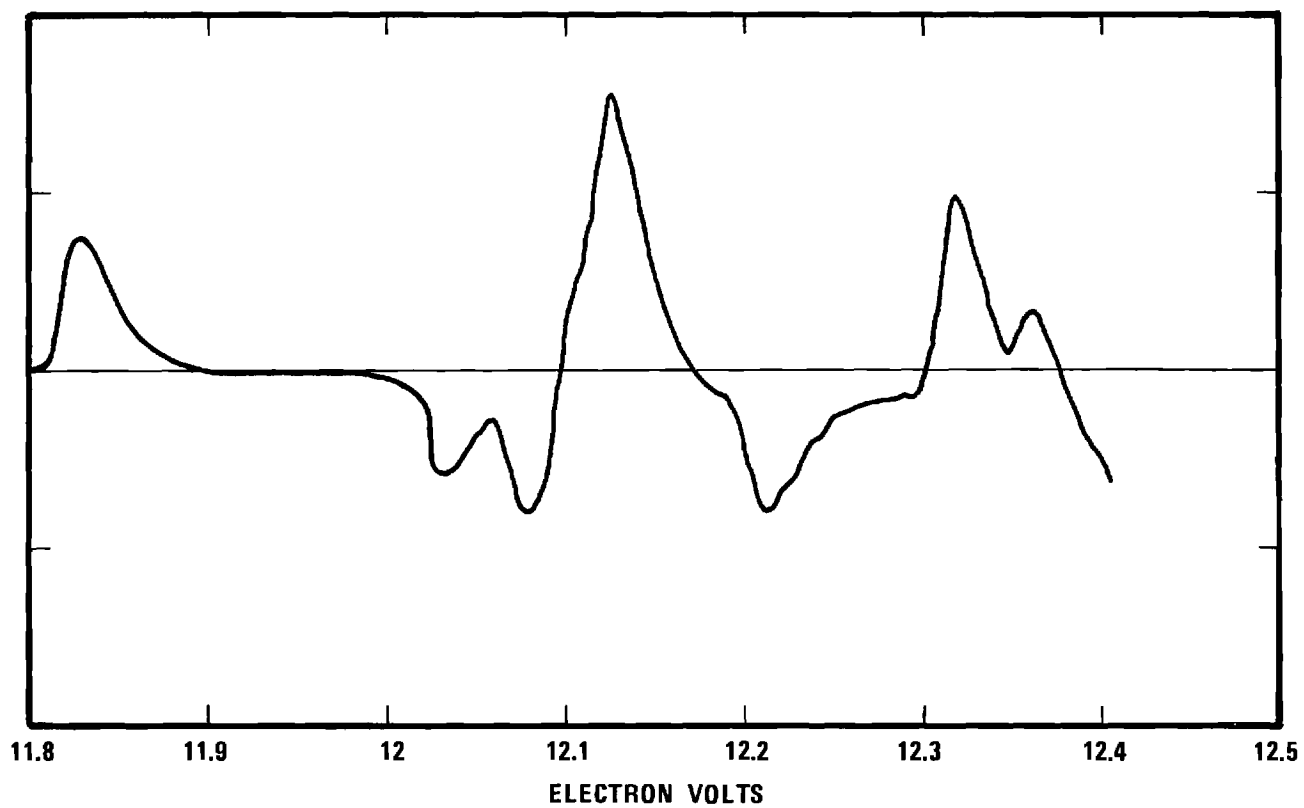


Figure 1. Second derivative of ionization efficiency data of Wilson and McGee (3) for the determination of $I(\text{BH}_3)$.

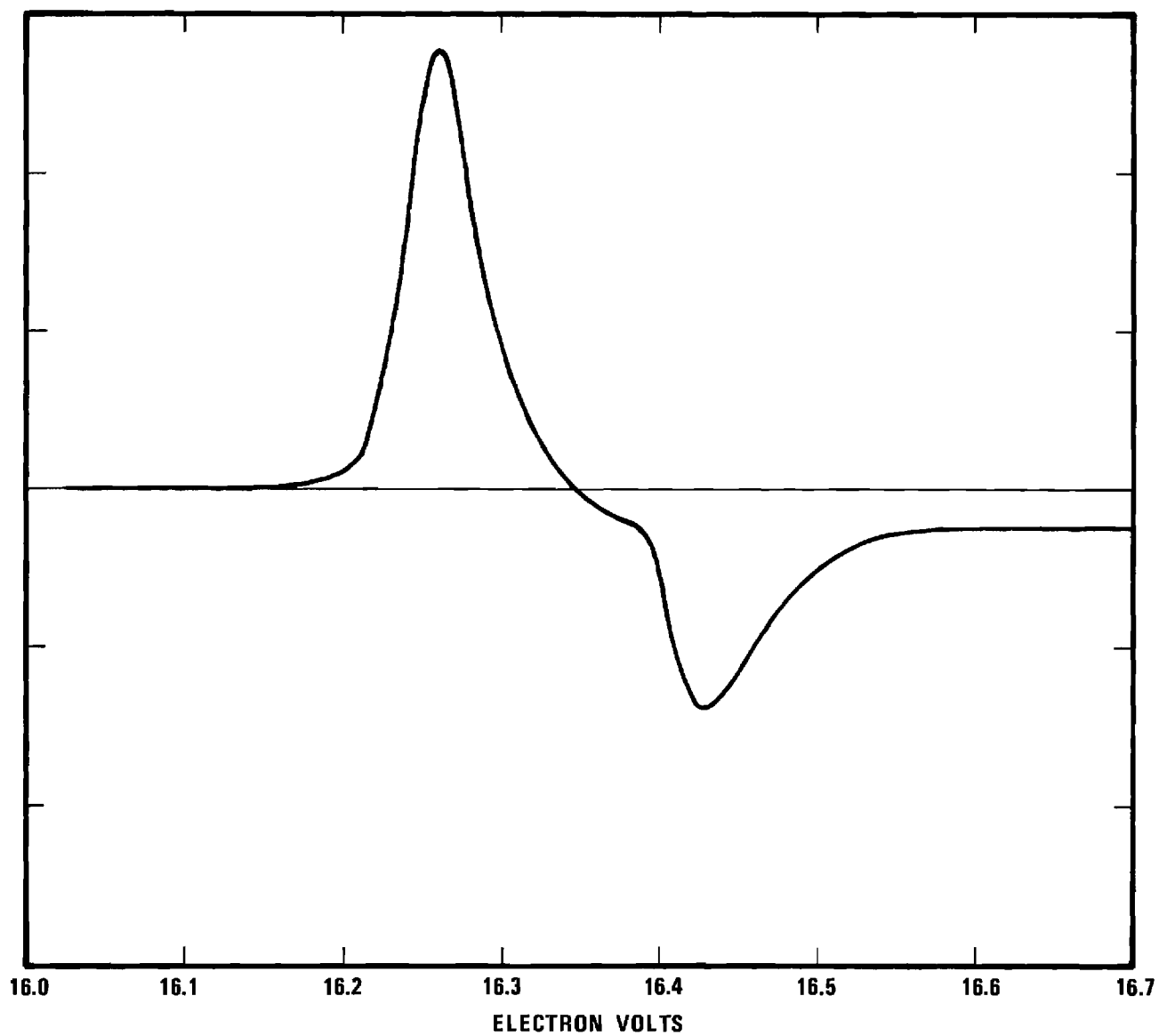


Figure 2. Second derivative of ionization efficiency data of Wilson and McGee (3) on Ar^+ used to calibrate the energy scale.

Although these interpretations of the data on $I(BH_3^+)$ are not absolutely unequivocal for a variety of reasons, the above argument does serve to illustrate the method. We are exploring further its utility in cryochemistry.

E. Electric Arc and Exploding Wire Apparatus

The apparatus described below is part of a study on various methods of energy input into low temperature systems. Since most chemical reactions proceed very slowly - or not at all - at cryogenic temperatures it is necessary to provide a certain activation energy. The products formed in such reactions will usually exist in equilibrium only at high temperatures, and it is important to quench them as rapidly as possible to such a low temperature that the reaction rate decreases to virtually zero ("frozen equilibrium"). Two promising ways to achieve this goal are electric arcs and exploding wires in a low temperature environment, especially submerged in a liquid cryogenic environment, like liquid nitrogen.

1. Submerged Electric Arc. The energy source for the arc is a DC power supply which delivers about 1/2 amp. at a voltage that can be varied continuously from 0 to 3000 V. DC rather than AC was chosen because test experiments showed that the DC arc is more stable and attains higher temperatures at less power input. Also, in a DC arc the anode gets considerably hotter than the cathode and consequently evaporates much faster (which is important if dissimilar electrodes are used). The current is limited by a power resistor of 3000 or 15,000 ohms. Since the resistance of the burning arc is comparatively small the actual voltage across the electrodes is usually only 30 to 60 V. The high voltage source is required to stabilize the arc which otherwise could easily be quenched by the surrounding liquid.

Three different arrangements are of practical interest for chemical reactions:

a. One or both of the electrodes participate in the reaction; the surrounding liquid is inert. Test runs have been made with graphite electrodes and with various alkali metals (Li, Na, K). In the latter case, the anode consists of a graphite crucible filled with the alkali metal; the cathode is a tungsten welding electrode which burns off very slowly. The liquid used in the test runs was liquid nitrogen, but it could be readily replaced by argon or another noble "gas" to ensure chemical inertness.

b. The electrodes are inert and surrounded by the reactants. For instance, an argon-fluorine compound might be produced by an electric arc burning in a mixture of liquid argon and liquid fluorine.

c. Both the electrodes and the surrounding liquid participate in the reaction. In one of the test runs, an arc was run between graphite electrodes under liquid nitrogen. In this case the formation of carbon-nitrogen compounds like cyanogen (C_2N_2) is expected.

2. Exploding Wires. In this experiment a capacitor bank is discharged through a thin wire. The heat evolved by the exceedingly high current vaporizes the wire in less than a millisecond; temperatures of up to 10^5 °K can be reached. In our apparatus, the energy is stored in five capacitors with a total capacity of 32 μ F. The circuit can be closed by a spark gap switch which is triggered by an automobile ignition coil. Details may be found in the attached circuit diagram (Figure 3).

Test runs were made with wires of various metals and graphite thread. All metal wires could be vaporized completely; the graphite thread, however, consists of thin fibers and has therefore a tendency to disintegrate rather than to vaporize. Only at high energies (250 J corresponding to 4000 V) was it possible to vaporize most of the carbon. Whereas the explosions in air produced a loud noise, there was no sound at all when the wire was immersed in water or liquid nitrogen. There is a shock wave, however, which may shatter the reaction vessel. The idea of an all-glass reactor was therefore abandoned. Currently an all-metal reactor is being constructed. Since the reactor has to be vacuum tight and most ordinary seals fail at cryogenic temperatures, the top demountable seal of the vessel will be soldered together with Wood's metal to allow easy disassembling.

We have also designed and fabricated a multiple array of exploding wires such that eight wires may in turn be exploded in the same reactant mixture. This arrangement, of course, will yield exactly eight times the amount of product as is obtained from the earlier single-shot devices.

The experiments to be done with the exploding wire apparatus are similar to those involving the electric arc. The arc is easier to handle experimentally; on the other hand, the exploding wire technique seems especially promising for the production of unusual compounds since very high temperatures can be reached and the following quench is exceedingly rapid.

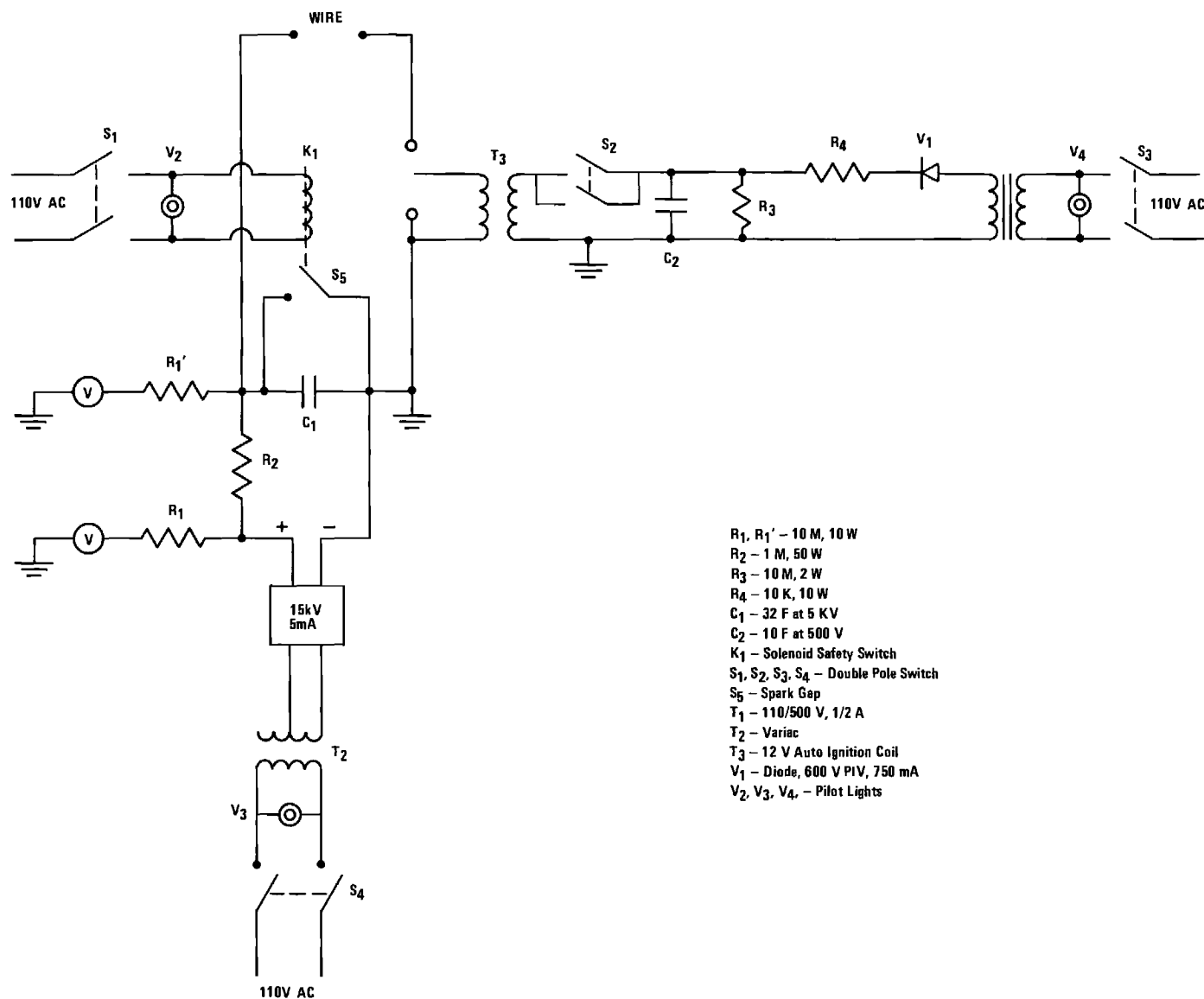


Figure 3. Diagram of power supply and triggering circuitry for exploding wire apparatus.

III. RESEARCH

Some of the most interesting problems in astrochemistry, particularly as regards cometary phenomena, are concerned with the types of compounds and reactions that occur under environmental conditions that are very extreme by terrestrial standards. Spectral observations prove the presence of CN, C₃, NH₂, C₂, OH, NH, and CH in comet heads. The parent compounds from which these species originate may be only conjectured, but in view of the very low temperature of the comet it seems clear that unusual and highly reactive parent species may well be present. Consequently, an important phase of this NASA program is the synthesis, reactivity, structure and energetics of principally C - H and N - H compounds that are of low molecular weight, are highly reactive, and which may exist only at very low temperatures. However, as long as these species are kept cold, they may be distilled, purified, reacted, etc. just as would any normal reagent at more ordinary temperatures.

Several studies in this low temperature, preparative chemistry are being pursued, and the progress on each is categorized below with respect to the particular sought-for product molecule.

For a long time it has been evident that the large body of knowledge in chemical theory has a particularly strong relevance to our experimental program in chemical synthesis, reactivity and energetics of unusual molecules at cryogenic temperatures. We have begun a completely application oriented theoretical program in molecular orbital calculations with the anticipation of enhanced interpretative, predictive and correlative inputs to the cryochemical experiments.

A. CYCLOBUTADIENE

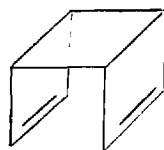
Cyclobutadiene is a cyclic and highly reactive dimer of acetylene. It has never been isolated, although it has been frequently discussed by organic chemists for many years. Acetylene is a postulated cometary constituent, and if this be true, then it seems entirely reasonable that the dimer, C_4H_4 , might also be present in icy cometary nuclei. Cyclobutadiene seems sure to exhibit interesting chemistry, the relevancy of which to cometary phenomena could be significant. Thus, it has seemed reasonable to explore (1) the synthesis, (2) proof of existence, (3) isolation, (4) energetics, and (5) the most simple reactivity of cyclobutadiene using the techniques of cryochemistry. It has further turned out, perhaps fortuitously, but none the less interestingly, that the only promising route to cyclobutadiene involves a newly synthesized parent substance in which the hydrocarbon is complexed with iron tricarbonyl. Now iron is also apparent in comet spectra at approximately 0.01 AU, and it is conceivable that this iron is present in the icy cometary nuclei as a complex with some highly reactive, unstable hydrocarbon such as cyclobutadiene. Nickel also forms similar highly reactive and volatile hydrocarbon and carbonyl complexes. It appears then, that both the parent molecule as well as the free hydrocarbon ligand could be of interest in cometary chemistry considerations. Molecules of cyclobutadiene with iron as well as the other transition metals may exist at low temperatures in configurations analogous to dibenzyl iron or ferrocene.

In previous reports we have discussed the preparation of the only known precursor of cyclobutadiene, cyclobutadieneirontricarbonyl (CIT), and we have discussed the structure, mass spectrum and ionization potential of this interesting iron complex. We have discussed the oxidation of CIT in ether solution by Ce^{IV} in still equivocal experiments designed to stabilize cyclobutadiene by using a hard cryogenic quench. We have discussed the pyrolysis of CIT to yield free cyclobutadiene, and from ionization efficiency measurements on these pyrolysis products, we have reported still somewhat rudimentary molecular energetic data on the compound.

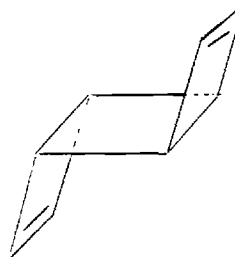
Most recently, we have been concerned with the dimerization of cyclobutadiene. Dimers of cyclobutadiene (C_8H_8) have been obtained by Nenitzescu⁴

4. M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, Ber. 97, 382 (1964)

and classified as syn-tricyclo [4.2.0.0^{2,5}] octa-3,7-diene (I) and anti-tricyclo [4.2.0.0^{2,5}] octa-3,7-diene (II).



I



II

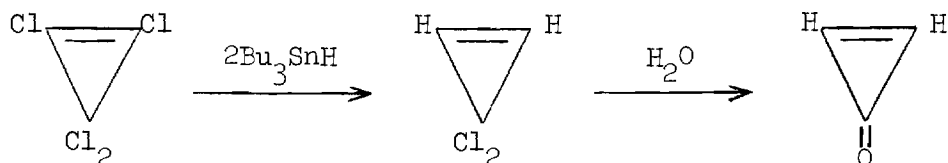
The formation of the syn dimer (I) by treating cis-3,4-dichlorocyclobutene with sodium amalgam in ether is postulated as occurring via the dimerization of free cyclobutadiene. Oxidation of CIT in Ce^{IV} solution also produced a 5:1 ratio of the syn and anti dimers of cyclobutadiene.⁵ Since CIT is obtained from the reaction of cis-3,4-dichlorocyclobutene and iron enneacarbonyl with less than 50 percent yield, we have decided to attempt to stabilize cyclobutadiene from the direct dehalogenation of cis-3,4-dichlorocyclobutene.

In order to avoid the possibility of dimerization of cyclobutadiene in the presence of air, nitrogen gas is bubbled through the reaction mixture. The apparatus is attached to the cryogenic inlet system and the product of the reaction is quenched at -180° to -196°C . After $2\frac{1}{2}$ hours of reaction, the product was observed mass spectrometrically at -196°C , and we failed to observe free cyclobutadiene. Instead, ether is the largest contributor to the spectrum while cis-3,4-dichlorocyclobutene and the dimer of cyclobutadiene make small and about equal contributions. In Nenitzescu's experiments, dehalogenation of cis-3,4-dichlorocyclobutene for 40 hours led to a 65 percent yield of dimer. Therefore, only a small amount of free cyclobutadiene (assuming this is formed as an intermediate) will be present at any one time. With such large amounts of ether and small amounts of free cyclobutadiene it will be difficult to adequately study cyclobutadiene in the mass spectrometer.

We are investigating the dehalogenation reaction of cis-3,4-dichlorocyclobutene both (1) directly without using ether as a solvent, and (2) in

5. L. Watts, J. D. Fitzpatrick and R. Pettit, J. Am. Chem. Soc. **88**, 623 (1966)

The original apparent synthesis by Breslow and Ryan of cyclopropenone consisted of the reaction of tetrachlorocyclopropene with two equivalents of tri-n-butyltin hydride at room temperature in paraffin oil to produce a volatile mixture of mono-, di-, and tri-chlorocyclopropenes. This mixture of chlorinated products is taken up in CCl_4 , then hydrolyzed with cold water to give an aqueous phase solution of the cyclopropenone. This sequence of reactions is as follows:



As is discussed in detail in the last report,⁷ tetrachlorocyclopropene is made from the dehydrohalogenation reaction of KOH with pentachlorocyclopropane, which, in turn, is synthesized from trichloroethylene and trichlorosodium acetate. The Bu_3SnH is obtained from the reaction of Bu_3SnCl and LiAlH_4 .

Our first attempt to reproduce this original synthesis was proved successful when both the dichlorocyclopropene and cyclopropenone were identified by nmr analysis. This preparation was done on a small scale and the purity was quite poor. We then completed a large scale preparation of the tetrachlorocyclopropene and tri-n-butyltin hydride which proved to be the most convenient stopping place before the final preparation of the ketone. By utilization of mass spectrometric and infrared analysis we were able to better control the preparations, and we obtained improved yields and much higher purity than in the first attempt. Tetrachlorocyclopropene can be kept indefinitely at room temperature. Bu_3SnH will react with air but it can be kept under argon sealed from air at room temperature. Dichlorocyclopropene, on the other hand, is itself a cryochemical which must be kept below -70° or it is lost by polymerization. At room temperature, dichlorocyclopropene, within seconds, will begin to turn from a clear white liquid to yellow, and then steadily darken to a deep brown. As a result of this preparation we have in hand enough reagents to produce 15 grams of the dichlorocyclopropene.

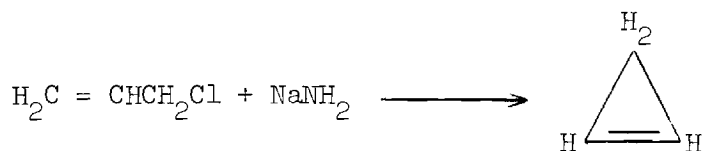
The original preparation of cyclopropenone resulted in a water solution. Trying to separate this solution by slowly warming from -196° to room temperature under vacuum and immediate analysis by the mass spectrometer proved unsuccessful. A dominant peak at $m/e = 19$ (H_3O^+) suggested that cyclopropenone might have hydrolyzed to acrylic acid as it is known to do.⁶ Also, to vaporize the solvent water, the solution must be heated to a temperature at which the ketone would rapidly polymerize. Cyclopropenone is known to polymerize above -20° . These data prove water to be an undesirable solvent.

We have found that the ketone can be synthesized in acetonitrile and perhaps other solvents which are polar enough to dissolve the ketone. We are attempting to find a more suitable solvent in which to perform the hydrolysis of the dichlorocyclopropene and which will, in turn, enable the product to be separated. An obvious choice of solvent is one greatly differing in volatility. Performing the reaction at atmospheric pressure in a non-volatile solvent, and following this by vacuum pumping may allow the ketone to be evolved as a free gas. Conversely, a very volatile solvent may be evaporated at a low enough temperature to leave behind an unpolymerized product.

According to Ryan,⁸ the hydrolysis reaction in pure dichlorocyclopropene results in a black polymer, liberating CO gas. But this same reaction, slowed and controlled by carrying it out at cryogenic temperatures, may possibly yield the unpolymerized ketone.

C. CYCLOPROPENE

As discussed in the last report,⁷ cyclopropene has been synthesized from the reaction of allyl chloride with sodium amide



8. G. Ryan, private communication. We are grateful to Mr. Gordon Ryan and Dr. R. Breslow of Columbia University, who have been most kind in giving us the benefit of their experience on a number of matters that occur in the preparation of cyclopropenone.

under conditions which allow the unstable cyclopropene to readily escape as a gas from the reaction mixture and be immediately trapped at 77°K. The trapped species has been analyzed mass spectrometrically, using our cryogenically adapted inlet systems.

Although the ionization potential of cyclopropene has been measured previously,⁹ there was some doubt as to whether the species existing at the time of electron impact would be the closed ring structure or its open chain isomer $\text{CH}_2=\text{C}=\text{CH}_2$. Since cyclopropene is reactive (polymerizes above -80°C), it could possibly "open up" during analysis at room temperature. Using the cryogenic inlet system, we have made both room temperature analyses and low temperature analyses of this product. The data did not indicate any significant difference in appearance potentials measured at the different temperatures. But there was an inordinately large range of scatter in the data (from 9.4 to 10.5 electron volts). This matter has yet to be fully explained as to whether our data are significantly different from the previous value of 9.95 eV. One would expect energetic data from open and closed structures to differ by the amount of the ring strain energy of about 27 kcal/mole.

By measuring the appearance potential of the ion fragments C_2H_2^+ and CH_2^+ from cyclopropene we were able to calculate heats of formation of 653 and 694 kcal/mole, respectively. By comparing with the measured ΔH_f° of 665 kcal/mole we can get an idea of the types of results and accuracy one can obtain for ΔH_f° which in turn may prove useful in assaying the results calculated for ΔH_f° of similar compounds such as cyclopropanone, cyclopropenone, and cyclobutadiene.

D. THEORETICAL PROGRAM IN MOLECULAR ORBITAL CALCULATIONS

In initiating a theoretical program within the context of our particular circumstances and expertise, several guidelines have been followed. We are not now nor do we expect to become chemical theoreticians. But rather we have taken strictly an engineering point of view with the objective of utilization of the best current theory as it may bear upon our particular problems of

9. K. B. Wiberg, W. J. Bartley and F. P. Lossing, J. Am. Chem. Soc. 84, 3980 (1962)

10. F. L. Carter and V. L. Frampton, Chem. Rev. 64, 497 (1964)

reactivity, stability, and energetics with unusual molecules at cryogenic temperatures. There is, of course, a vast difference between using molecular orbital theory, as opposed to developing such theory. It further turns out that within the last few years, new notions as well as efficient computer programs have been developed which seem to permit the calculation of quantities of chemical interest with useful, rather than purely academic, accuracy.

We have joined the Quantum Chemistry Program Exchange at the University of Indiana, and through this association we have obtained a computer program written by Professor Roald Hoffmann of Harvard¹¹ which has been frequently quoted and used by a number of investigators. This program performs extended Huckel theory and Hartree-Fock self consistent field molecular orbital calculations on molecules composed of first and second row atoms. The program determines molecular orbital wave functions, energy levels, bond orders, charge densities, and atomic charges. We are in the process of modifying this program for use with the unusual molecules in which we are interested.

We have also recently received a computer program applicable to hydrocarbons written by Professor Gilles Klopman of Case Western Reserve University.¹² This program gives more accurate results for the molecular parameters mentioned above, and also determines molecular ionization potentials and bond energies which are, of course, directly measurable with our experimental equipment and techniques. At present, we are modifying the program for use on the hydrocarbons in which we are interested, and we plan to extend this semi-empirical SCF molecular orbital approach to molecules other than hydrocarbons. We expect to compare the results of these two calculations with experimentally obtained values of ionization potentials, and heats of atomization (or bonding energies) of our unusual low temperature molecules.

11. R. Hoffmann, J. Chem. Phys. 39, 1397 (1963)

12. G. Klopman and M.J.S. Dewar, J. Am. Chem. Soc. 89, 3089 (1967). We gratefully acknowledge the kindness of Dr. Klopman in supplying us with a listing and a magnetic tape of his complete program.

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Fifth and Sixth Semi-Annual Reports
Research Project B-509

CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN
ATOMS AT TEMPERATURES BELOW 100°K

by

Henry A. McGee, Jr.

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Performed for

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Washington, D. C.

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I. INTRODUCTION

A. Space Chemistry. - This research program is concerned with the development of chemical information at cryogenic temperatures, particularly on systems that astronomers and astrophysicists feel are important in comets and in the atmospheric and surface chemistry of the planets. This objective rather quickly resolves itself into studies of low molecular weight compounds of the four reactive elements of maximum cosmic abundance, namely hydrogen, carbon, nitrogen and oxygen.

The approach here is not one of free radical stabilization, i.e., centered upon attempts to isolate labile species in inert matrices at very low temperatures which would otherwise be chemically lost with zero activation energy. The concentrations of such species are limited to a maximum of a few tenths of a per cent (usually much less), and hence, the importance of such systems in cosmic chemistry would seem to be minimal. The matrix technique, particularly when combined with ir or epr, does, of course, provide a powerful means to study the physical and chemical properties of free radicals.

By contrast, low molecular weight species which have singlet electronic ground states, i.e., species that are highly reactive but are not free radicals, are in an altogether different category. Examples of such substances are cyclobutadiene, cyclopropanone, oxirene, diimide, ammonium ozonide, benzyne, tetrahydrofuran, and many others. One would expect such species to exhibit an activation energy for reaction, but we would also expect this energy to be unusually small. If an activation energy exists, then substances such as these may be preparable as stable cryochemical reagents and a true chemistry at very low temperatures may be developed. Since the activation energies involved in these systems are small, it will usually be necessary to maintain the compounds below some critical temperature if they are to be manipulated as stable, pure reagents. Hence, all of the common operations of chemistry must be adapted to cryogenic temperatures. A central operation in any chemical investigation is analysis. In earlier reports on this grant, the development of unique cryogenically cooled reactor-inlet attachments to the time-of-flight mass spectrometer have been described in detail. The cryogenic mass spectrometer

continues to be the key analytical tool in the approach to low temperature chemistry that is being pursued in this laboratory with three large mass spectrometers presently in use in various aspects of this NASA research program.

The best characterization of those strange nomads of space, the comets, is the so-called "dirty snowball" model of Whipple as modified by Donn and Urey.¹ Here the comet's nucleus is considered to be composed of frozen ices of simple compounds such as NH_3 , H_2O_2 , C_2H_2 , etc., and some meteoric dust. However, it has been necessary to postulate highly energetic reactions occurring at very low temperatures in order to explain cometary phenomena observed by astronomers. It is possible, if not highly probable, that these reactions involve as yet unknown species which are stable when cold but which react vigorously upon slight warming. The search for the existence of such species and the study of their chemistry and energetics continues to be the primary objective of this NASA program. One should also recall that the atmosphere and surfaces of the Jovian planets are very cold (even Mars is much colder than earth), and hence, the equivalents of earthbound meteorology, geochemistry, and possibly other areas of geophysics in which chemistry is important, must be understood, as it applies to that particular planet, in terms of low temperature chemistry. A build-up of general knowledge in the phenomenological chemical behavior of species likely to be present will also be valuable inputs to the engineering designs of landing vehicles for both manned and unmanned explorations of the future.

B. Industrial Chemistry. - As this work has developed, we have found rather eager interest on the part of segments of the chemical process industry in many of these same sorts of reactions. These people are interested in energy storage and conversion and in chemical synthesis. Our way of life depends upon the inexpensive availability of a wide variety of chemicals in tonnage quantities, and any process or technique which offers hope of economy or variety in these syntheses is sure to attract attention. The low temperature procedures developed here represent a totally new dimension of preparative chemistry, and, since industrial chemistry is preparative chemistry, they also represent new dimensions (however embryonic) of industrial chemistry. We are

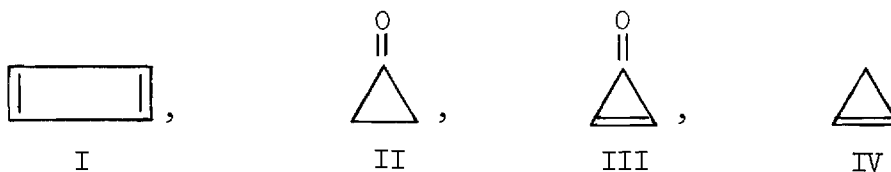
working hard toward expanding our long-time and fruitful dialogue with segments of the chemical process industry into activities of a concrete collaborative nature.

The existence of very substantial industrial interest in the research and teaching programs of this laboratory is, we think significant, and is worth bringing to the attention of NASA. Research and teaching in this laboratory are completely intermeshed and are of equal importance. Students get strong backgrounds of formal training in both engineering and in chemistry. Their thesis research in cryochemistry and kinetics seems to stretch the student in both the areas of engineering concern and in the more scientific concerns in that each involves complex problems in experimental design; each has definite and significant implications as regards generalization to large scale operation, and each has first-rate scientific merit. Not only the "space-defense" industry, but also the general chemical process industry manifests its interest in such students by their position and salary offers which are in the national upper 10 per cent for all new Ph.D.'s in science and engineering.

As a unit of a technological Institute which is beginning to realize its potential for greater contributions to the economy and well-being of the entire South, we are vitally interested in both the development of technology and in the utilization of that technology. Judging by past performance, it would appear that this NASA program can function very well in both of these regards.

II. RESEARCH

A major part of this NASA program in space chemistry is the synthesis, energetics, and chemical characterization of low molecular weight, highly reactive compounds of C, H, N and O. Progress has occurred with cyclobutadiene(I), cyclopropanone(II), cyclopropenone(III), and cyclopropene(IV).



Compounds I, II, and III are central issues in the theory and practice of organic chemistry. They have been postulated as reaction intermediates, and their direct observation has been vigorously sought by numerous investigators for many years, but with little or no success.

The new techniques of cryochemistry are applicable to the isolation and characterization of such compounds.

A. Cyclobutadiene. - Cyclobutadiene is a highly strained cyclic dimer of acetylene² that has been directly, but not definitively, observed in only one experiment which was based on kinetic mass spectrometry in flash photolyzed cyclobutadieneirontracarbonyl (CIT).³ We now report the mass spectrum, ionization potential, and the indefinite free existence of condensed cyclobutadiene at very low temperatures from the pyrolysis and rapid cryo-quench of CIT. These new data, though compelling, are however, still not completely definitive, but it seems clear that any absolute identification and characterization of cyclobutadiene will demand the techniques of cryochemistry. We may also reasonably expect the preparation of cyclobutadiene as a neat cryochemical reagent provided only that the activation energies for its very facile diene reactions, although very small, are nonetheless finite.

The apparatus consists of a pyrolysis furnace mounted inside a cryogenically cooled inlet system attached to a Bendix time-of-flight mass spectrometer.⁴ The furnace was constructed of a 5 mm OD Pyrex tube wound with Nichrome wire providing a heated length of 3.5 cm. The furnace was mounted coaxially inside an 11 mm ID monel quenching tube which was kept at -196° and 10^{-6} torr. Thus, the pyrolysis was conducted at low pressures and short contact times, and the products must travel only a few mm from the furnace exhaust port before being quenched.

Each pyrolysis run lasted 2 hours with inlet pressures of CIT of 10^{-2} to 10^{-1} torr (indicated at a distance of 93 cm from the furnace) and with furnace temperatures at 320° to 380° . Upon controlled warm-up, the quenched products vaporized and travelled less than 8 cm with no associated warming before controlled energy electron bombardment in the source. The principle products of pyrolysis are shown in Table 1, and each species was also observed in the

Table 1. Pyrolysis Products and Appearance Temperatures

<u>Compound</u>	<u>Temperature ($^{\circ}\text{C}$)</u>	<u>Relative Quantity</u>
CO	-196	large
C_2H_2	-155	medium
CO_2	-145	small
C_4H_6	-120	small
C_4H_4	-105	large
C_6H_6	-90	large
C_8H_8	-80	medium

earlier flash photolysis of CIT.³ At -105° , a large peak at m/e 52, C_4H_4^+ , and a small peak at m/e 54, C_4H_6^+ , were observed. Continuous pumping at -110° for 6 hours failed to completely remove C_4H_6 . The C_4H_6 was identified as 1,3 butadiene and the mass spectrum of C_4H_4 reported here (see Table 2) was obtained by subtracting the mass spectrum of 1,3 butadiene from the observed total mass spectrum at -105° .

The isomers of cyclobutadiene, butatriene and vinylacetylene, have been prepared and each exhibited both a different mass spectrometric pattern and a different ionization potential as shown in Tables 2 and 3. To avoid possible misinterpretation from temperature effects, the ionization potentials of cyclobutadiene, vinylacetylene, and butatriene were determined at -100° , -108° , and -90° , respectively. These ionization potentials were also calculated using a semi-empirical SCF treatment recently developed by Dewar and Klopman.⁵ The experimental and theoretical results are summarized in Table 3.

Table 2. TOF Mass Spectra of C_4H_4 Isomers at 70 eV

<u>m/e</u>	<u>C_4H_4 from Pyrolysis of CIT</u>	<u>Butatriene</u>	<u>Vinylacetylene</u>
52	100%	100% (100%) ^a	100% (100%) ^b
51	59	70 (72-80)	56 (50.2)
50	51	51 (54)	49 (41)
49	17	26 (24)	19 (13)
48	1	8 (--)	8 (2.8)
39	5	1 (--)	1 (0.85)
26	26	18 (21.2)	12 (11.0)

(a) Measured with a magnetic mass spectrometer (CEC, model 21-103), W. M. Schubert, T. H. Libbicoet and W. A. Lanka, *J. Am. Chem. Soc.* 76, 1929 (1954). Additional peak at m/e 53 of 14.7-22.2 per cent evidently arises from reaction during inlet.

(b) Measured with a magnetic mass spectrometer (CEC, model 21-101), Selected Mass Spectral Data, API Research Project 44.

Table 3. Experimental and Theoretical Ionization Potentials for C_4H_4 Isomers

<u>Isomer</u>	<u>Experiment</u>	<u>Theory</u> ^a
Cyclobutadiene	9.55	8.9
Vinylacetylene	9.9 (9.9 ^b)	9.42
Butatriene	9.25	8.99

(a) Calculated using a semi-empirical SCF MO treatment developed by M.J.S. Dewar and G. Klopman, *J. Am. Chem. Soc.* 89, 3089 (1967)

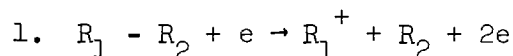
(b) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p. 261.

The ionization potentials at m/e 52, 78 and 104, presumably C_4H_4 , C_6H_6 , and C_8H_8 , respectively, were determined from the low temperature evolved gases by the linear extrapolation method using ionization efficiency curves recorded directly from the electrometer using a Hewlett-Packard (Model 700/AR) X-Y plotter. The observed IP of C_8H_8 was 9.1 eV, and since the value for cyclo-octatetraene is 8.6 eV,⁶ the $I(C_8H_8)$ observed here is postulated as cyclobutadiene dimer. The mass spectrum and ionization potential at m/e 78, C_6H_6 , are in agreement with that of benzene. The formation of benzene in the pyrolysis can occur by the reaction of cyclobutadiene and acetylene or by the polymerization of acetylene at these pyrolysis temperatures (320° to 380°). Benzene was in fact observed upon passing pure acetylene through the furnace at 380° .⁷ The reaction of cyclobutadiene and acetylene to form Dewar benzene and then benzene itself has been suggested by Pettit.⁸

From these comparisons of the mass spectra and ionization potentials of the C_4H_4 species, and from the formation of benzene and cyclobutadiene dimer, we conclude that cyclobutadiene was produced from the pyrolysis of CIT and quenched as a compound which is stable and probably isolable below about -90° . We feel that this constitutes the most definitive study of this long-sought molecule that has appeared.

B. Three Carbon Strained Ring Compounds. - As discussed in previous reports, a major effort of our work has been to apply the techniques of cryochemistry to the synthesis and study of a family of small, 3-carbon strained ring compounds: cyclopropene, cyclopropanone, and cyclopropenone. These compounds, because of their strained structure, are all highly reactive, and they exhibit only a fleeting existence at room temperature while functionally serving as reaction intermediates. We have now shown that they can be isolated and stored indefinitely at low temperatures. We have synthesized these compounds and studied their molecular energetics by the use of cryogenic inlet systems adapted to a mass spectrometer.⁴ From the measurement of ionization and appearance potentials of the compounds and fragments, we wanted to calculate heats of atomization, bond dissociation energies and ring strain for comparison with similar quantities obtained from theoretical calculations.

Energetic data from the measurement of appearance potentials of fragment ions are based on the following type reaction:



and equation:

$$2. \quad \begin{aligned} \text{A.P.}(R_1^+) &= \Delta H_r = \Delta H_f^O(R_1^+) + \Delta H_f^O(R_2) - \Delta H_f^O(R_1 - R_2) + E^* \\ &= D(R_1 - R_2) + R_1 + E^* \end{aligned}$$

where: R_1 - group of atoms bonded to another group, R_2

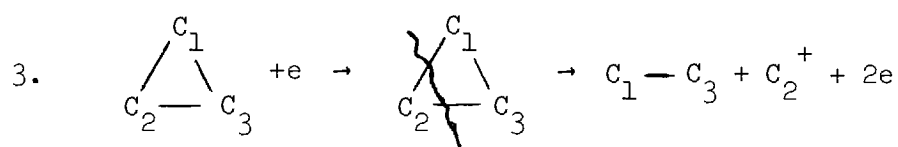
A.P. - mass spectrometrically measured appearance potential

ΔH_f^O - heat of formation

E^* - excess energy of any fragment (includes translational, vibrational and rotational)

$D(R_1 - R_2)$ - bond dissociation energy.

In the case of ring compounds, fragmentation requires that two bonds be broken, and we wanted to study and interpret this rather more complex phenomenon, i.e.,



The preliminary interpretation of the data from the first compound investigated, cyclopropanone, proved to be inconclusive, and hence, a critical error analysis of expressions like Equation 2 had to be undertaken with compounds previously studied and interpreted by other workers in the mass spectrometric field. Possible sources of errors to be investigated were:

- (a) accuracy of A.P.
- (b) choice of fragmentation process and products
- (c) ΔH_f^0 of fragment, usually a number from the thermochemical literature
- (d) ionization and appearance potential values for both ground states and excited states
- (e) excess energy of fragments (translational and vibrational)

Excess energies of the fragment ions were studied by the method of Franklin.⁹ This method is based on the theory and fact that fragment ions with a thermal distribution of velocities will exhibit a mass spectrometric peak shape which reflects the one-dimensional spread in velocities of the fragment ion after ionization. The width of each peak is directly proportional to the square root of ion mass and temperature. Any deviation from the standard width at room temperature is related to a change in ion temperature from which one can calculate the translational energy of the ion fragment and the translational energy of the neutral fragment. Franklin has further shown that this total excess translational energy is a definite fraction of the total (translational, rotational, and vibrational) excess energy.¹⁰

There is some doubt as to whether a particular ion observed in the mass spectrometer is a ring or an open structure. Since these unusually reactive cryogenic species presumably polymerize through a free radical structure, several LCAO-MO-SCF computer programs are being used to predict whether the ionization potentials of these various species differ enough energetically to be detected by a mass spectrometric measurement. Also, in the simultaneous breaking of two ring bonds, each fragment would initially be produced as an excited diradical, the energy of which may be calculable. Presently, only the computer programs limited to H and C are working correctly,⁵ and data on cyclopropene are discussed later. Additional computations on C, H, and O molecules should be available soon.

(a) Cyclopropane

Cyclopropane was investigated because it is similar to our unusual cryogenic molecules and because previous work on its energetics was available.¹¹ Appearance potentials of the fragments were measured and processes were chosen that came closest to being energetically consistent as described by Equation 2. Later work¹⁰ showed that some of the ions possessed considerable excess energy and, then, that the processes chosen in the previous work were incorrect. Cyclopropane exhibited a variety of shapes of ionization efficiency curves which could be classified as to their value in energetic deductions.

Ionization potentials are obtained by comparing the unknown ionization efficiency curves to those of known standards. The shapes of unknown fragments usually fall distinctly into one of two classes: (1) they are nearly identical in shape with the standard, or (2) they possess a much longer initial curved tail. For the first type, any method of comparing the unknown and calibrating curves can be used with good results. The second type of curve is caused by more than one process contributing to the formation of the ion, and the overall resulting curve is the arithmetic sums of these individual processes. For a many-process ionization, the overall curve will have a long, shallow curve. This type of curve is impossible to compare to a standard and cannot be used to deduce energetic quantities. But, if the overall curve arises from only a few processes, it may have a long, but steep, curved tail. This case can be handled by the method of initial breaks.

With accurate appearance potentials and excess energies in hand, the ΔH_f of cyclopropane was calculable from data on three ions, and it was shown that the products were not present as diradicals, but in their ground states. This molecule, then, provided a foundation to discuss the energetics of other cyclic compounds.

(b) Cyclopropene

Cyclopropene slowly polymerizes at dry ice temperature (-78°). We synthesized this molecule by the reaction of allyl chloride with sodium amide, under conditions where the unstable cyclopropene could readily escape from the reaction mixture and be immediately trapped at 77°K .¹² The final product was purified by simple trap to trap distillation. This molecule was

investigated using both the low temperature inlet system (wherein the molecule was kept at -140° until analyzed) and at room temperature. Mass spectra and appearance potentials measured at both temperatures appeared to be equivalent. This indicated that if the ring opened or a diradical formed upon warming, that it did so in only such small quantities that the product was energetically undetectable. All fragment ions were formed with little or no excess energies. But no fragments had a satisfactorily shaped curve to measure the appearance potential accurately. This is shown in Table 4 where all calculated ΔH_f° for

Table 4. Mass Spectrometric Data on Cyclopropane and Cyclopropene

Fragment m/e	I.P. (e.v.) or A.P.		Excess Energy		$\Delta H_f^{\circ a}$			Curve Shape	
	<u>This Work</u>		Kcal./Mole.		Kcal./Mole.				
	<u>Exp.</u>	<u>Theory</u>	<u>Exp.</u>	<u>Lit.</u>	<u>This Work</u>	<u>Lit.</u>	<u>Exp.</u>	<u>This</u>	<u>Work</u>
42 (Parent)	10.3		10.2				1	13	Good
27	13.7		13.5	30			5		Long Tail
26	14.0		13.6	15			21		Long Tail
15	16.0		16.9	15			-40		Long Tail Shallow
14	18.5		18.8	90	120		15		Long Tail
40 (Parent)	9.8	9.7	9.9				41	67	Good
39	11.0		11.1						
27	13.5			0			100		Long Tail Shallow
26	16.4			0			-10		Long Tail Shallow
15	16.0			0			0		
14	15.0			15			77		

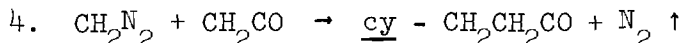
(a) ΔH_f° of parent as calculated from experimental A.P. of fragment ion using Equation 2.

cyclopropene are in considerable error. Note the good results for the I.P. of cyclopropene as calculated by the previously discussed computer program.

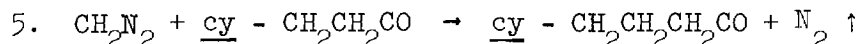
To test the temperature stability of the molecule, samples were thermostated at constant temperatures, then quenched to 77°K, and then warmed to determine whether the molecule had been destroyed and whether there were any gaseous decomposition products. The soak-temperatures ranged from -140° to room temperature and the product was stored under vacuum. We found no decomposition products, but a polymer which was noticeably formed only at about room temperature. In fact, a one-week room temperature exposure did not completely destroy cyclopropene as analysis showed both the molecule and a high molecular weight compound (m/e 80) which appeared to be the dimer. Thus, the compound appears to be much more stable than anticipated from other work. The polymer appeared to be a white waxy solid which smears upon contact at room temperature. The polymer was heated to near 300°, but it remained stable and showed no decomposition accompanied by off-gas evolution. The polymer was soluble in benzene, slightly soluble in gasoline, and insoluble in water, acetone, and methanol.

(c) Cyclopropanone

Cyclopropanone is a small ring compound that has been often proposed as a reaction intermediate, and at the time this work was begun, the species had never been isolated. We used a direct approach to its synthesis using the reaction of diazomethane with ketene.



Room temperature synthesis attempts have always yielded the butanone which was viewed as resulting from further reaction of diazomethane with cyclopropanone.



Diazomethane and ketene were prepared, purified, and characterized mass spectrometrically. The reaction was carried out in a cooled, evacuated trap by arranging, at liquid N₂ temperatures, a condensed ring of diazomethane

above a solid ring of ketene (in great excess). By then plunging the trap into a liquid refrigerant at -150° , the solid yellow diazomethane became a viscous liquid which slowly ran down into and reacted with the now also liquid ketene producing a white solid and a volatile gas. The product gas was monitored mass spectrometrically and was identified as N_2 . The rate of evolution of off-gas was constant with time, supporting the idea of a concentration independent, liquid-liquid reaction on the wall of the vessel.

After the excess reactants (which were proven to be entirely ketene) were removed by warming, the solid was transferred to the cryogenic inlet system where it was warmed and product peaks at m/e 56 and m/e 70 were studied at -90° and -75° , respectively. The relative volatilities of the two compounds allowed then to be separated sufficiently to obtain their mass spectra and energetic values. The vapor pressure, mass spectra, and energetic values of the heavier species were essentially¹³ the same as those obtained in this laboratory from a pure sample of cyclobutanone (K & K Laboratories, Inc.). Likewise, the data for the lighter product were identical to that reported for cyclopropanone by Shaafsma, et al.¹⁴ Both cyclopropanone and cyclobutanone yield the same ions upon electron bombardment revealing their similar structure. On the basis of these data, we concluded that cyclopropanone had been isolated.

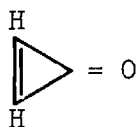
We also studied cyclopropanone at room temperature, and similar to cyclopropene, obtained the same I.P. for the parent indicating no major change in structure due to warming. However, this proved to be a very inefficient operation as most of the sample (greater than 95%) was polymerized, and the sample barely lasted long enough for the study.

We have studied the temperature stability of this molecule by the same techniques as discussed under cyclopropene. This molecule is much more reactive than cyclopropene. Some polymerization was apparent at -90° , a temperature at which cyclopropanone exerts little vapor pressure. It is difficult to tell whether the compound is a liquid or a solid at this temperature. Because of the localization of the polymer at the site where it was condensed as a solid, it appears that the polymerization reaction is at least begun, if not completed, as a solid or liquid before it reaches the vapor phase. Although a one-hour room temperature soak completely destroyed the cyclopropanone, no volatile decomposition products were observed. The polymer was a

white powder which, when heated to 200° , proved to be thermally unstable. The first product observed was m/e 56 which was interpreted as trapped cyclopropenone and not as polymer decomposition. Then heavier, but unidentified, products were observed. The polymer was soluble in benzene, slightly soluble in gasoline, somewhat soluble in acetone and alcohol, and not soluble in water. The original appearance potentials are now being reinvestigated in terms of what was learned from other cyclic compounds. Also, the computer calculation of the I.P. and ΔH_f are now underway.

(d) Cyclopropenone

Cyclopropenone,

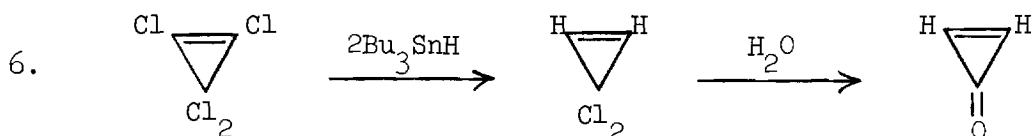


is a highly strained, small ring system that appears to possess considerable conjugative stabilization. Studies with the substituted molecule date from 1959, and compelling, but not absolutely conclusive, evidence for the synthesis of the parent ketone has appeared.¹⁵ The original synthesis yields the ketone in aqueous solution, but attempts to isolate the substance, in work done by different research groups, whether by removal of the solvent by distillation, or by vapor phase chromatography under a variety of conditions have failed. Cyclopropenone is lost by polymerization just as is true of the hydrogenated analog, cyclopropanone.¹³ Although the olefin appears to be more stable than the saturated compound, it cannot be kept in water solution as it hydrolyzes to form acrylic acid.¹⁵

Both of these ketones are interesting cryochemical systems. The cyclopropenone is particularly interesting in view of the failure of standard techniques in attempts to isolate the substance during the almost two years since its initial identification. The lack of published literature on the molecule since then also casts some doubt on its existence. The cryochemical equipment and procedures that have been developed in this laboratory are being applied to the isolation, energetics, and reactivity questions surrounding

this molecule. In view of the equivocal data, even with the great interest in the past of many investigators, it may well be that the techniques of cryo-chemistry may be the only way to effectively study this molecule.

The original apparent synthesis by Breslow and Ryan of cyclopropenone consisted of the reaction of tetrachlorocyclopropene with two equivalents of tri-n-butyltin hydride at room temperature in paraffin oil to produce a volatile mixture of mono-, di-, and tri-chlorocyclopropenes. This mixture of chlorinated products is taken up in CCl_4 , then hydrolyzed with cold water to give an aqueous phase solution of the cyclopropenone. This sequence of reactions is as follows:



Our first attempt to reproduce this original synthesis was proved successful when both the dichlorocyclopropene and cyclopropenone were identified by nmr analysis. This preparation was done on a small scale and the purity was quite poor. Later, by utilization of mass spectrometric and infrared analysis, we were able to better control the preparations, and we obtained improved yields and much higher purity than in the first attempt. Tetrachlorocyclopropene can be kept indefinitely at room temperature. Bu_3SnH will react with air but it can be kept under argon sealed from air at room temperature. Dichlorocyclopropene, on the other hand, is itself a cryochemical which must be kept below -70° or it is lost by polymerization. At room temperature, dichlorocyclopropene, within seconds, will begin to turn from a clear white liquid to yellow, and then steadily darken to a deep brown.

The original preparation of cyclopropenone resulted in a water solution. Trying to separate this solution by slowly warming from -196° to room temperature under vacuum and immediate analysis by the mass spectrometer proved unsuccessful. A dominant peak at $m/e = 19$ (H_3O^+) suggested that cyclopropenone might have hydrolyzed to acrylic acid as it is known to do. Also, to vaporize the solvent water, the solution must be heated to a temperature at which the ketone would rapidly polymerize. Cyclopropenone is known to polymerize above -20° . A polymer is formed during the slow warming but we cannot say definitely

it is from cyclopropenone as it could also be from unreacted dichlorocyclopropene. These data prove water to be an undesirable solvent.

The ketone can also be synthesized in acetonitrile and perhaps other solvents. We are attempting to find a more suitable solvent in which to perform the hydrolysis of the dichlorocyclopropene and which will, in turn, enable the product to be separated. An obvious choice of solvent is one greatly differing in volatility. Performing the reaction at atmospheric pressure in a non-volatile solvent, and following this by vacuum pumping may allow the ketone to be evolved as a free gas. Conversely, a very volatile solvent may be evaporated at a low enough temperature to leave behind an unpolymerized product.

According to Ryan,¹⁶ the hydrolysis reaction in pure dichlorocyclopropene results in a black polymer, liberating CO gas. But this same reaction, slowed and controlled by carrying it out at cryogenic temperatures, may possibly yield the unpolymerized ketone.

We plan to carry out the above described experiments in the next few weeks. Results from the computer calculation of the most stable structure for cyclopropenone should also be available within the next few weeks.

III. FUTURE PLANS

The nature of our continued research with the above series of small strained-ring systems has already been described. Several new systems seem particularly promising, and hence, some expansion in scope will occur during the ensuing year.

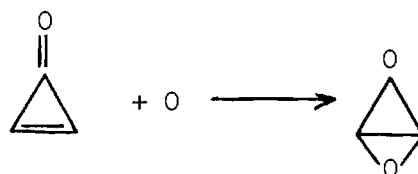
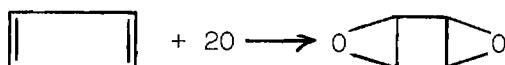
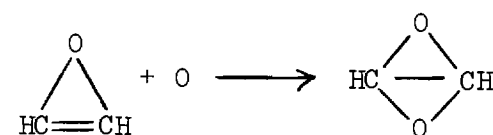
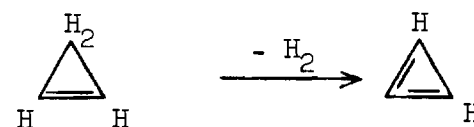
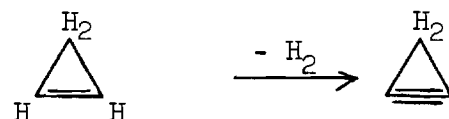
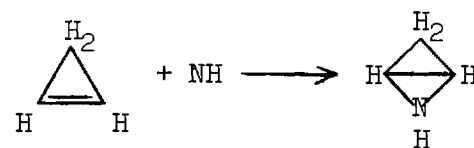
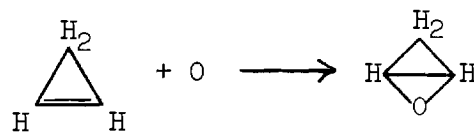
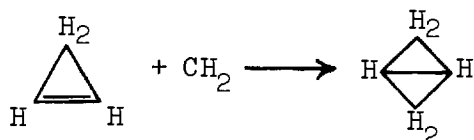
(a) Oxirene. Although we have been unable to perform any definitive experiments, we propose to continue work toward the synthesis of this highly strained, unsaturated, heterocycle,



The most promising approach still seems to be the addition of ^1D excited O atoms to outline at low temperatures.

(b) Cryogenic Reactions of New Molecules. Successful synthesis of the unusual and reactive compounds of Chapter II opens the door to exploration of their chemistry. For example,

7.

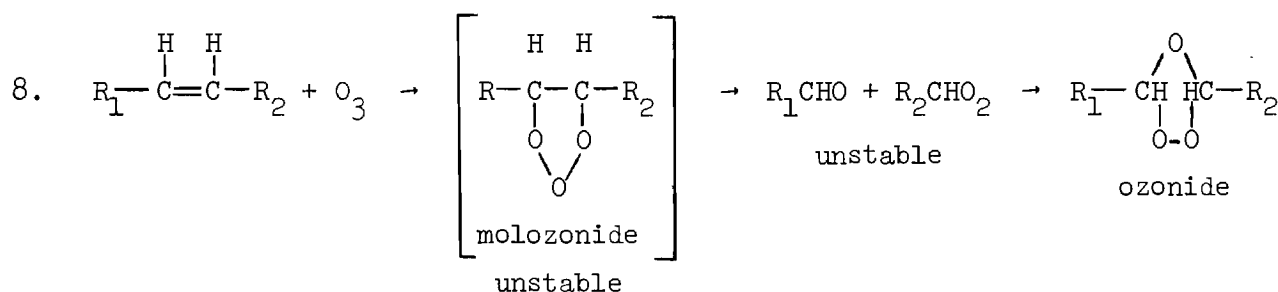


All of these suggested product molecules are presently unknown and may well be non-existent, even at cryogenic temperatures, in view of high strain in the bonds. But these typical examples of cryochemical reactivity, as well as many others that could be written, seem logical and interesting follow-ups to our successful syntheses of the required (and previously unavailable) unusual cryochemical reagents.

(c) Ozonides. Ozone may well be an important cometary constituent as well as a constituent of the atmospheres or surfaces of the Jovian planets. It is also a highly reactive cryogenic liquid whose chemical characteristics are still rather obscure.

In earlier reports on this NASA program, we reported rather unsuccessful attempts to confirm the much debated synthesis of hydrogen superperoxide, H_2O_4 , from the reaction of atomic hydrogen with liquid O_3 at $77^\circ K$. These experiments were plagued by frequent and ill understood explosions. We propose to continue these studies utilizing our improved technique and equipment that has been developed in the meantime.

Ozone is believed to react with olefins to form ozonides via the formation of an unstable transitory adduct called molozonide, but such a species has never been directly observed.



We propose to study the above reaction at very low temperatures with a number of simple unsaturated hydrocarbons (for example, ethylene, acetylene, dicyanoacetylene, etc.) with the objective of isolating the molozonide (if it exists) or any other reactive intermediate. With success here, energetic, stability, and reactivity studies will be conducted in the usual manner.

(d) Nitrogen Compounds. A family of N-H compounds may be postulated: triazene ($\text{H}_2\text{N}-\text{N}=\text{NH}$), triazane ($\text{H}_2\text{N}-\text{NH}-\text{NH}_2$), tetrazene ($\text{H}_2\text{N}-\text{N}=\text{N}-\text{NH}_2$), etc. In earlier reports on this NASA program, we have shown that the simplest dinitrogen compound, diimide (N_2H_2), may be made from the cryogenically quenched atomic oxygen-ammonia flame. One may also postulate that "Rice's blue stuff" quenched from pyrolyzed HN_3 may be a cyclic trimer, $(\text{NH})_3$, or either ozone-like since NH is isoelectronic with O. Finally, it was also recently shown in low temperature matrix experiments that atomic fluorine will abstract hydrogen from HN_3 to yield the N_3 radical.

We propose to study the reactions of NH (from HN_3), and N_2H_3 (from hydrazine) and N_2H_2 (from $\text{O} + \text{NH}_3$ flame) in attempts to form three and four membered cyclic and acyclic compounds of this family. We also propose to study the formation of cyclic N_6 from the dimerization of two N_3 free radicals. The molecular energetics, the region of thermal stability and the identification of the reaction or decomposition products from all of these studies will be accomplished with the aid of the cryogenic mass spectrometers in the usual way.

(e) Cyanogen Azide. Cyanogen azide, N_3CN , is an unstable and highly reactive molecule which has recently been synthesized, and it has been the object of several reactivity studies.¹⁷ Upon pyrolysis, it yields NCN radicals which then dimerize to form $\text{NC}-\text{N}=\text{N}-\text{CN}$ which is itself an orange-red, highly reactive, volatile compound.

We propose to make a series of exploratory studies of the chemistry of cyanogen azide at very low temperatures with a view toward the development of information pertinent to the origin of CN emission from comets. For example, the discovery of an H-C-N-O compound in which the cyanogen group was only weakly bonded (say $D(\text{M-CN}) < 1 \text{ ev}$) would be a good candidate species for low intensity photolysis.

IV. ADDITIONAL INFORMATION

After careful arrangements to insure efficiency and continuity, NASA approved a proposed leave-of-absence to allow the Principal Investigator to serve the first nine months of 1969 as a visiting professor in the Chemistry and Chemical Engineering Division at the California Institute of Technology.

His salary will be paid jointly by Caltech and Georgia Tech, together with a very small contribution from this NASA grant. During this leave-of-absence, the Georgia Tech Foundation has made funds available to allow monthly return visits by Dr. McGee for consultations with his research students and for the continued supervision of this NASA research program. Dr. McGee's work at Caltech will involve seminars, lectures, consultations with Research Fellows, etc. on matters of the same or very closely related areas of research as are now underway in his laboratory at Georgia Tech. It should be possible to enlist at least one Post-Doctoral Fellow at Caltech who would begin work at Caltech and then move on to the Georgia Tech laboratories at an appropriate time.

Joint investigations are also being developed. Already, an experiment with cyclopropanone immersed in liquid nitrogen has been transported from Atlanta to Pasadena. Unique facilities and expertise at Caltech, combined with long experience in cryochemistry at Georgia Tech, permit broader and more definitive studies than would be possible at either Institute alone. We anticipate and are working toward long-term collaborative research programs.

Other campus functions of the Principal Investigator include service on a Board responsible for the administration of a large (\$300,000/year) NASA Sustaining University Grant and on a small committee appointed by the Chancellor of the University System of Georgia to advise him in the selection of a new President for Georgia Tech. Dr. McGee has been named Meeting Program Chairman of the 67th National Meeting of the American Institute of Chemical Engineers to be held in Atlanta in February 1970. In this position he is responsible for the entire technical program of this national Institute meeting.

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FINAL REPORT

Research Project B-509

CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND
OXYGEN ATOMS AT TEMPERATURES BELOW 100°K

by

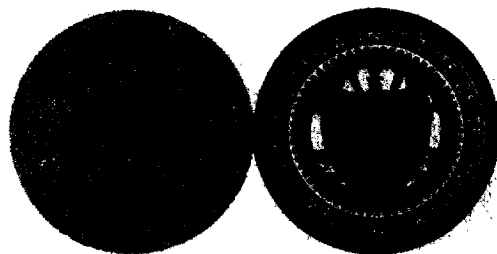
Henry A. McGee, Jr.

NASA Grant NGL-11-002-005 (formerly NsG 337)

August 1973

Performed for

National Aeronautics and Space
Administration
Planetary Programs Office
Washington, D.C.



School of Chemical Engineering
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

CHEMICAL REACTIVITY OF HYDROGEN,
NITROGEN, AND OXYGEN ATOMS AT
TEMPERATURES BELOW 100°K

Final Technical Report
on
Grant NGL-11-002-005

National Aeronautics and Space Administration
Planetary Programs Office
Washington, D. C. 20546

ABSTRACT

This research has been concerned with the synthesis of unusual compounds by techniques employing cryogenic cooling to retard their very extreme reactivity. Examples of such species that were interesting in this program are diimide (N_2H_2), cyclobutadiene (C_4H_4), cyclopropanone ($\text{C}_3\text{H}_4\text{O}$), oxirene ($\text{C}_2\text{H}_2\text{O}$), and many others.

New and generally applicable analytical techniques using the mass spectrometer were developed. These instrumental adaptations permitted the qualitative and rough quantitative analysis of compounds such as the above. Special purpose cryogenically cooled inlet arrangements were designed such that the analyses incurred no warm-up of the cold, and frequently explosively unstable, compounds. Controlled energy electron impact techniques were used to measure critical potentials and to develop the molecular energetics and thermodynamics of these molecules and to gain some insight into their kinetic characteristics as well.

Three and four carbon strained ring molecules have been studied. Several reactions of oxygen and hydrogen atoms with simple molecules of H, N, C, and O in hard quench configurations have been studied. And the quench stabilization of BH_3 , though of little astrophysical interest, has been explored as a model system in cryochemistry. Unfortunately, the species could not be prepared as a stable cryochemical.

This research program was initiated on January 1, 1966 and terminated on June 30, 1971 when the principle investigator moved to Virginia Polytechnic Institute and State University. The research formed the doctoral theses of five students and the masters thesis of one student. The program was continued at VPI&SU under grant NGR 47-004-080 effective July 1, 1971.

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CHAPTER I

INTRODUCTION AND BACKGROUND INFORMATION

This research program has been concerned with the development of chemical information at cryogenic temperatures, particularly on systems that astronomers and astrophysicists feel are important in comets and in the atmospheric and surface chemistry of the Jovian planets. Each of these astronomical objects is very cold, and clearly insofar as chemistry plays a role in the behavior of these objects, that chemistry must be occurring at very low temperatures by terrestrial standards. This objective rather quickly resolves itself into studies of low molecular weight compounds of the four elements of maximum cosmic abundance, namely hydrogen, carbon, nitrogen and oxygen.

The approach here is not one of free radical stabilization, i.e., centered upon attempts to isolate labile species in inert matrices at very low temperatures. All evidence suggests that the activation energy for the reaction of low molecular weight free radicals is zero (or close to it), and hence it will be possible to prepare these species in "stable" forms only by such diffusional inhibition techniques. The resulting concentrations of labile species are limited to a maximum of a few tenths of a per cent (usually much less), and hence the importance of such systems in cosmic chemistry would seem to be minimal. The matrix technique, particularly when combined with ir or epr instrumentation, does, of course, provide a powerful means to study the physical and chemical properties of free radicals.

By contrast, low molecular weight labile species which have singlet electronic ground states, i.e., species that are highly reactive but are not free radicals, are in an altogether different category. Examples of such substances are cyclobutadiene, cyclopropanone, oxirene, diimide, ammonium ozonide, benzyne, tetrahydrofuran, and many others. One would expect

such species to exhibit an activation energy for reaction, but we would also expect this energy to be unusually small. If an activation energy exists, then substances such as these may be preparable as stable cryochemical reagents and a true chemistry at a very low temperatures may be developed. Since the activation energies involved in these systems are small, it will usually be necessary to maintain the compounds below some critical temperature if they are to be manipulated as stable, pure reagents. Hence, new cryogenic manipulative techniques had to be developed, for ideally one must transpose all of the common or usual operations of bench scale chemistry to permit their convenient utilization at cryogenic temperatures. The most important operation in any chemical investigation is analysis. Several unique cryogenically cooled reactor-inlet attachments to the time-of-flight mass spectrometer have been developed under this grant. The cryogenic mass spectrometer has proven to be an efficient analytical tool in low temperature chemistry.

The best characterization of those strange nomads of space, the comets, is the so-called "dirty snowball" model of Whipple as modified by Donn and Urey.¹ Here the comet's nucleus is considered to be composed of frozen ices of simple compounds such as H_2O , NH_3 , H_2O_2 , C_2H_2 , etc., and some meteoric dust. However, it has been necessary to postulate highly energetic reactions occurring at very low temperatures in order to explain some of the cometary phenomena that are observed by astronomers. It is possible, if not highly probable, that these reactions involve as yet unknown species which are stable when cold but which react vigorously upon slight warming. The search for the existence of such species and the study of their chemistry and energetics was one of the primary objectives of this NASA research program. Other than the comets, the atmosphere and surfaces of the Jovian planets are also very cold (even Mars is much colder than earth), and hence the equivalents of earthbound meteorology, geochemistry, and possibly other areas of geophysics in which chemistry is important, must be understood, as it applies to that particular planet, in terms of low temperature chemistry. A build-up of general knowledge in the phenomenological chemical behavior of species likely to be present in such environments will be valuable inputs to the engineering designs of landing vehicles for both manned and unmanned explorations of the future.

As this work has developed, we have found rather eager interest on the part of segments of the chemical process industry in many of these same sorts of reactions. These people are interested in energy storage and conversion and in chemical synthesis. Our way of life depends upon the inexpensive availability of a wide variety of chemicals in tonnage quantities, and any process or technique which offers hope of economy or variety in these syntheses is sure to attract attention. The low temperature procedures developed here represent a totally new dimension of preparative chemistry, and since industrial chemistry is preparative chemistry, they also represent new dimensions (however embryonic) of industrial chemistry. This broad interest in developing such a new dimension of industrial chemistry in addition to the above enumerated areas of application in space chemistry, have formed the objectives of this program.

Accomplishments under this grant have been in the areas of (1) instrumentation development, (2) the development of phenomenological chemical information at cryogenic temperatures, (3) the energetics of low molecular weight, highly unstable and reactive molecules which have been synthesized by cryochemical procedures, and (4) in the training of doctoral students. The details of accomplishments in these several areas have been presented in a series of semi-annual progress reports and in a series of reprints of journal articles and theses which have from time to time been forwarded to NASA as they were published. These details will not be enumerated here. It is, however, appropriate to include a capsule resume of the completed research.

CHAPTER II

RESEARCH RESULTS - EQUIPMENT DEVELOPMENT

Before chemistry at very low temperatures will progress very far, the common operations of bench scale experimentation must be translated to the point of convenient utilization at cryogenic temperatures, and perhaps the most fundamental operation of all is that of chemical analysis. The analytical facility that was invented during this program was designed for the study of the synthesis, stability, reactivity, and energetics of that interesting class of compounds which usually must be synthesized and maintained below some rather low temperature if the compound is to exist as a stable entity or chemical reagent. Examples of such compounds that are either known or pseudo-known are H_2O_3 , H_2O_4 , BH_3 , HNO , NO_3 , N_2H_2 , NH_4O_3 , etc. Manipulations with these species must be conducted at temperatures below the onset of that loss process having the lowest activation energy, and this may be 100°K or lower.

A. General Design Considerations

Both the synthesis reactions and the subsequent studies of the reactivity and energetics of the species of interest must be conducted in cryogenically cooled systems. Experience has shown that simple transfer operations such as pipetting, liquid flow, or vaporization and recondensation become difficult operations when the working substance is thermally unstable at cryogenic temperatures. Also the purification techniques that might be applicable to such systems are complicated by the temperature requirement, and hence each will require development prior to its use. Therefore, it was desirable to combine into one device, insofar as it was possible, the features of a versatile chemical reactor, some capability for separative operations, and chemical analysis by mass spectrometric means.

Almost without exception, reactions which proceed at cryogenic temperatures involve at least one reactant which is a free radical and which is usually generated by electric discharge, pyrolysis, photolysis, or by chemical reaction (such as a low pressure flame). So the experimental arrangement should also be versatile enough to reasonably accommodate these several free radical generation operations.

The mass spectrometer was selected as the primary analytical device for these investigations because, unlike electron spin resonance

or infrared, which have both been widely and successfully used in related experiments, the mass spectrometer detects all species. It also affords a direct observation of the species of interest and the output data require a minimum of equivocal interpretation. Very small quantities are adequate for analysis. An identification may be obtained in the present system provided only that a species exert a vapor pressure of about 3×10^{-6} torr and that the vapor will, upon electron impact, give a sufficient intensity and variety of either positive or negative ions having a lifetime at least of the order of 50 microseconds. The identification is also aided by the use of an ionizing electron beam of controlled energy, and by the control of the temperature of the inlet system which takes advantage of the relative volatility and hence the separability of the several components that may be present from a particular experiment. The open structure of the source of the Bendix spectrometer, which makes it possible to assemble complex hardware adjacent to and even within the source itself, was the deciding factor in the selection of that machine. Many other adaptations of the TOF instrument in situations where this open source structure has been advantageous have been recently summarized.² The disadvantages of the TOF instrument stem from the low duty cycle of 0.005 which results from its control pulse of 0.25 microseconds at a frequency of 20 Kc, i.e., the machine is effectively off 99.5 per cent of the time. The only earlier mass spectrometer adaptation that seems reasonably related to the present arrangement was described by Blanchard and LeGoff.⁴ In their apparatus, the walls of the ionization chamber were cooled with liquid nitrogen, and the system was employed in unsuccessful attempts to condense and revaporize I atoms.

The innovation of cryogenic mass spectrometry is described in some detail below. But the system could be viewed in some sense, as rather similar to a heated filament inlet system for use with the Bendix instrument that was developed by Biemann³ and in which thermally sensitive organic substances contained in a tiny capsule may be positioned inside the source adjacent to the ionizing electron beam of the instrument. Heating the capsule produces vaporization directly into the electron beam, and hence there are few collisions and therefore little reaction or degradation before ionization. Our system is similar, but it operates at the far opposite end of the temperature spectrum.

B. Mechanical Description

A schematic of the apparatus appears in Figure 1 where the reactor-inlet system is shown in operating position near the electron beam. The reactor-inlet system is suspended from a vacuum header and consists of a thermostated refrigerant chamber made of copper for rapid thermal equilibration which was nickel plated on the outside to reduce the emissivity and hence the refrigerant use rate. The monel reactor and condensation tube in which the low temperature species are prepared and manipulated is inside this refrigerant chamber. Thermostating is accomplished by offsetting the natural inward heat leak with a controlled influx of refrigerant which is adjusted to be slightly in excess of that required to just balance the natural heat leak. Fine control is then maintained automatically by a recorder-controller (Leeds and Northrup Company, Adjustable Zero-Adjustable Range-Speedomax H) which controls the power dissipated in 100 ohm constantan heaters wound on the inside of the chamber. Electrical trimming of the heat balance can be much more precisely controlled than is possible with flow control of the liquid refrigerant. Proportional control of these heaters was not required since simple two-position operation resulted in oscillations about the control point which increased to a maximum of only $\pm 0.5^{\circ}\text{K}$ when the apparatus was cooled to near 77°K .

A gas pressurized refrigerant delivery system maintains the flow of liquid N_2 . Close control and monitoring of the influx of refrigerant is accomplished by adjusting a micrometer valve until the desired flow rate is attained as indicated by a flowrator in the frigerant chamber exhaust line. From the measured vented gas flow rate, one can immediately deduce the liquid refrigerant use rate.

The end of the condensation tube nearest the source is fitted with any one of several flat extension pieces which are positioned to protrude into the ionization chamber of the spectrometer when an analysis is being performed; a channel in this extension piece conducts the sample from the condensation tube into the ion source. The inlet port itself (0.089 cm dia.) may be positioned at any point relative to the electron beam including its being actually submerged in the beam, and hence the cold gaseous sample emerges from the inlet tube directly into the ionizing electron beam, and ionization of the sample occurs prior to any wall collisions. A sample molecule must be considered to be background after

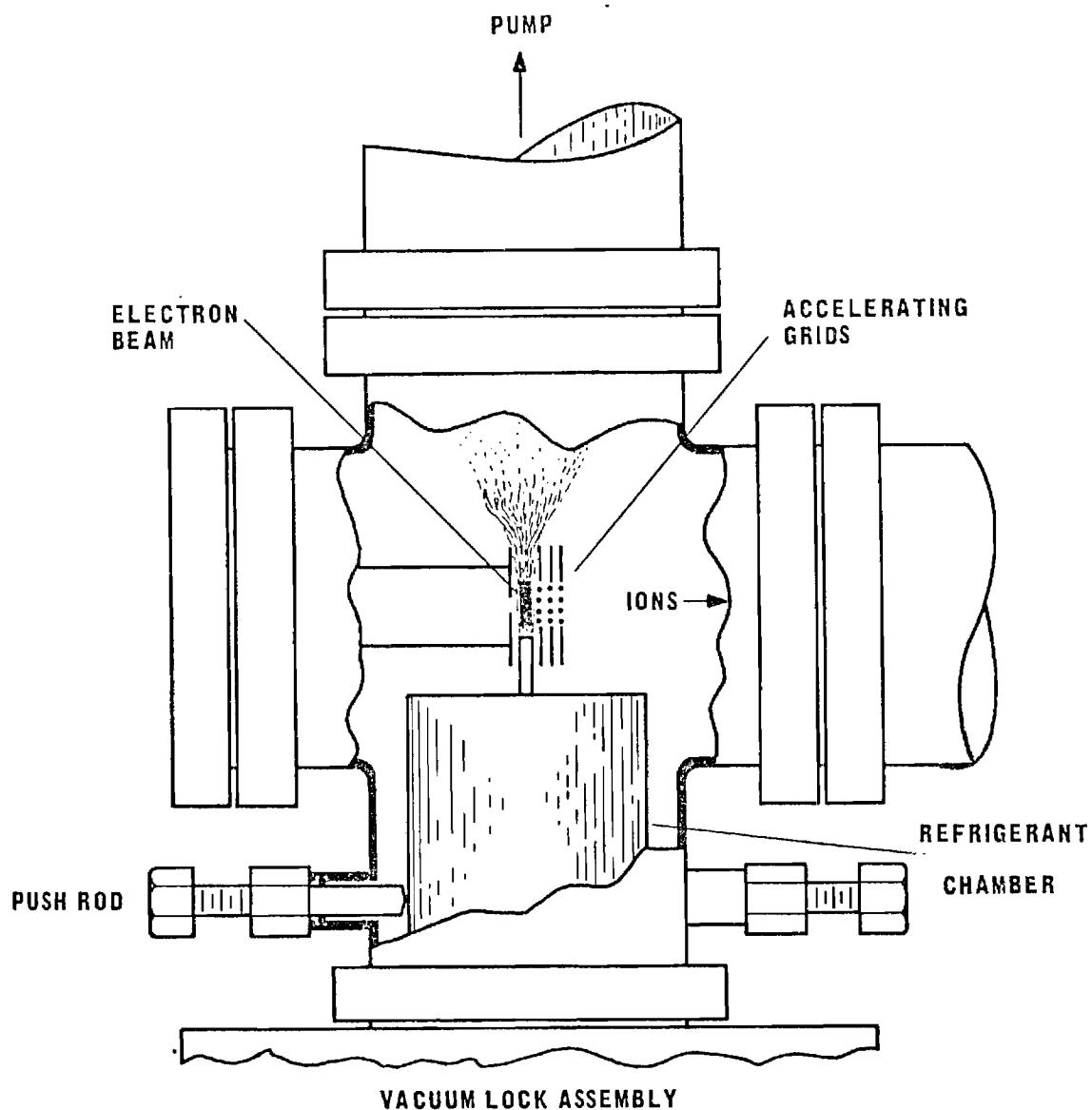


Figure 1. Top view of the "Cross" vacuum chamber of the TOF mass spectrometer which contains the source structure and which is depicted with the cryogenic reactor-inlet system in analytical position.

only one such wall collision. Design calculations, which were confirmed subsequently by experimental measurements, show that the 0.4 x 1.6 cm cross section of the nickel plated copper extension piece provides sufficient conductivity along its 2.5 cm length to insure that the sample is not heated significantly above the temperature of the refrigerant chamber when it passes through the inlet channel. The maximum calculated ΔT was 0.8°K and the measured value was somewhat less than 2°K. The difference was probably due to the thermal resistance at the solder joint where the extension piece joins the refrigerant chamber. These ΔT 's were however quite acceptable. The lateral positioning of the reactor inlet device is accomplished with a screw, and an observation port is provided to visually follow the advance of the extension piece into the ion source structure. Sidewise positioning adjustments in the plane perpendicular to that of Figure 1 are made during this advance by a pair of oppositely placed, vacuum sealed push rods which are mounted on the "cross" vacuum chamber. This rather delicate alignment situation is apparent in Figure 1. Fast pumping in the source region is provided by a nominal 750 l/sec system. The reactor-inlet system passes through a vacuum lock arrangement so that the system can be withdrawn for adjustment without the necessity of breaking the vacuum in the mass spectrometer.

C. Ion Source Collision Dynamics

Maximum detectability corresponds to the observation of usable spectra at the lowest sample pressures, hence at the lowest temperatures of the condensed samples that are of interest here, and therefore in the region of greatest thermal and chemical stability of these rather labile compounds.

As originally developed by Clausing⁵, it is possible to calculate the intensity of molecules effusing into a vacuum from a circular inlet port of area πr^2 which has some particular ratio of length to radius, L/r . The molecular intensity, N_θ at any solid angle, $d\omega$, located at some angle, θ , with respect to the center line of the port (see Figure 2), may be developed in the form of the cosine distribution function multiplied by a deviation factor, J , which is a complicated function of L/r and θ ,

$$N_\theta = [(N_t/\pi)(\cos \theta)(d\omega/dA)]J \quad (1)$$

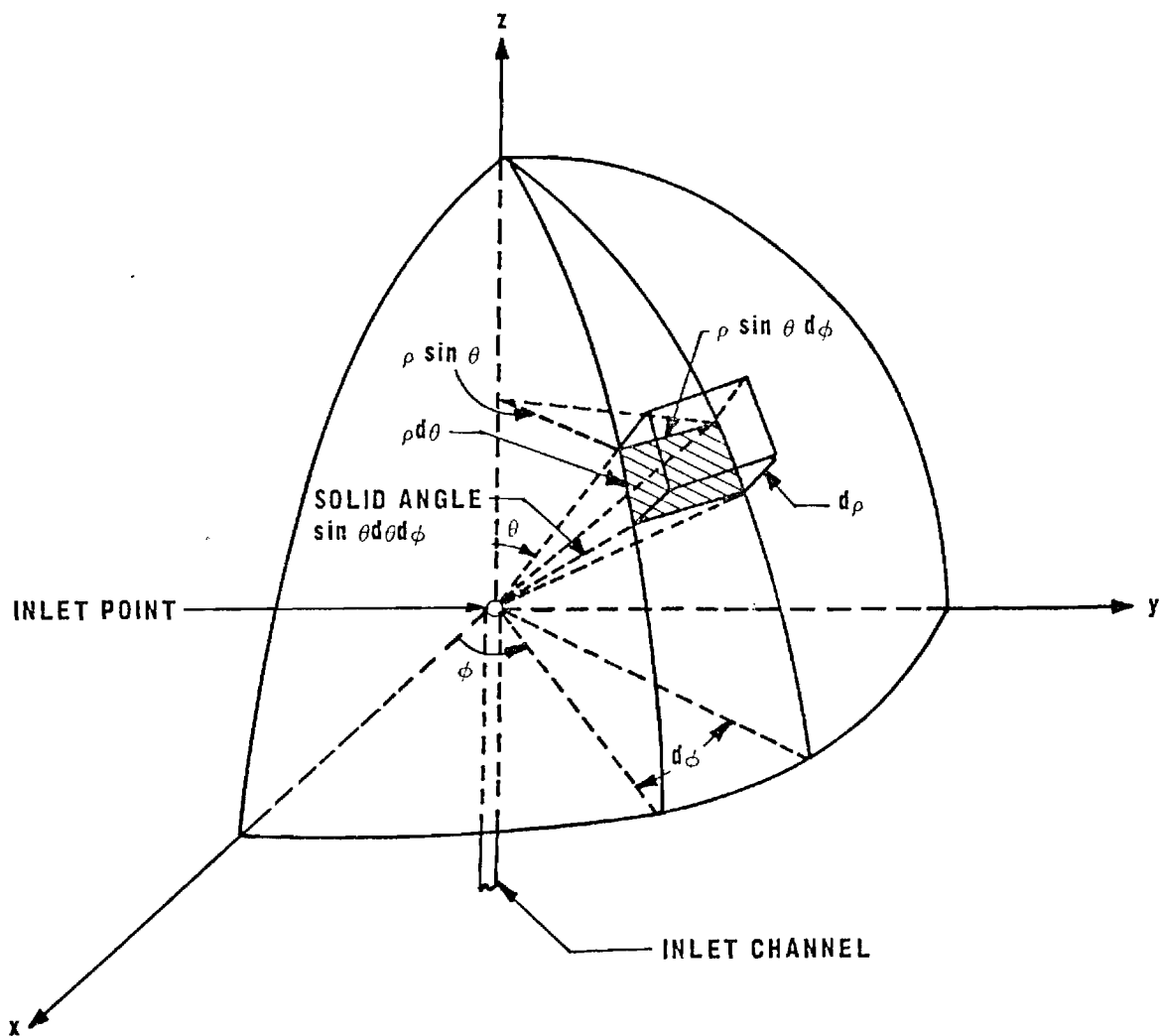


Figure 2. Spherical coordinate system for calculating the number density of molecules at any point, (ρ, θ, ϕ) , for the efflux of a gas through a hole in a thin edge orifice.

From the variation of J with L/r and θ^5 , it is evident that both the intensity at any angle and the total flow will be a maximum for a sharp edge orifice for which case J has its maximum value of unity. N_t is the rate at which molecules enter the sample inlet channel and is given by the product of the molecular number density in the sample reservoir, the average molecular speed, and the inlet area, i.e., by $PA/(2\pi mkT)^{1/2}$. We are concerned, of course, with the ionization of molecules which have suffered no collisions since leaving the inlet port. The sensitivity, S , is directly proportional to the number of these molecules that are ionized per unit time which is given by the product of the electron flux, N_e , the molecular or the target number density, $D(x,y,z)$, and the ionization cross section, σ_i . Considering the case for which the cosine distribution of intensities is correct, i.e., $J = 1$ or a sharp edge orifice, the number of molecules emitted per unit of time through the shaded solid angle, $d\omega$, shown in Figure 2 is $N_{t\theta}d\omega$ where $d\omega = \sin\theta d\theta d\phi$. Hence, the molecular flux at that point is given by $N_{t\theta}(d\omega/dA)$ where $dA = \rho^2 \sin\theta d\theta d\phi$. The number density of molecules, $D(\rho, \theta)$, at any point is given by the molecular flux divided by the average molecular velocity,

$$D(\rho, \theta) = (N_{t\theta} \sin\theta d\theta d\phi) / (\bar{v} \rho^2 \sin\theta d\theta d\phi) \quad (2)$$

which reduces to

$$D(\rho, \theta) = \frac{N_{t\theta}}{\bar{v} \rho^2} \quad (3)$$

and since $N_{t\theta} = N_t \cos\theta / \pi$,

$$D(\rho, \theta) = \frac{N_t}{\pi \bar{v} \rho^2} \cos\theta \quad (4)$$

Equation (4) gives the number density of molecules at any point in spherical coordinates and corresponds to Equation (1). Transforming Equation (4) into rectangular coordinates yields the expression

$$D(x, y, z) = \frac{N_t}{\pi \bar{v}} \cdot \frac{z}{(x^2 + y^2 + z^2)^{3/2}} \quad (5)$$

Since the probability that a given molecule will be ionized during a single pass through the electron beam is very small, it can be assumed that the number of target molecules is undiminished as a result of ionization and is therefore correctly represented by Equation (5).

The sensitivity, S , becomes,

$$S = K \int_{\text{covol.}} N_e \sigma_i dN(x, y, z) \quad (6)$$

where

$$dN(x, y, z) = D(x, y, z) dV(x, y, z) \quad (7)$$

and N_e and σ_i are the electron flux and ionization cross section, respectively. Figure 3 illustrates the general rectangular effective collision covolume of the electron beam of cross section, $2a \times 2b$ and length, $(c_2 - c_1)$, where c_1 and c_2 are the perpendicular distances from the inlet port to the nearest and far faces of the beam, respectively. Assuming that σ_i and N_e are constants and using Equation (5) and (7), Equation (6) can be written, using symmetry properties, as

$$S = (4N_t N_e \sigma_i K / \pi \bar{v}) \int_0^a \int_0^b \int_{c_1}^{c_2} [z / (x^2 + y^2 + z^2)^{3/2}] dx dy dz \quad (8)$$

After some manipulations, this equation can be integrated to yield,

$$S = \{ 4N_t N_e \sigma_i K / \pi \bar{v} \} \{ a \ln[\gamma_2(b + \beta_1) / \gamma_1(b + \beta_2)] \\ + b \ln[(\alpha_2 + \beta_2 - a)(\alpha_1 + \beta_1 + a) / (\alpha_2 + \beta_2 + a)(\alpha_1 + \beta_1 - a)] \\ + c_2 \tan^{-1}(a/c_2) - 2c_2 \tan^{-1}[ac_2 / (\alpha_2 + b)(\alpha_2 + \beta_2)] \\ + 2c_1 \tan^{-1}[ac_1 / (\alpha_1 + b)(\alpha_1 + \beta_1)] - c_1 \tan^{-1}(a/c_1) \} \quad (9)$$

where, $\alpha = (b^2 + c^2)^{1/2}$; $\beta = (a^2 + c^2)^{1/2}$; $\gamma = (a^2 + b^2)^{1/2}$; and where the factor, J , has been taken to be constant and equal to its maximum value of unity. Equation (9) predicts the approximate number of molecules ionized per unit time with the near face of the electron beam a distance c_1 away from the sample inlet port for the case where (1) the flow out of the inlet channel is molecular, (2) the inlet channel is a thin edge orifice, i.e., cosine distribution of intensities from the inlet port, (3) the axis of the inlet channel is aligned with the center axis of the electron beam, and (4) the inlet port is approximately a point source.

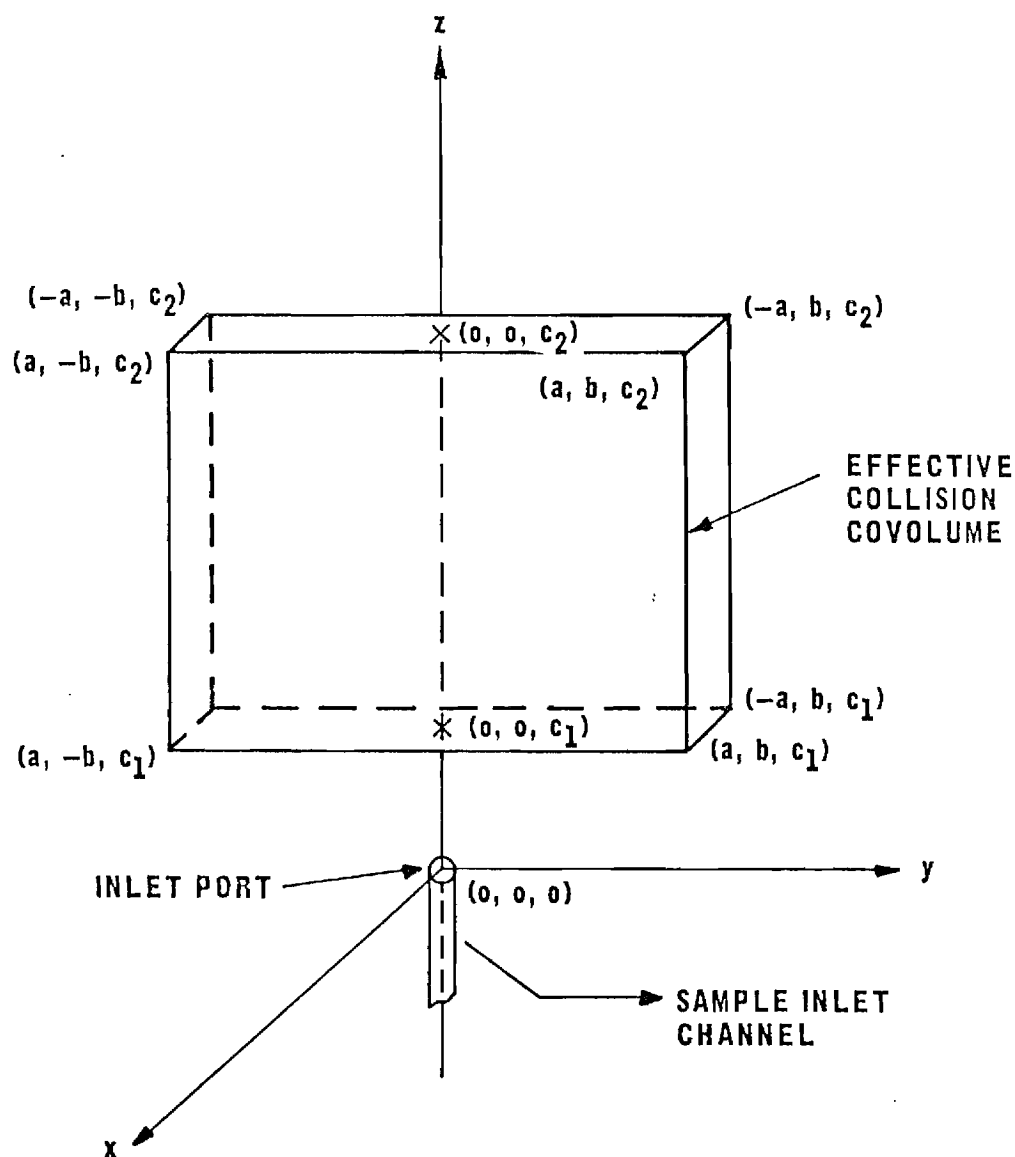


Figure 3. Rectangular coordinate system for integrating over the effective collision covolume to determine the total sensitivity for a given position of the inlet port relative to the electron beam.

For the perpendicular arrangement of the inlet port relative to the electron beam, the geometrical parameters in the Bendix source structure, a , b , and $(c_2 - c_1)$, are 0.038 cm, 0.318 cm, and 0.50 cm, respectively. for the coaxial arrangement these parameters are 0.25 cm, 0.318 cm, and 0.076 cm, respectively. Substitution of these values into Equation (9) for various values of c_1 gives the variation in sensitivity for the two arrangements as a function of the distance of the sample inlet port from the electron beam. The factor $S \bar{v} / N_t N_e \sigma_i K$ (more conveniently written $F\bar{v}$) was computed from Equation (9) for both the perpendicular and coaxial arrangements for values of c_1 between $c_1 = 0$ and $c_1 = 3.0$ cm at intervals of 0.005 cm. Some of the values of this factor are tabulated in Table I. $F\bar{v}$ is equivalent to the fraction of molecules effusing from the inlet port per unit time that appear in the effective collision covolume of the electron beam multiplied by the average molecular speed (i.e., $N_b \bar{v} / N_t$) where N_b is the number of molecules in the collision covolume. The paramount importance of minimizing the distance between the inlet port and the electron beam is clear, for if the inlet port is only two mm away from the beam, the sensitivity is down by a factor of four for the perpendicular case. From Table I it was concluded that both the perpendicular and coaxial arrangements provide about the same sensitivity at equal displacements from the near face of the electron beam. These predicted trends have been experimentally verified; e.g., moving the inlet port about 6 mm away from its optimum position results in sensitivity losses of an order of magnitude.

The major deductions from these results were: (1) that the coaxial arrangement and the perpendicular arrangement are equivalent so far as sensitivity is concerned, and (2) the investigation of species that are destroyed in a single collision should be performed with the sample inlet port as close as possible to the electron beam, within less than 3 mm if possible. In view of deduction (1), and the mechanical conveniences discussed earlier, it was concluded that the perpendicular arrangement was preferable to the coaxial arrangement, and the system was designed in that way.

The sensitivity for a stable species also decreased appreciably as the distance of the inlet port from the electron beam was increased, despite the fact that, unlike the cryochemical species, there is an appreciable background due to the stable species. A stable CO_2^+ ion current from CO_2 was observed, and the variation of this current with distance of the inlet

TABLE I. Variation of Sensitivity with Relative Configuration of Electron Beam and Inlet Port

Configuration	Geometrical Parameters (cm)				$\bar{v} F^*$ (from Eq. (9))
	a	b	c_1	c_2	
Perpendicular Arrangement	0.038	0.32	0.0	0.5	0.156
	0.038	0.32	0.2	0.7	0.0387
	0.038	0.32	0.8	1.3	0.0070
	0.038	0.32	1.4	1.9	0.0028
	0.038	0.32	2.0	2.5	0.0015
Coaxial Arrangement	0.250	0.32	0.0	0.076	0.134
	0.250	0.32	0.2	0.276	0.0594
	0.250	0.32	0.8	0.876	0.0087
	0.250	0.32	1.4	1.476	0.0036
	0.250	0.32	2.0	2.076	0.0018

* F is the fraction of molecules entering the inlet channel per unit time that appear in the collision covolume and is equivalent to $S/\sigma_i N_t N_e K$. Maximum detectability with respect to the relative configuration of the electron beam and the inlet port corresponds to a maximum value of F .

port from the electron beam was studied. Figure 4 illustrates the variation that was obtained. It can be seen that the intensity decreases by a factor of about 13 when the inlet port is moved from its optimum position, where the electron beam is in grazing incidence, to a distance about 2.5 cm away from the near edge of the electron beam. This is an order of magnitude less than the factor of about 150 indicated from Table I for an unstable species, i.e., with no allowed background sample, but the decrease still represents a considerable loss of sensitivity.

The above calculations are for the case where the inlet port is a thin edge orifice which corresponds to the optimum design for a circular channel. A better arrangement would be a thin edge slit which would take advantage of the entire effective length (0.64 cm) of the electron beam. This would be particularly advantageous for the perpendicular arrangement.

It should be noted that if it is not necessary to maintain a minimum pressure, i.e., a minimum temperature, in the inlet system, then a greater sensitivity can be obtained by using a long inlet channel rather than a thin edge orifice. The limiting variable in this case would be the total sample influx that can be handled by the mass spectrometer pumping system. A more directed flow is obtained with a channel and would result in more molecules in the region of the electron beam for the same total mass flow rate through the inlet port.

Calculation of the sensitivity for this case would involve integration over the effective collision covolume where the factor J is included.⁵ The integral involved is a very complicated function of L/r and θ would be very difficult to compute.

A qualitative indication of the sensitivity permitted with various channels can be obtained without integrating over the collision covolume. That is, the fraction of molecules, n , entering an inlet channel of finite length which finally emerge within an angle θ with respect to the axis of the channel can be computed from the following integral

$$n = \int_0^{\theta} J \sin 2 \theta \, d \theta \quad (10)$$

where J is the deviation factor discussed above.

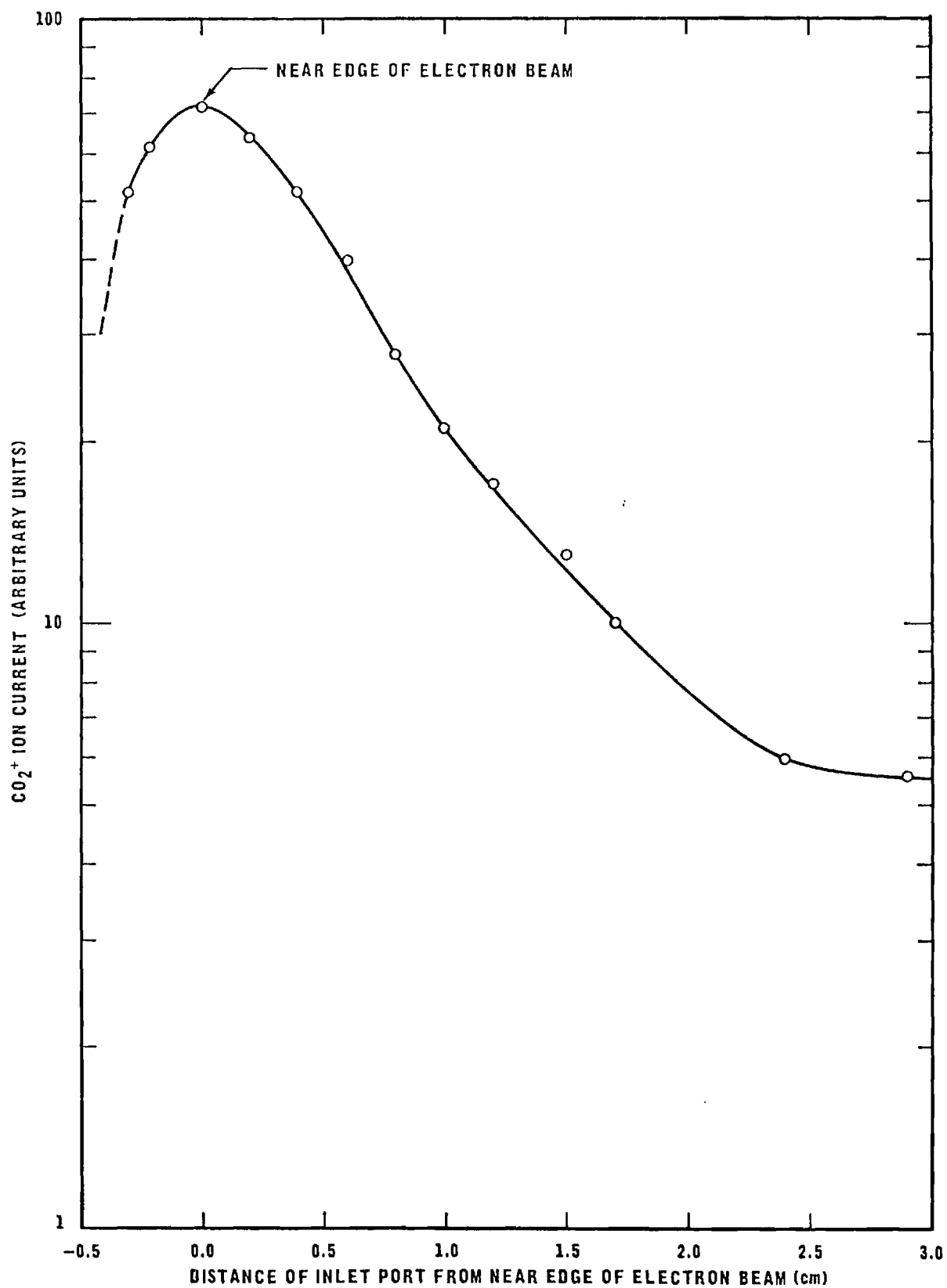


Figure 4. Variation of sensitivity with relative configuration of electron beam and inlet port for the perpendicular arrangement using CO_2 as a test gas.

The value of n has recently been computed numerically and tabulated for numerous values of the parameters L/r and θ .⁶ Using these results, the fraction of molecules that actually effuse from the inlet port within an angle θ with respect to the channel axis was calculated and is summarized in Table II. The first row (i.e., for $L/r = 0$) is for the case of an infinitely thin edge orifice for which $J = 1$. It is quite obvious from Table II that the flow of sample becomes increasingly more directed in the forward direction for larger values of the length to radius ratio, L/r . For instance, the fraction of molecules emitted within an angle $\theta = 20^\circ$ is more than twice as great for a channel with $L/r = 10$ than for an infinitely thin orifice. These results indicate that a long exit channel would be quite desirable for experiments in which it is permissible for the cold sample to be maintained at pressures of several torr.

Table II. Fraction of Molecules Effusing From a Cylindrical Channel Within an Angle θ With Respect to the Axis of the Channel.

L/r	20°	30°	40°	50°	60°	70°	80°
0	0.1170	0.2500	0.4132	0.5868	0.7500	0.8830	0.9699
.1	0.1219	0.2594	0.4269	0.6034	0.7670	0.8971	0.9774
.2	0.1267	0.2686	0.4401	0.6188	0.7820	0.9084	0.9817
.5	0.1405	0.2940	0.4749	0.6573	0.8154	0.9272	0.9835
1.0	0.1610	0.3294	0.5185	0.6974	0.8383	0.9311	0.9838
1.2	0.1682	0.3411	0.5313	0.7059	0.8400	0.9315	0.9839
1.5	0.1784	0.3563	0.5461	0.7133	0.8415	0.9321	0.9840
2.0	0.1933	0.3763	0.5609	0.7179	0.8438	0.9332	0.9843
3.0	0.2167	0.3996	0.5721	0.7241	0.8471	0.9346	0.9848
4.00	0.2329	0.4100	0.5787	0.7283	0.8493	0.9352	0.9848
6.00	0.2509	0.4225	0.5871	0.7334	0.8519	0.9364	0.9850
10.0	0.2663	0.4341	0.5949	0.7385	0.8542	0.9373	0.9850

CHAPTER III

RESEARCH RESULTS - CRYOCHEMISTRY

Studies have been conducted on a variety of chemical systems with the general objective of developing new chemistry under the extreme condition of cryogenic cooling. Some new phenomena have been observed. Although the compounds discussed here may seem large, they are not so large as to be meaningless vis a vis the astrophysical questions that are at hand. For example, in the last two or three years, similar compounds have been observed in space by radio astronomy including H_2CO , CH_3OH , NH_3 , HCN , HCCCN , HCOOH , CH_3CCH , HNCO , and HNC . Some of these same compounds appear in the following discussion of results from our cryochemical investigations. Some of these compounds also have biological significance, and they are of great concern in exobiology. Mass spectrometric cracking patterns and molecular energetics by electron impact techniques have been the primary means of characterization. In this chapter, we present a cursory summary of these research results.

A. Three Carbon Strained Ring Compounds - Cyclopropene, Cyclopropanone, and Cyclopropenone.

CO_3 is a possible important species in the atmosphere of Mars. We became interested in this compound and in closely related species such as the isoelectronic cyclopropanone. This latter compound would have a higher probability of successful synthesis than would CO_3 . These species possess abnormal bonding in the form of small valence angles, and this leads to poor bonding orbital overlap and weak bonds--a condition that is commonly described by the term "ring strain." This abnormal bonding creates a driving force for the molecule to enter into those reactions that would lead to relief of

this strain. Thus, at room temperature, the reactivity may be so great that some molecules exhibit only a fleeting existence. Our interest is in the quench stabilization of such species. The primary effort in this work was to investigate four ring compounds and, from mass spectral and energy measurements at low temperatures, to derive a consistent body of calculated results which would relate such quantities as heats of formation (ΔH_f^0), bond energies (E), bond dissociation energies (D^0), activation energies (ΔH_{act}), and ring strain. Studies at room temperature versus those at low temperatures were used to discern changes in structure, decomposition, etc. with temperature for these reactive molecules. The causes and results of the instability of these molecules would necessarily determine procedures and precautions for their convenient handling. When this work was begun, two of the target molecules, cyclopropanone and cyclopropenone, had never been isolated as pure species and much of the work involved synthesis and separation problems. Cyclopropene, a reactive olefin; cyclopropane, an energetic model for cyclopropanone; and cyclobutanone, a by-product of the cyclopropanone synthesis, were also investigated.

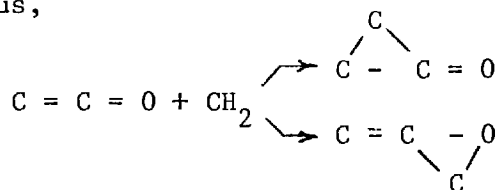
Although it had long been postulated as a reaction intermediate and although it had shown fleeting, but detectable, existence, cyclopropanone had not been isolated as a pure species. Shortly after this work was begun, two papers appeared almost simultaneously, both describing the low temperature synthesis (-78^0) from ketene and diazomethane in solutions of methylene chlorine⁷ and liquid propane⁸. These reports on the stability and the polymerization of the reactive product agreed with the results from our study.

In an unusual and unique process, we synthesized cyclopropanone by the direct liquid-liquid, solvent free, reaction of diazomethane and ketene at -145° . This is a synthesis with many novel and interesting facets. It is very unusual to find a liquid-liquid reaction which will proceed at such a low temperature without any external form of activation. The reactor, submerged in a coolant at -145° , quickly conducted away the heat of reaction and prevented the molecule from decomposing. The species had been reported to decompose into CO and C_2H_4 upon its formation in the gas phase⁹. The low temperature also served to slow the rate of cyclopropanone polymerization. The use of low temperatures, pure reagents, and a great excess of ketene led to yields of better than 50 per cent cyclopropanone with the four membered ketone ring, cyclobutanone, as the only side product. Although cyclopropanone can be kept indefinitely at -196° , it appears to begin to slowly polymerize at -90° and reacts so rapidly at room temperature that samples are destroyed within minutes. This reactivity at room temperature causes a severe analysis problem and cyclopropanone can be conveniently studied only at low temperatures.

Although cyclopropanone had been reported to decompose upon its formation in the gas phase reaction of CH_2N_2 and CH_2CO , after quenching to -196° , we found that heating the molecule to room temperature produced no evidence of decomposition or structural changes, but rather an increase in the rate of polymerization. The polymer formed was a white, porous looking solid. The ionization potentials, appearance potentials, and excess energies of the principal ions from cyclopropanone and cyclobutanone were experimentally measured, both over the quenched product and after purification, and their molecular energetics were calculated therefrom. The ionization potentials of cyclopropanone and cyclobutanone were measured to be 9.1 eV and 9.4 eV,

respectively. Both of these values were supported by molecular orbital calculations that were performed in this laboratory and which are discussed later in this report. The important massspectral and critical potential measurements on cyclopropanone are summarized in Table III. With diazomethane in excess, the reaction products were largely C_4 and some C_5 ketones, but very little of the C_3 ketone. In metal systems which catalyzed the decomposition of CH_2N_2 , cyclopropane was observed due to the reaction of CH_2N_2 with its decomposition product ethylene at very low temperatures.

There was also some evidence for the formation of the unknown species allene oxide from the attack of the CH_2 upon the C-O rather than the C-C bond of ketene. Thus,



It is also interesting to note that the IP of cyclopropanone is more than an eV lower than that of its open chain isomer acrolein at 10.25 eV. This is due to the increased ground state energy of cyclopropanone plus the decreased energy of its ion due to the ability of the ring to accommodate the positive charge. The appearance potential of $C_2H_4^+$ and CH_2CO^+ are 10.2 and 9.9 eV respectively which are lower than the IP's of the parent species themselves. This again is expected in view of the highly strained (see following discussion) ring system which needs very little energy to break.

Cyclopropene, described in the literature as very reactive and explosive, was investigated both because of this reactivity and as an energetic model for cyclopropanone. It was found to be much easier to handle than one would expect from the literature as it was synthesized,

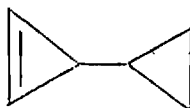
TABLE III

Summary of Mass Spectral and Critical Potential Data On
Cyclopropanone and Its Coproduct Cyclobutanone

m/e	C ₃ H ₄ O at -90 ^{oa}	Appearance Potentials (eV)	C ₄ H ₆ O at -70 ^{oa}	Appearance Potentials (eV)
70			20	9.4
56	15	9.1	3	
42	15	9.9	100	11.0
41	5		14	
39	4		16	
38	4		5	
37	4		5	
36	3		2	
28	100	10.2		13.0
27	35	12.9	12	14.1
26	34	13.5	8	
15				15.7
14		11.6	7	16.7

^aTemperatures of -90^o and -70^o for the C₃ and C₄ ketones respectively were levels at which the species exerted convenient vapor pressures in the cryogenic mass spectrometric inlet system. It was however not possible to completely separate the C₃ ketone from the C₄ species due to the similarity of their vapor pressures.

distilled, and transferred at room temperature with no change in structure and with only an insignificant loss from polymerization (which only became noticeable at room temperature). A one week exposure to room temperature destroyed most, but not all of the species. Some dimer was also formed,



Unfortunately, the mass spectrum of cyclopropene consists of very intense ion peaks corresponding to the positively charged, intact ring and very weak ions resulting from ring fragmentations. The ionization efficiency curves of the weak ion signals were of such poor quality that reliable experimental appearance potentials could not be obtained and hence it was impossible to unambiguously develop the molecular energetics. The ionization potential of cyclopropene was measured to be 9.6 - 9.7 eV which was supported by our molecular orbital calculation of 9.6 and close enough to a literature value of 9.95 eV to attribute the differences to experimental errors.

Cyclopropene was studied at -145° and room temperature ($\sim 25^{\circ}$). Although it is known to polymerize at -80° and although the polymerization is believed to be a reaction of the excited double bond diradical¹⁰, no experimentally detected change in the ionization potential (9.6 - 9.7 eV) from -145° to 25° proved that any formation of a triplet species occurs in such small amounts as to be experimentally unimportant.

Cyclopropanone was similarly studied at -90° and at 25° . Although it was seen to polymerize quite rapidly at room temperature and although many of its reactions in solution are postulated to proceed through the ring

opened dipolar ion (23 kcal/mole more stable than the closed ring¹¹), no change in the ionization potential with temperature (9.1 eV) likewise implies no detectable presence of these structures. A difference in structure would, of course, have invalidated physical data taken at room temperature. Mass spectral and energetic data are summarized in Table IV.

According to Breslow¹², the reaction of tetrachlorocyclopropene with tri-n-butyltin hydride at room temperature produces a volatile mixture of chlorocyclopropenes which, when collected in CCl_4 and hydrolyzed with water, produces cyclopropanone in water solution. Breslow postulates the existence of the free ketone, not the gem diol, even in water solution; however, he states that all attempts to separate and isolate the molecule have led to ". . . at least partial polymerization of the compound." He also reports that the ketone may be extracted from water solution by polar solvents and that it is much less reactive and more stable than its saturated analog, cyclopropanone. His paper strongly suggests that cyclopropanone was synthesized and implies that the failure to isolate cyclopropanone was due only to its tendency to polymerize.

Based on our previous work on cyclopropanone and these reactivity statements, we reasoned that cyclopropanone would most certainly be stable enough for cryogenic mass spectrometric analysis once it was separated from its solution. Since it could be extracted, the obvious approach was to find a polar solvent which would allow separation of the ketone at a low enough temperature to prevent polymerization. Although the reported¹² synthesis and nmr analysis for cyclopropanone were reproduced, we were unable to isolate the ketone by any of the following techniques: extraction of the

TABLE IV

Summary of Mass Spectral and Energetic Data on Cyclopropene

m/e	Intensity At -140°	Appearance Potential (eV)
40	60	9.7
39	100	10.9
38	36	
37	23	
36	6.8	
28	< 5	
27	< 2.3	
26	5.7	
15	< 0.6	
14	5.7	
13	< 2.3	

ketone from water solution using different solvents; performing the hydrolysis step in water soluble solvents; partial hydrolysis of the dichlorocyclopropene sample with less than the stoichiometric amount of water; and drying of the solutions to remove dissolved water. We are unable to reasonably explain these failures, and hence we conclude that this very interesting compound must be ascribed as being as elusive as ever.

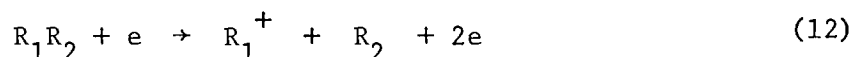
B. Excess Energy in Molecular Fragmentations.

The literature abounds with examples of fragmentations that contain excess energy. In general, the parent molecular ion contains no excess translational energy and rarely does it contain excess vibrational energy as well. For fragment ions however, the probability of excess energy increases with increase in the number of bonds that are broken. In general, for a molecule R_1R_2 in which $I(R_1) < I(R_2)$, R_2^+ will usually appear with excess energy. Thus we expect at least half of all fragment ions will occur with excess energy. Also we observe that a more abundant fragment ion has less excess energy and vice versa. Thus the ions of low abundance from the necessary breaking of two bonds in the 3-carbon ring compounds will very likely contain excess energy.

Recently a technique for determining excess energy from a peak shape analysis, i.e., based upon the focusing properties of the energetic ions, has been developed for the TOF spectrometer¹³. In addition, this measured kinetic energy of a fragment ion has been rather well correlated with the total excess energy, E^* , in the fragmentation event by the relation,

$$\bar{e}_t = E^* / \alpha N \quad (11)$$

where α is an empirical constant which was found to be approximately the same for a large number of fragmentation processes in a wide variety of molecules, and N is the number of classical oscillators in the parent molecule. The form of this expression comes from a consideration of the distribution of energy E^* among N classical oscillators. In the fragmentation event,



the excess energy is

$$E^* = A(R_1^+) - \Delta H_r^0 \quad (13)$$

The total translational energy of the fragments, \bar{e}_t , is calculated from the measured translational energy of the fragment ion, \bar{e}_i , from momentum balance considerations, and the result is

$$\bar{e}_t = \left(\frac{M_i + M_n}{M_n} \right) \bar{e}_i - \left(\frac{M_i}{M_n} \right) (3/2kt) \quad (14)$$

where M_i and M_n are the masses of the ion and the neutral species from the fragmentation event. From measurements of $A(R_1^+)$ and thus E^* and from measurements of \bar{e}_i and thus \bar{e}_t on a wide variety of molecules, α was found to be very nearly equal to 0.44 for all fragmentations.

A consideration of the ion optics in the Bendix TOF machine leads to the following expression for \bar{e}_i

$$\bar{e}_i = (N_o^2 / 3.69) (qE_s)^2 (W_{1/2}^2 / M) \quad (15)$$

where \bar{e}_i is in eV, N_o is Avogadro's number, q is the charge on the ion, E_s is the ion accelerating potential in the source, $W_{1/2}$ is the peak width at half-height and M is the mass of the ion. The broadening of an ion signal results from the fact that ions are formed in the source with

initial velocities in the direction of acceleration, hence they do not all start from rest, and thus their flight times are different. The method employed here then merely uses the degree of broadening to determine the initial kinetic energy of the ions.

Instrumental factors that affect the intensity of an ion peak in a multiplicative manner did not significantly affect the peak shape. However all of the ion focusing controls were crucial to the measurements.

The excess energies were a function of energy as typically shown in Figures 5 and 6. The data of Figure 5 were reproductions of previous work to authenticate our technique. The curves vary widely in character depending on the potential energy surface of the activated complex. The data of Figure 6 for CH_2^+ from cyclopropane are particularly interesting. Neglecting the rapidly falling data very near the AP, and extrapolating the more gentle higher energy data to the AP yields $\bar{e}_1 = 0.35$ eV and $E^* = 103$ kcal/mole which is in good agreement with earlier data on this process. Rather if we accept this unusual phenomenon (which we have observed only in these strained ring systems) the energetics can be interpreted by assuming that C_2H_4 and CH_2^+ are produced in excited triplet states. As the bombarding electron energy is increased, some ions are produced as excited triplets with little excess energy while others degenerate to the ground electronic singlet states with the concomitant production of large amounts of excess vibrational and translational energy in the fragments. At some still higher electron energy, almost all of the fragments are produced in the ground electronic states with excess vibrational energy and the upper curve is produced.

The extrapolated excess energies at the appearance potentials for all ions studied here are summarized in Table V. The precision of the data

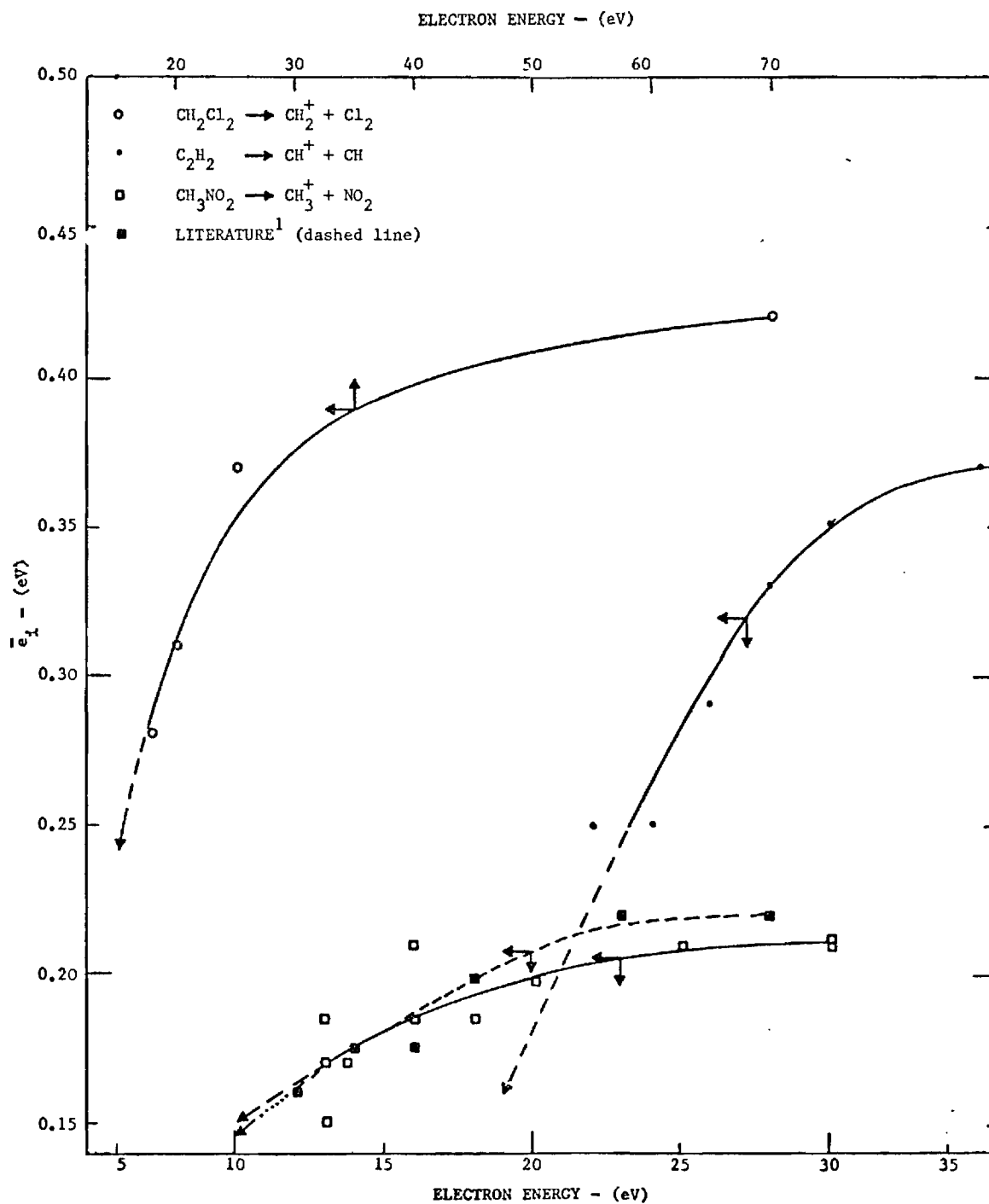


Figure 5. \bar{e}_1 Versus Electron Energy for Verification of Experimental Technique

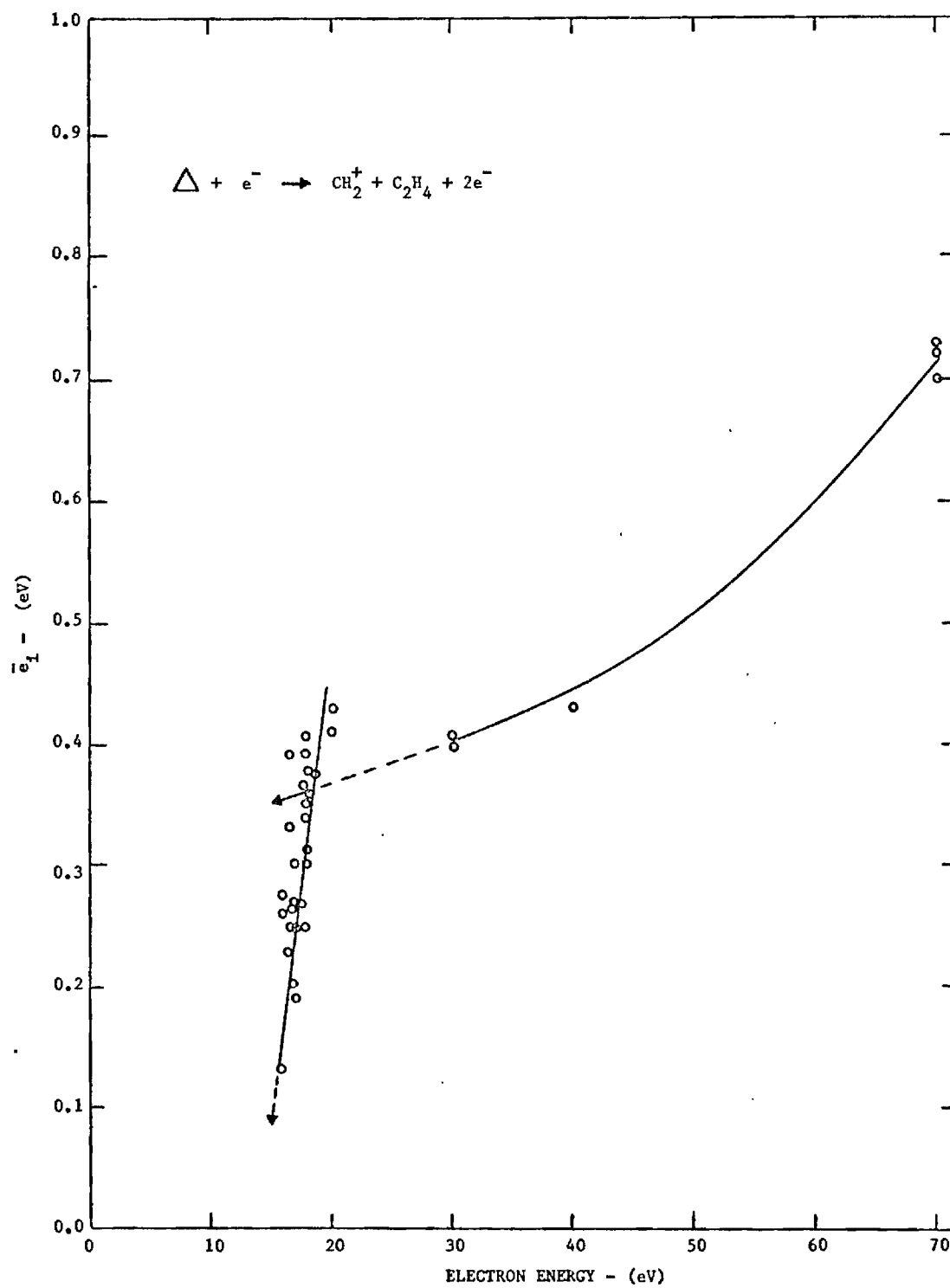


Figure 6. \bar{e}_1 Versus Electron Energy for $\text{cy-C}_3\text{H}_6 \rightarrow \text{CH}_2^+$

TABLE V

Summary of Excess Energies (kcal/mole) at AP
for All Compounds Studied in This Research

Parent Molecule	Ion	\bar{e}_i	\bar{e}_t	E^*	Literature ¹ E^*
CH_2Cl_2	CH_2^+	5.5	6.5	28	36
C_2H_2	CH^+	3.7	7.0	21	19
CH_3NO_2	CH_3^+	3.5	4.2	29	29
cy- C_3H_6	C_2H_3^+	1.4	2.1	19	21
	C_2H_2^+	1.4	1.8	16	15
	CH_2^+	8.0	11.5	103	113
		1.6		18	
	C_2H_4^+			--	
	CH_3^+			0	
	C_2H_4^+	1.54	2.2	17	
cy- $\text{C}_3\text{H}_4\text{O}$	$\text{C}_2\text{H}_2\text{O}^+$	1.22	2.2	17	
	$\text{C}_2\text{H}_2\text{O}^+$	1.53	2.5	26	
cy- $\text{C}_4\text{H}_6\text{O}$	C_2H_4^+	1.27	1.7	18	
	C_2H_3^+	2.25	3.1	33	
	CH_2^+	2.08	2.3	24	
	CH^+	1.5	1.8	12	
cy- C_3H_4	C_2H_2^+	1.25	2.0	13	

1. M. A. Haney and J. L. Franklin, J. Chem. Phys., **48**, 4093 (1968).

varies greatly, but the resulting correlated excess energies, E^* , have explained the molecular energetics of this family of strained ring compounds as is evident in the following section of this report.

C. Derived Molecular Energetics.

The molecular energetics of highly reactive cryochemicals is important in understanding both their reaction kinetics and stability characteristics as well as, of course, their thermodynamics. In this research, the molecular energetics were developed by electron impact techniques. One of the major problems in the interpretation of such data is the occurrence of energy of excitation in either or both of the ion and neutral fragments in the ionization process itself. The cyclic, strained compounds are a convenient mechanism for the general study of this problem, and the data are, of course also directly applicable to these compounds of astrophysical interest.

In our work, it was found to be very common for the fragments produced upon electron impact of ring compounds to possess excess translational and vibrational energy, but rare for the measured appearance potential to correspond to a fragment in an excited electronic state. This excess energy may be viewed as residual energy from the formation of multiple bonds in the fragments. The introduction of a rearrangement correction term for the energetic difference in the initial and final ring fragmentation products, i.e., the excess energy of the fragmentation process, allowed us to assign ring bond energies to particular bonds and enabled bond dissociation energies and an estimation of ring opening activation energies to be calculated which seem to relate well to literature data from various other kinds of experiments.

Cyclopropane was investigated as an energetic model from which the molecular energetics of cyclopropanone could be discussed. The literature on cyclopropane discusses strain energies, heats of formation, ionization and appearance potential measurements, structure, mechanisms, and reactions. If our mass spectrometric data could be correlated with other existing data for this molecule, a similar and confident interpretation of the new molecule, cyclopropanone, would be possible. The energetics of cyclopropane were successfully explained by the insertion of an energetic rearrangement term, $R(R_1)_g^{ex}$, in the equations for calculating bond energies, $D^O(R_1-R_2)$ and $D^O(R_1^+-R_2)$. This energetic rearrangement term represents the energy difference between a hypothetical initial diradical and the final ground state structure for the fragments which result from breaking two carbon-carbon (C-C) ring bonds. From our measurements with cyclopropane, we were able to calculate the following values (kcal/mole) which compared well with literature data:

$$\Delta H_f^O = 13 \pm 3 \quad (\text{lit.} = 12.7)$$

$$\text{ring strain} = 36 \quad (\text{lit.} = 27 \text{ relative to paraffins})$$

$$E(\text{C-C}) = 75$$

$$D^O(\text{C-C}) = 52 \quad (\text{lit.} = 49)$$

$$\Delta H_{act}(\text{ring opening}) = 65 \quad (\text{lit.} = 65)$$

and wherein the ring strain is localized to the carbon-carbon ring bonds.

Heats of formation in the gas phase of cyclopropanone and cyclobutanone were calculated from our mass spectrometric data to be 27 ± 8 and 13 ± 5 kcal/mole. Bond energies were used to calculate additional ring

strains of 36 and 19 kcal/mole with respect to cyclopropane and cyclobutane, respectively. By a procedure analagous to the one used for cyclopropane, the following values were prediced for cyclopropanone:

$$E(C-C^{\dagger}) = 66; E(C-C) = 40$$

$$D^0(C-C^{\dagger}) = 45; D^0(C-C) = 20$$

$$\Delta H_{act}(C-C^{\dagger}) = 61; \Delta H_{act}(C-C) = 35$$

It would be quite interesting to predict an activation energy for ring opening at the C-C (rather than the C-C[†]) bond in cyclopropanone in order to support or dispel the theory that cyclopropanone reactions in solution proceed with a low activation energy via the ring opened dipolar ion. The latter value above supports the theory¹¹ that cyclopropanone solution reactions do indeed proceed via such a ring opened dipolar ion, but this conclusion is totally dependent upon inclusion of the rearrangement energy term. Without the inclusion of $R(R_1)_g^{ex}$ terms, mass spectrometric results would predict a stronger bond at the distant carbon-carbon bond, $d(C-C) = 1.58 \text{ \AA}$, than the shorter carbon-carbon bond, $d(C-C^{\dagger}) = 1.49 \text{ \AA}$. This result particularly points out the necessity of the rearrangement term.

In this work, an experimental procedure was developed to calculate, from mass spectrometric data, the ΔH_f^0 for molecules to within about ± 5 kcal/mole. Any lack of precision in the appearance potential and excess energy measurements is partially overcome by using more than one fragment ion to calculate ΔH_f^0 . This measurement is only worth the trouble for molecules

[†] carbonyl carbon

with structures from which it is not possible to make a good estimate of ΔH_f^O from other more precise methods. It is particularly adaptable to small rings because the fragments are produced in ground electronic states and correspond to molecules for which ΔH_f^O and ionization potential are usually known and need not be measured. However, it is necessary to check for the occurrence of excess translational and vibrational energies. This technique is simply the reversal of the normal energetic treatment from which the heat of formation of the fragment ion is calculated from the appearance potential by knowing the ΔH_f^O of the parent molecule.

During the course of this work, secondary efforts were needed to develop techniques for the measurement of appearance potentials of ions with long-tail ionization efficiency curves (a more asymptotic-like approach to zero intensity with decreasing electron energy). The determination of critical potentials from ionization efficiency curves that have standard shaped curves (positive slope at zero intensity) is obtainable by any number of methods with varying degrees of precision. These methods include initial break, semi-log matching, retarding potential difference, linear match, and extrapolated difference techniques. On the other hand, the appearance potential of ions with long-tail curves required methods that would separate the curve into sections pertaining to single processes each of which must be interpreted individually. The appearance potential of some of these long-tail, low abundance ions were experimentally undeterminable by any of the above electron impact methods. In any event, by looking for good match of the curves over the first two eV of the curve, one could obtain higher precision and still have a method that emphasizes the initial onset region of the ionization efficiency curve.

An effort was made to apply molecular orbital theory to these ring systems. This work involved no development of molecular orbital theory but merely the application of each of four available computer programs to these ring molecules^a. Although MO calculations have been performed for some time, it is only in the last few years that new notions, particularly semi-empirical theory, as well as efficient computer programs have been developed which seem to permit the calculation of quantities of chemical interest to within useful accuracies. The four programs used in this work were written by Klopman¹⁴ and Baird¹⁵, both working with M. J. S. Dewar, Pople¹⁶ and Hoffmann¹⁷. We wished to calculate the ionization potential and heats of atomization (ΔH_a) for comparison with experimental data and to use the molecular orbital theory to help predict the structure of these reactive molecules. For these very reactive species, experimental structure determinations may be a long time forthcoming and it was hoped that mass spectrometric data reinforced by molecular orbital theory could provide some valuable insights. Because of the inability of molecular orbital calculations to predict known molecular structures or even most stable structures from which accurate ΔH_a and ionization potentials could be calculated, theoretical chemists have had to adjust molecular parameters by empirical means such that ΔH_a and ionization potentials could be calculated accurately (on the average)

^aAll four programs were obtained from the Quantum Chemistry Program Exchange at Indiana University.

for broad classes of compounds whose actual experimental bond lengths and angles are similar enough to allow a set of "standard" molecular geometries to be used for all molecules in the calculations.

Of the four molecular orbital programs used in this work, the Baird and Klopman programs calculated usable numbers for ΔH_f^O and ionization potentials while only the Pople program appeared to show any promise of structure prediction. Because of the insensitivity of the ionization potential to geometry changes and the good accuracy of calculated versus experimental ionization potentials, the Klopman and Baird programs appear to be usable for calculating ionization potential for cryogenic ring molecules. However, the strong geometry dependence (especially the C-C ring bonds) of both Baird and Klopman programs prevents the use of these two programs for calculating ΔH_f^O until some confidence is gained in assigning standard geometries to abnormal rings. This assignment is further complicated for ring molecules having unmeasured geometries. Although the triplet calculations appear usable for parent molecules, the application to fragments appears to be also dependent on some better understanding of standard geometries. This confidence in assigning standard geometries may be obtainable by working with many known strained rings, or for a particular ring molecule with a family of substituted derivatives of known structure and properties, good agreement may result from calibrating the programs for this family of molecules as has been done for the cyclopropane and cyclopropene families¹⁸. Once this confidence is gained, the programs offer a strong potential for mass spectrometric identification and distinction

between closed ring and open chain isomers whose ΔH_a and ionization potential usually differ significantly. For very unstable molecules not amenable to nuclear magnetic resonance or infrared analysis, this seems a very worthy goal.

Although parts of the molecular orbital programs may not yet be sufficiently accurate for absolute use, they still offer the possibility of relative comparison of different structures, triplets, isomers, etc. from which qualitative trends or relative quantitative data can be used for mass spectrometric analytic decisions and calculations. Also included in this area is the prediction of relative stabilities of competing products.

D. Cyclobutadiene - The Cyclic Dimer of Acetylene.

Acetylene is a likely cometary constituent and indeed cyanoacetylene ($\text{N}\equiv\text{C}-\text{C}\equiv\text{CH}$) has been recently observed in certain regions of space by radio astronomers. This five atom molecule is, of course, strikingly large.

We were thus attracted to a study of cyclobutadiene, which is the 8-atom cyclic dimer of acetylene that had successfully eluded all attempts, many of them very extensive, of synthesis. The molecule was expected to be energetic and intensely reactive. Theoretical calculations have disagreed as to the nature of the ground state of cyclobutadiene, for, depending upon the method of calculation, both singlet and triplet states are predicted. The many experimental failures of synthesis by conventional techniques and the divergent results of theoretical calculations when combined with the seeming relevance of the species in certain astrophysical problems, led us to undertake the synthesis and characterization of cyclobutadiene by our newly developed cryochemical procedures.

Several chemical procedures were explored. An earlier report of indirect evidence for the isolation of cyclobutadiene from the reaction of CIT* with ceric ion at 0° was based on the identification by gas chromatography of very small amounts of methyl benzoate produced by the reaction of the isolated cyclobutadiene with methyl propiolate in the presence of a large amount of cyclobutadiene dimer¹⁹. This research, reported in 1965 created quite a stir, and it was written up in Chem. and Engineering News. In our research, cyclobutadiene was both liberated from CIT and observed to react immediately with methyl propiolate and other dienophiles upon pyrolysis in the injector of a gas chromatograph. In view of the conditions maintained in the earlier reported experiment¹⁹, the formation of methyl benzoate could be due to this process instead of the assumed reaction of isolated cyclobutadiene with methyl propiolate, and thus this earlier report, though promising, must be discounted accordingly.

We conducted the oxidation of cyclobutadieneirontricarbonyl (CIT) at 0° , the volatile products were transported at 0° , and were then quenched at -180° to -196° in the cryogenic inlet arrangement attached to the mass spectrometer. Upon slow, controlled warming, free cyclobutadiene, was not detected, but cyclobutadiene dimer was observed.

The dehalogenation of cis-3,4-dichlorocyclobutene with sodium amalgam at room temperature followed by immediate quenching of the volatile products at -180° to -196° in the cryogenic inlet system also failed to yield evidence of cyclobutadiene although cyclobutadiene dimer was again observed.

*Cyclobutadieneirontricarbonyl

We also attempted the radio frequency discharge of cis-3,4-dichlorocyclobutene at room temperature at pressures of 10^{-1} torr followed by immediate quenching at -196° . HCl , C_2H_2 , C_2HCl , C_4H_4 , C_4H_2 , $\text{C}_4\text{H}_3\text{Cl}$, and $\text{C}_2\text{H}_2\text{Cl}_2$, were observed upon slow controlled warm-up in the cryogenic inlet system, but the mass spectra and ionization potentials of the C_4 species showed it to be vinylacetylene rather than cyclobutadiene as is evident in Table VI. The C_4 spectrum at -120° has been corrected for the presence of diacetylene, $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$, m/e 50, which was produced in the discharge and which revaporized at the same temperature as did the C_4 species. The comparison spectra of Table VI were determined at temperatures of equivalent vapor pressures.

Pyrolysis of CIT was conducted in a specially designed furnace inlet system to the mass spectrometer in which the furnace exhaust was only 1/8 inch from the ionizing electron beam. With pressures of CIT of 10^{-2} to 10^{-1} torr and furnace temperatures of 350° to 400° , cyclobutadiene was produced along with cyclobutadiene dimer, benzene, 1,3-butadiene, vinylacetylene, acetylene, and carbon monoxide. The ionization potential of cyclobutadiene was measured to be 9.3 to 9.4 eV. In the pyrolysis of CIT followed by a rapid quench inside the cryogenic inlet system, C_4H_4 was revaporized and detected at -100° , but the IP was measured to be 9.5 to 9.6 eV as shown in Table VII. Although the mass spectrum and ionization potential of this C_4H_4 species were different from its isomers vinylacetylene and butatriene (see Table VIII) the evidence for the existence of a stable cyclobutadiene at low temperatures was not totally conclusive because of the unavoidable presence of vinylacetylene. The nearness of the ionization potentials and vapor pressures was such that we were never able to measure either the mass spectrum or the IP of the pure species.

TABLE VI

Summary of Important Mass Spectral and IP Data

From C_4H_4 Synthesis ExperimentsWith $C_4H_4Cl_2$

m/e	C_4H_4 From rf Discharge of $C_4H_4Cl_2^a$	Vinylacetylene at -108°	Butatriene at -90°
52	100	100	100
51	59	56	72
50	51	49	51
49	21	19	26
48	7	8	8
39	1	1	1
26	11	12	18
Ionization Potential (eV)	9.7-9.9	9.8-9.9	9.2-9.3

^aThis C_4 species was observed at -120° after quenching the discharge products to -196° followed by slow controlled warm-up for sequential revaporization and analysis.

TABLE VII

Ionization Potentials of C_4H_4 Isomers

<u>Compound</u>	<u>Exp.</u>	<u>Theoretical</u> ^c
cyclobutadiene (singlet)	9.3 - 9.4	8.83, 8.56
cyclobutadiene (triplet)	8.2 - 8.6 ^a	8.43
vinylacetylene	9.8 - 9.9 (9.9) ^b	9.60
butatriene	9.2 - 9.3 (9.4) ^a	8.99, 9.16

^aE. Hedaya, et. al., J. Amer. Chem. Soc., 91, 1875 (1969).

^bF. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, New York, 1957, pp. 261.

^cThese theoretical calculations were performed in our laboratory using LCAO-MO-SCF computer programs obtained from the Quantum Chemistry Program Exchange at the University of Indiana.

TABLE VIII

Summary of Important Mass Spectra From CIT
Pyrolysis and Quench Experiments

m/e	C ₄ H ₄ from Pyrolysis of CIT ^a	Vinylacetylene at -108°	Butatriene at -90°
52	100	100	100
51	59	56	70
50	51	49	51
49	17	19	26
48	1	9	8
39	5	1	1
26	26	12	18

^aThis C₄ species was observed at -105° after quenching the products from the pyrolysis of CIT at 380° to -196° followed by slow controlled warm-up for sequential revaporization and analysis.

The larger percentage of vinylacetylene after the quench accounts for the somewhat higher IP of the revaporized C_4 components. The only other measured IP is for triplet cyclobutadiene produced by the pyrolysis of photo- α -pyrone at $800^\circ C$ ²⁰. The agreement with our theoretical value for the triplet is encouraging.

Critical potential measurements on fragment ions sufficient to allow a calculation of the heat of formation of cyclobutadiene were accomplished, but the resulting calculations were inconclusive. Calculations from several perspectives using AP data on several ions yielded values clustered near 30 kcal/mole and near 70 kcal/mole. The discrepancy was probably due to excess energy in the ionization processes, but experimental difficulties prohibited the necessary measurements.

The mechanism of the pyrolysis of CIT was examined. The formation of benzene was evidently due to the reaction of cyclobutadiene and acetylene and not due to the pyrolysis of acetylene. Vinylacetylene was also not due to the pyrolysis of acetylene. The lack of formation of these species from acetylene was demonstrated by blank pyrolysis experiments under the same conditions using only pure acetylene.

Cyclobutadiene was observed to react as expected with dienophiles in the copyrolysis of CIT with methyl propiolate or with dimethyl acetylenedicarboxylate. The reaction of cyclobutadiene with oxygen from the copyrolysis of CIT and oxygen, produced furan. This result agreed with that of flash photolysis of CIT²¹ in the presence of oxygen but disagreed with that of the pyrolysis of photo- α -pyrone²⁰ in the presence of oxygen in which 2-butene 1,4-dione had been produced. The lack of reaction of cyclobutadiene with CH_3 or CH_2 in the copyrolysis of CIT with methyl

bromide or with dibromoethane again suggested that cyclobutadiene produced from CIT had a singlet ground state.

A preliminary account of these results was published, however, because of the remaining uncertainties detailed above, a more complete communication must await further experiments.

E. Cryoquenched Reactions of Oxygen Atoms with Simple Hydrocarbons.

The reactions of oxygen atoms with several simple hydrocarbons followed by rapid quenching to cryogenic temperatures have been studied with the use of low temperature mass spectrometry. The rapid quenching was carried out in an attempt to stabilize the initial reaction products, and the inlet system permitted the detection of any compounds which might be stable only at low temperatures. The systems that were studied were the reactions of oxygen atoms with acetylene, ethylene, and ethane which were 99.6, 99.8 and 99.9 per cent pure respectively as obtained from the supplier, and hence no purification was attempted.

The atoms were produced by means of an efficient radio frequency electrodeless electric discharge arrangement which consisted of a 50-turn copper coil 33 mm O.D. and made of 14 gauge wire. An impedance matching network insured the maximum power transfer from the transmitter to the plasma and hence, maximum production of atomic species. The network was very simple as is evident in Figure 7. The transmitter, operating at 3.5 mHz, had an output impedance of 52 ohms, and hence the network, with its 50 turn coil and plasma core, must be adjusted to 52 ohms. Proper adjustment was indicated by a SWR of near unity. The discharge was self igniting, would operate in pyrex with no cooling, and would maintain an intense discharge

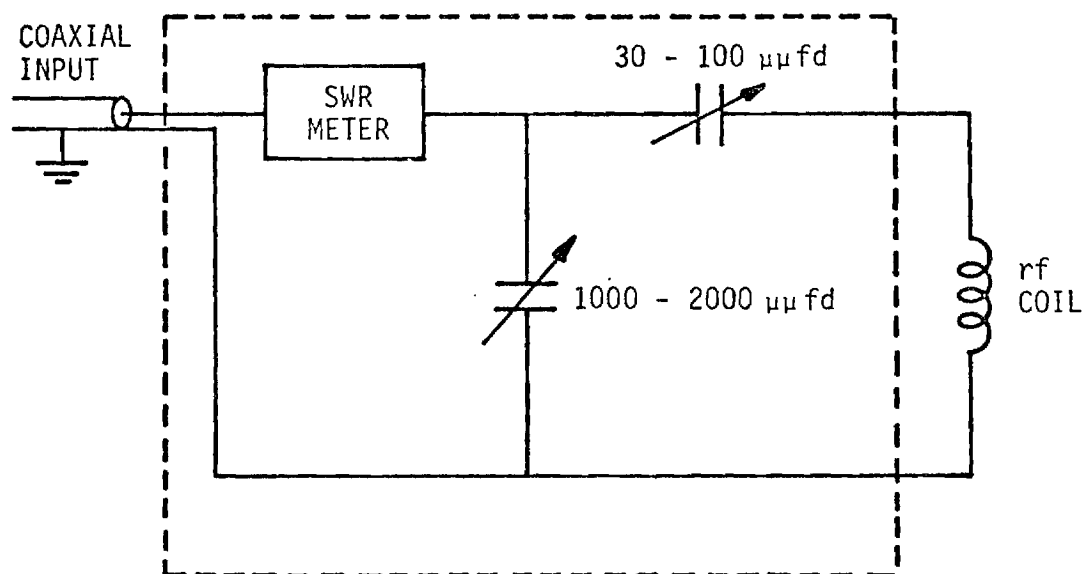
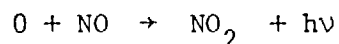
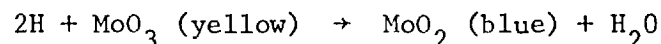


Figure 7. Impedance matching network.

in, e.g., hydrogen at pressures up to 80 torr. Tests for the presence of O and H atoms using the emission from



and the yellow to blue color change in



were always positive, but no attempts at quantitative analysis were ever attempted.

The resulting mixture of atomic O and both ground state and excited molecular O₂ species contacted the second gaseous reactant in a pyrex reactor cooled to very low temperatures, thereby resulting in fast quenching of the reaction products. The quenching temperature was varied from 77⁰ to 100⁰ K and the reactions occurred in a pressure range of 0.5 to 2.5 torr. The low temperatures were produced by immersing the reactor in a dewar of a suitable liquid refrigerant which was stabilized with an automatic temperature control system. The reaction products were studied during a controlled warm-up from the quenching temperature by use of the low temperature inlet system.

The reaction of oxygen atoms with ethane followed by a rapid quench to 90⁰K produced small amounts of ethanol as the only reaction product in strong contrast to the room temperature reaction which produces CO₂, CO, ethanol, CH₂O, CH₃CHO, and H₂O. These results are an example of a successful attempt to stabilize the initial reaction product by low temperature quenching, and they thus shed light on the reaction mechanism. The reaction probably occurred by an insertion of an excited ¹D oxygen atom into the carbon-hydrogen bond rather than by reaction of the ground state ³P which would have abstracted an H atom and resulted in a different product array. Unlike the case with either C₂H₄ or C₂H₂, the reaction with C₂H₆ seemed to catalyze the formation of O₃. No O₃ was observed when operating with the lighter

hydrocarbons nor when pumping only discharged O_2 -He through the reactor under the same reaction conditions. However, the O_3 formation could have been a physical artifact of the reactor design as well.

The reaction of oxygen atoms with ethylene followed by a rapid quench to 90°K produced products with appearance temperatures as shown in Table IX.

No new or unusual products were observed, and hence these results were first thought to be rather disappointing. However, the presence of relatively large amounts of ethylene oxide supported a proposal by Cvetanovic^{22, 23} that the initial reaction product was an energy-rich ethylene oxide molecule. The increased quantities of ethylene oxide produced in the present work was then a result of the low temperature quenching. Formaldehyde, methanol, and formic acid were probably formed from the free radical scavenger action of O_2 that was also present in the reaction zone. These results then are a second example of a rapid quench stabilizing the initial product and thereby giving us insight into the reaction mechanism.

The reaction of atomic oxygen with acetylene followed by a rapid quench to 90°K produced carbon dioxide, glyoxal, formic acid, water, a red compound or complex disappearing at -123° , and a white solid which slowly changed to a yellow and finally to a brown color on exposure to the atmosphere at room temperature. These products and their appearance temperatures appear in Table X. The red color and double C_2H_2 evolution were not reproduced in blank experiments. The red substance was tentatively explained in terms of a charge transfer complex between unreacted acetylene and formic acid wherein the acid proton of the formic acid interacts with

TABLE IX

Products from the Reaction of Discharged Oxygen with C_2H_4 Followed by Quench to $90^\circ K$

<u>Temperature Range, $^\circ C$</u>	<u>Product</u>
-176 to -152	unreacted C_2H_4
-163 to -131	CO_2
-145 to -121	HCHO
-127 to -94	CH_3CHO and $CH_2OCH_2^*$
-82 to -54	CH_3OH
-65 to -10	H_2O
-60 to -10	HCOOH

*The mass spectral data permitted a product ratio estimate of acetaldehyde to ethylene oxide of 30:70.

TABLE X

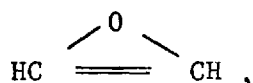
Products from the Reaction of Discharged Oxygen with
 C_2H_2 Followed by Quench to 90°K

<u>Temperature Range, °C</u>	<u>Evolved Cpd.</u>	<u>Observation</u>
-163 to -135	Unreacted C_2H_2	
-163 to -135	CO_2	
-135 to -116	secondary C_2H_2	red color fading
-103 to -79	O_2	yellow color fading
-82 to -54	$(CHO)_2$	yellow color fading
-50 to -20	$HCOOH$	
-79 to -20	H_2O	
room temperature		white, fluffy solid

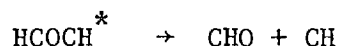
the π electrons of the acetylene. The red color of the complex would be caused by the transfer of electrons from the acetylene to the formic acid. This electron transfer would be to a lower excited state and cause a shift toward longer wavelengths of absorption. This type of absorption is well known, for example, when chloranil (yellow) and hexamethylbenzene (colorless) are mixed, an intensely red solution is formed²⁴. In our studies, the proposed charge transfer complex would exist only at low temperatures. Upon warming, the bonding would weaken and the C_2H_2 would be evolved.

We have also found that this same sort of reaction configuration but with benzene rather than C_2H_2 will also yield red deposits at $90^\circ K$. Charge transfer complexes of benzene are well known²⁵.

Glyoxal is yellow, and thus its evaporation would explain the observed color change, but the origin and significance of the accompanying slight O_2 evolution was not established. The room temperature solid was not identified but was found to contain functional groups of aldehydes and esters. Upon exposure to the atmosphere, it gradually became yellow and finally dark brown after about 48 hours. The expected initial reaction product, ketene, was not detected presumably due to the insufficient speed of the quench. $O(^3P)$ does react at $20^\circ K$ in an argon matrix to yield ketene. Interestingly, $O(^1D)$ would be expected to react with C_2H_2 to form oxiene,



a very strained and presently unknown species. The initial hot species would decompose



and these radicals would react further to form the observed product distribution.

The results obtained from the study of these three reactions indicated that, depending on the molecular complexity and the energetics of the initial reaction products, a variety of intermediates could be stabilized by low temperature quenching.

F. Cryoquenched Reaction of O Atoms with NH_3 .

The products of the reaction of atomic oxygen with ammonia with an immediate quench to 90°K are presented in Table XI.

When the $\text{O};\text{NH}_3$ reaction was conducted at room temperature with no quenching, NO and N_2O were the main products. When cooled below -115° the peaks due to these oxides began to decrease indicating that a portion of their precursors were being removed from the reaction zone by the quench. This removal was never completely effective since some NO and N_2O remained even when quenching at 90°K .

The product mass was yellow as previously reported over 40 years ago²⁶, but the color was due to the normally unstable diimide, N_2H_2 , rather than HNO or NH_3O as was then proposed. The color bleached as the N_2H_2 was removed between -125° and -110° . The ionization potential of diimide was measured to be 9.8 ± 0.2 eV in good agreement with a previous value²⁷.

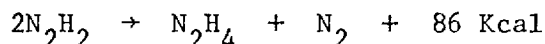
The AP of N_2H_2^+ from N_2H_4 was found to be 11.3 ± 0.2 eV.

Hydrazine could have been formed from the dimerization of two NH_2 radicals or from the disproportionation of diimide,

TABLE XI

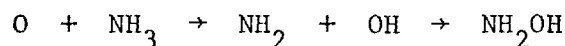
Products of the Reaction of Discharged
Oxygen with NH_3 Followed
by Quench to 90°K

<u>Temperature Range, $^\circ\text{C}$</u>	<u>Product</u>
-183 to -141	NO
-125 to -110	N_2H_2 , N_2 , N_2O , unreacted NH_3
-61 to 1	H_2O
-50 to -15	N_2H_4
-1 to > 1	NH_2OH
room temperature	NH_4NO_3



which would also explain the evolution of N_2 with the appearance of N_2H_4 .

The detection of NH_2OH was important in that it had previously been proposed to exist as an intermediate in the oxidation of NH_3 ²⁸. The compound could have been formed by



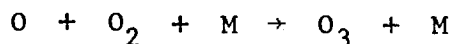
or by direct insertion. The conversion is exothermic by 119 kcal/mole.

G. Cryoquenched Reaction of H Atoms with NO.

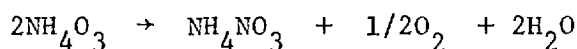
The reaction of hydrogen atoms with nitric oxide followed by a rapid quench to 77°K produced only small amounts of nitrous oxide and water. The expected intermediate, HNO, was not detected; however, the presence of nitrous oxide and water indicated that HNO was produced during the reaction process²⁹. The failure to stabilize and detect HNO is supported by a concurrent study made by Robinson³⁰.

H. Low Temperature Reaction of Ozone and Ammonia.

While discharged oxygen and NH_3 produced a yellow colored product mass upon quenching to 90°K as described above, quenching to 77°K produced an orange-red mass which proved to be formed by the reaction of condensed ozone with the NH_3 . In subsequent experiments, a layer of ammonia was condensed on top of a layer of ozone at 77°K. A bright yellow deposit was produced, and as the reactor was slowly warmed, the yellow color changed to a orange-red. In another experiment, the orange-red solid could be formed at 90°K if the discharged oxygen was first forced to strike the liquid oxygen cooled surface before contacting the gaseous NH_3 . The preliminary cold wall contact evidently led to ozone,



The orange-red solid bleaches at -70° and white solid NH_3NO_3 is produced. Ozone and oxygen appear over a wide temperature range of -153° to -112° during slow warming. Thus we conclude that the original product was NH_4O_3 which decomposed according to



This proposal is in keeping with earlier related observations^{31,32}.

I. The Lower Boron Hydrides.

Borane, BH_3 , should be a stable species at sufficiently low temperatures, as should, for that matter, BH as well. The simplest known boron hydride is diborane, B_2H_6 , which is itself a very energetic and uniquely bonded molecule. And BH_3 and BH should be even more energetic. Thus the objective here was the identification and determination of the energetics of these molecules by mass spectrometric techniques, and an attempt to prepare each as a stable liquid or solid phase by utilization of cryogenic reactor techniques. A secondary effort was made to produce H_2BF in order to obtain more information concerning unstable trivalent compounds of boron.

The boron hydrides, particularly B_2H_6 , and also the higher alkylated boranes had received considerable attention because of their practical usefulness, especially as rocket and jet aircraft fuels. In addition, much interest and controversy has been focused upon the unusual bonding present in these compounds due to their so-called "electron deficient" nature.

Initial attempts to detect BH_3 in the pyrolysis of B_2H_6 and dimethylanilineborane involved the introduction of the pyrolysis products into the ionization region of the mass spectrometer by effusion through small diameter orifices. This approach had been used successfully in this laboratory in the study of CF_2 ³³ as well as in other investigations of unstable molecules and free radicals³⁴. However, BH_3 could not be detected in a lengthy and sometimes frustrating series of hot filament and tubular furnace pyrolysis experiments. When BH_3 was finally observed by introducing the pyrolysis products directly into the electron beam without the presence of a beam collimating orifice, it became clear that future investigations of unstable species should be conducted, if possible, in this manner. Whereas CF_2 was not lost upon effusion through a 0.032 inch diameter orifice³³, BH_3 suffered decomposition or reaction under similar experimental conditions.

A radio frequency discharge of B_2H_6 failed to produce evidence of BH_3 . If BH_3 were actually formed in the discharge, it would have been depleted by the time the discharge products reached the ionization region of the mass spectrometer approximately one foot away. This became apparent only later during the cryogenic quenching experiments when it was found that BH_3 could not be successfully transferred through a 1-1/2 foot long by 3/8 inch diameter tube which had been cooled over its entire length to a temperature approximately that of the melting point of oxygen (54.8°K).

BH_3 was finally detected successfully in the pyrolysis of B_2H_6 in tubular furnaces of quartz, aluminum, and stainless steel at pressures of 10^{-4} to 10^{-2} torr and at temperatures of 250° to 400°. BH_3 was also produced by the pyrolysis of B_2H_6 on incandescent filaments of platinum,

tungsten, nichrome, zirconium, molybdenum, niobium, titanium, and tantalum. The ionization potential of BH_3 was determined by two independent methods to be 12.32 ± 0.1 eV. By combining this with a value of 14.88 ± 0.05 eV for $A(\text{BH}_3^+)$ from B_2H_6 , $D(\text{BH}_3 - \text{BH}_3)$ was calculated at 2.56 eV or 59 kcal/mole.

The appearance potentials of B^+ , BH^+ , BH_2^+ , BH_3^+ , and B_2H_5^+ from B_2H_6 , as well as from BH_3 wherever applicable, were determined. Although several of these values are in major disagreement with other studies, the numbers presented are considered to be accurate because of the experimental precision, and the excellent self-consistency of the resulting numbers. The latter is demonstrated by three determinations of $D(\text{BH}_3 - \text{BH}_3)$ as approximately 2.6 eV from the appearance potentials of three separate fragment ions. All of the appearance potential data from B_2H_6 and BH_3 are summarized in Table XII.

The experimental appearance potentials permitted the direct determination of either the values of or the lower and/or upper bounds for $D(\text{B}^+ - \text{H})$, $D(\text{BH}^+ - \text{H})$, $D(\text{BH}_2^+ - \text{H})$, $D(\text{BH}_3 - \text{BH}_3)$, $D(\text{BH}_3^+ - \text{BH}_3)$, $I(\text{B}_2\text{H}_6)$, and $I(\text{B}_2\text{H}_5)$. The calculation of $D(\text{B} - \text{H})$, $D(\text{BH} - \text{H})$, $D(\text{BH}_2 - \text{H})$, and $I(\text{BH}_2)$ was made possible by introducing the spectroscopic value of $I(\text{BH}) = 9.77$ eV³⁵. The values are consistent with some of the data from spectroscopic, kinetic, and mass spectrometric studies and also are upheld by theoretical arguments in several cases. These calculated energetic quantities are summarized in Table XIII.

The utilization of the derived bond energies to calculate the heat of formation of B_2H_6 as -40.9 kcal/mole at 298°K allowed an analysis of the errors in the experimental bond energies from this research. This was accomplished by comparing the calculated heat of formation from our data with an experimental value of 7.53 kcal/mole³⁶ which is believed to

TABLE XII

Appearance Potentials of Fragment Ions from BH_3 and B_2H_6

Fragment Ion	Appearance Potential from Parent in eV (This Work) ^c		Appearance Potential from Parent in eV (Literature)	
	BH_3	B_2H_6	BH_3	B_2H_6
B^{10+}	15.83 ^a	18.39 ± 0.02		18.7 ± 0.1^d 19.5 ± 0.2^e
B^{10}H^+	13.66 ± 0.02^b	16.39 ± 0.3		14.9 ± 0.1 16.6 ± 0.2
$\text{B}^{10}\text{H}_2^+$	12.95 ± 0.05	15.5 ± 0.05		13.4 ± 0.1 13.5 ± 0.5
$\text{B}^{11}\text{H}_3^+$	12.32 ± 0.1	14.88 ± 0.05	11.4 ± 0.2^f	13.1 ± 0.2^g 12.1 ± 0.2^g
$\text{B}^{11}_2\text{H}_5^+$		11.84 ± 0.1		11.9 ± 0.2 11.3 ± 0.5
$\text{B}^{10}\text{H}_6^+$				11.9 ± 0.1 12.1 ± 0.2
$\text{B}^{10}_2\text{H}_5^+$				11.9 ± 0.1 12.0 ± 0.3

^aCalculated as $A(\text{B}^+)$ from B_2H_6 or (18.39 eV) minus $D(\text{BH}_3 - \text{BH}_3)$ or 2.56 eV .^bError represents maximum deviation from average of experimental values.^cAverage of experimental values.^dW. S. Koski, et. al., J. Amer. Chem. Soc., **80**, 3202 (1958).^eJ. L. Margrave, J. Phys. Chem., **61**, 38 (1957).^fT. P. Fehlner and W. S. Koski, J. Amer. Chem. Soc., **86**, 2733 (1964).^gFragment ion is $\text{B}^{10}\text{H}_3^+$.

TABLE XIII

Bond Energies and Ionization Potentials Calculated or Estimated
from Appearance Potential Measurements

Bond Energy or Ionization Potential	Energy, eV		
	This Research	Literature	
		Experimental	Calculated or Estimated
D(B - H)	3.64	< 3.51 ³⁵	3.39 ^a , 3.40 ^b
D(BH - H)	4.83		4.7 ^c
D(BH ₂ - H)	3.58	3.2 ^d	3.2 ^c
D(B ⁺ - H)	2.17	< 2.04 ³⁵	3.0 ^c
D(BH ⁺ - H)	5.23		5.2 ^c
D(BH ₂ ⁺ - H)	0.63		0.9 ^c
D(BH ₃ - BH ₃)	2.56	1.7 ^d , > 2.39 ^e	1.23 ^h , 1.61 ⁱ 2.25 ^j , < 1.66 ^k
D(BH ₃ ⁺ - BH ₃)	< 3.67; > 3.04		
I(B ₂ H ₆)	< 11.84; > 11.21	11.9 ^f , 12.1 ^g	
I(BH ₂)	9.37	9.8 ^d	8.2 ^c
I(B ₂ H ₅)	> 8.26		7.86 ^f

^aA. C. Hurley, Proc. Royal Soc. (London) Ser. A., 261, 237 (1961).

^bF. O. Ellison, J. Chem. Phys., 43, 3654 (1965).

^cW. C. Price, et al., Discussions Faraday Soc., 35, 201 (1963).

^dT. P. Fehlner and W. S. Koski, J. Amer. Chem. Soc., 86, 2733 (1964).

^eE. J. Sinke, et al., J. Chem. Phys., 41, 2207 (1964).

^fW. S. Koski, et al., J. Amer. Chem. Soc., 80, 3202 (1958).

^gJ. L. Margrave, J. Phys. Chem., 61, 38 (1957).

^hR. E. McCoy and S. H. Bauer, J. Amer. Chem. Soc., 78, 2061 (1956).

ⁱT. P. Fehlner and W. S. Koski, ibid., 87, 409 (1965).

^jR. P. Clarke and R. N. Pease, ibid., 73, 2132 (1951).

^kM. E. Garabedian and S. W. Benson, ibid., 86, 176 (1964).

be a correct number. This calculation involved $D(\text{BH}_3 - \text{BH}_3)$, the heat of sublimation of boron, the dissociation energy of hydrogen, and two times the value of the heat of atomization of BH_3 . If all values except the latter are assumed to be accurate, it may be seen that an error of 24.2 kcal/mole in the heat of atomization of BH_3 , i.e., $D(\text{BH}_2 - \text{H}) + D(\text{BH} - \text{H}) + D(\text{B} - \text{H})$, would produce the rather large disagreement between the two heats of formation. That is, an average error of approximately 8 kcal/mole or 0.35 eV exists in the derived bond energies of BH , BH_2 , and BH_3 . This is believed to be the case as opposed to assigning what would be a considerable error to $D(\text{BH}_3 - \text{BH}_3)$. The errors are not believed to be due to the experimental appearance potential values, but to be inherent in the electron impact method of energy determinations, e.g., Franke-Condon problems.

Free BH_2 was not detected in the pyrolysis of B_2H_6 even though the experimental conditions under which BH_2 was reportedly synthesized in earlier studies in another laboratory were essentially reproduced³⁷.

Equilibrium partial pressures calculated from free energies of reaction based on the bond energies from this research and entropy values from estimated thermodynamic tables showed that the pyrolysis of B_2H_6 should produce approximately equal amounts of BH_2 and BH_3 . However, by again employing the experimental bond energies, the magnitudes of the activation energies for the dissociation of B_2H_6 into BH_2 and into BH_3 were estimated and a comparison of the resultant kinetic rate constants indicated that BH_2 would not play a significant role in the kinetics of the pyrolysis of B_2H_6 .

The quench of the products of the pyrolysis of B_2H_6 in the cryogenic reactor inlet system at temperatures as low as approximately the melting point of oxygen ($54.8^\circ K$) failed to produce evidence of stabilized BH_3 . That is, BH_3 was not observed either by monitoring the pyrolysis and quenching operation or by monitoring the gas evolved from the deposit upon warm-up. However, the observation of an increase in the H_2^+ ion peak at approximately $60^\circ K$ followed by a decrease in its intensity at higher temperatures led to the initial conclusion that BH_3 had been stabilized at the quenching temperature, but was reacting or decomposing to liberate H_2 as the temperature of the system was increased. This concurred with an earlier x-ray detection of an unidentified phase with a triple point of $60^\circ K$ in the quenched products of a microwave discharge of B_2H_6 ³⁸. A subsequent blank experiment in which unpyrolyzed B_2H_6 and H_2 were subjected to the cryogenic quench produced the same variation of the H_2^+ ion peak upon warm-up. The final conclusion was that H_2 was trapped in the B_2H_6 matrix and liberated at approximately $60^\circ K$.

H_2BF was not detected in similar cryogenic quenching experiments in the products of an rf discharge of BF_3 and B_2H_6 . However, HBH_2 was observed upon warm-up of the quenched discharge products to about $90^\circ K$. The lowering of $A(BF_2^+)$ to approximately 13 eV was evidence that HBH_2 and not BF_3 was the parent compound since $A(BF_2^+)$ from BF_3 is 16.2 eV³⁹. Also, the appearance of HBH_2^+ and BF_2^+ peaks at a temperature slightly lower than that at which peaks from BF_3 begin to appear agreed with the reported similarity of the vapor pressures of HBH_2 and BF_3 ⁴⁰. Finally, the

approximate 1:1 ratio of m/e ion peaks 31 and 49 concurred with a mass spectrometric study of HBF_2^{40} .

CHAPTER IV
SUMMARY LISTS

A. Graduate Theses

1. "Mass Spectrometric Study of the Products Obtained from Fast Cryogenic Quenching of Several Reactions Involving Atomic Hydrogen or Atomic Oxygen"

Author: D. B. Bivens
Degree: Ph.D. in Chemical Engineering

2. "Synthesis, Stability and Energetics of Cylobutadiene"

Author: P. H. Li
Degree: Ph.D. in Chemical Engineering

3. "Synthesis and Mass Spectra of Cyclopropene and Cyclopropenone"

Author: M. A. Bell
Degree: M.S. in Chemical Engineering

4. "The Preparation of Some Highly Reactive, Three Membered Ring Organic Compounds as Cryochemical Reagents, and the Low Temperature Mass Spectrometric Study of Their Stability and Molecular Energetics"

Author: R. J. Holt
Degree: Ph.D. in Chemical Engineering

5. "Mass Spectrometric Studies of the Synthesis, Energetics, and Cryogenic Stability of the Lower Boron Hydrides"

Author: J. H. Wilson
Degree: Ph.D. in Chemical Engineering

B. Publications

1. "A Refrigerated Inlet Arrangement for Mass Spectrometric Studies of Unstable Species at Cryogenic Temperatures, " Rev. Sci. Instr. 37, 561 (1966), T. J. Malone, W. J. Martin and H.A. McGee, Jr.
2. "Low Temperature Synthesis," Chem. Eng. Prog. 62, 113 (1966), D. B. Bivens, T. J. Malone, J. H. Wilson and H. A. McGee, Jr.
3. "Mass Spectrometric Studies of the Synthesis, Energetics, and Cryogenic Stability of the Lower Boron Hydrides," J. Chem. Phys. 46, 1444 (1967), J. H. Wilson and H. A. McGee, Jr.
4. "Mass Spectrometry in Cryochemistry," presented at 157th National ACS Meeting, Minneapolis, April, 1969 and reviewed in Chem. and Eng. News, 47, No. 17, 50 (1969), H. A. McGee, Jr.
5. "Mass Spectrum and Ionization Potential of Condensed Cyclobutadiene," Chem. Comm., 592, 1969, P.H. Li and H. A. McGee, Jr.
6. "Cryochemical Technology," Cryog. Technol., 7, 109 (1971), R. J. Holt and H. A. McGee, Jr.
7. "Cryochemical Synthesis of Cyclic Three Carbon Compounds", J. Am. Chem. Soc., in press, R. J. Holt and H. A. McGee, Jr.
8. "Molecular Energetics in Highly Strained Three Carbon Ring Compounds", R. J. Holt, H. A. McGee, Jr., and E. F. Rothgery, in preparation.

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