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School of Chemical Engineering  
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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.

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## 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, C<sub>3</sub>, NH<sub>2</sub>, C<sub>2</sub>, 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.

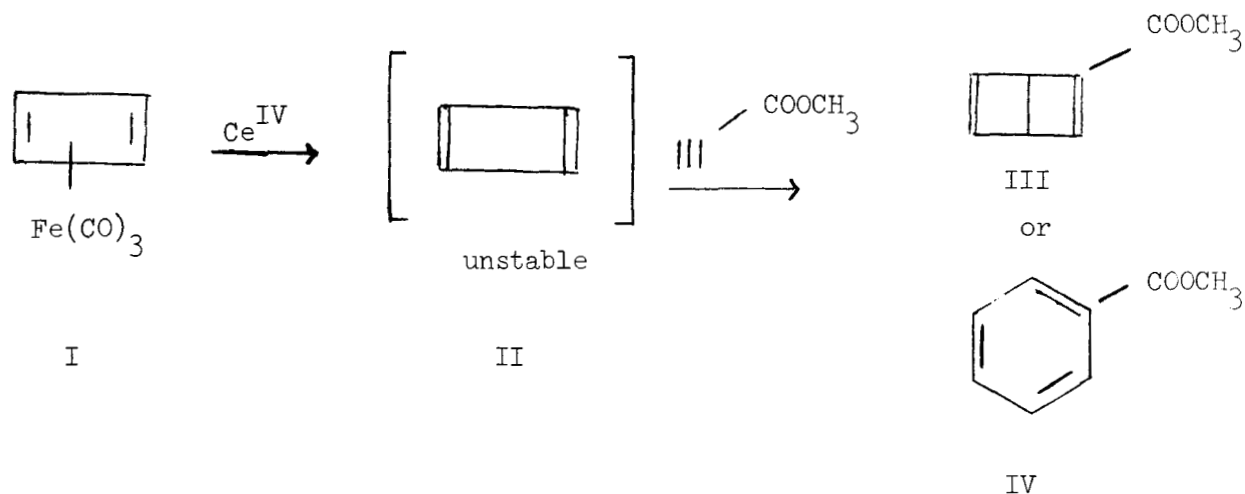
#### A. CYCLOBUTADIENE

##### 1. Synthesis

The synthesis of cyclobutadiene, C<sub>4</sub>H<sub>4</sub>, has been of interest to organic chemists for a long time.<sup>1</sup> 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.<sup>2</sup> 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,

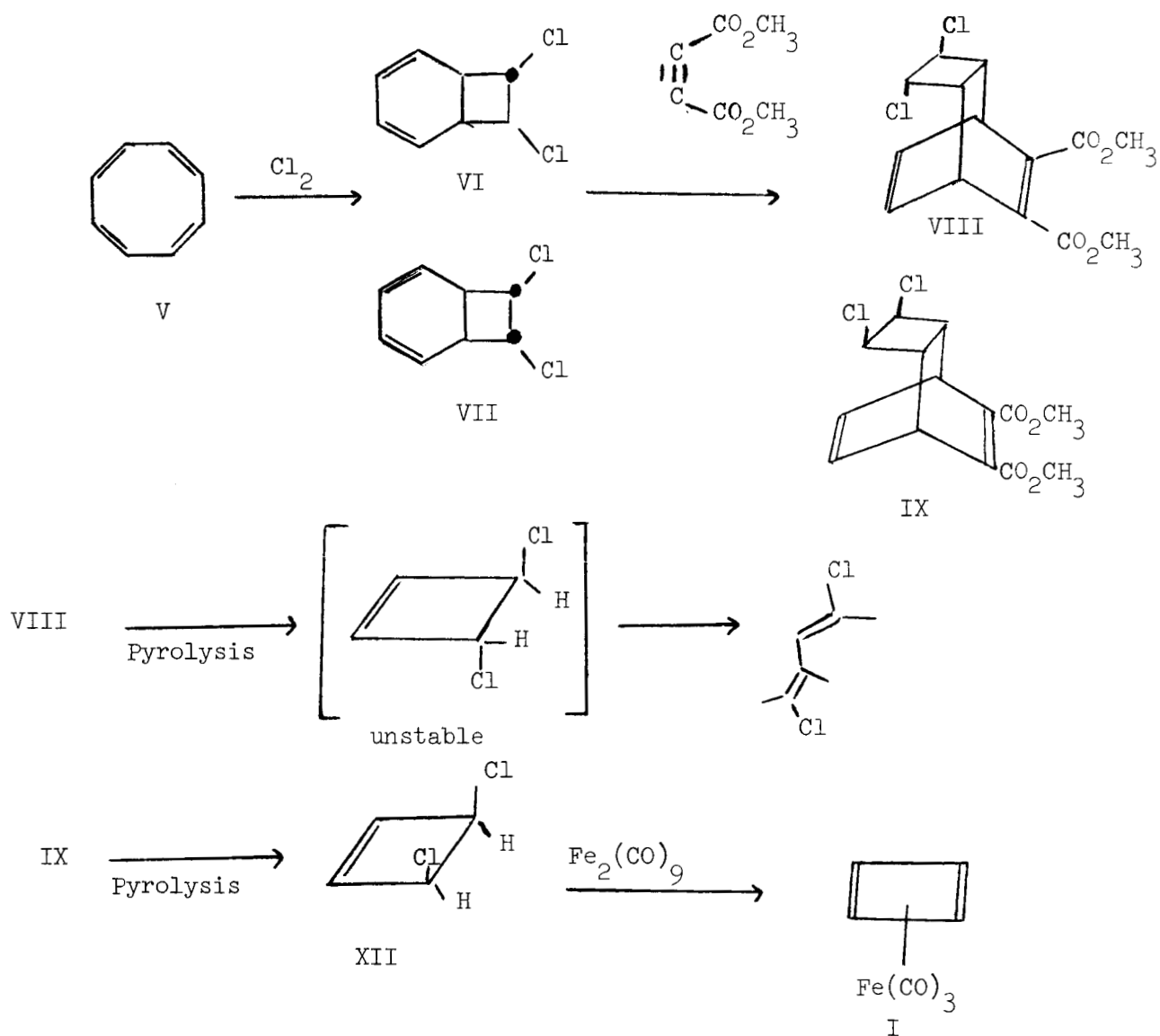


wherein the free cyclobutadiene(II) was never isolated or directly identified. In one experiment the gases evolved from the  $\text{Ce}^{\text{IV}}$  decomposition at  $0^\circ$  were passed through a short tube containing a plug of glass wool and condensed in a trap immersed in liquid nitrogen. After 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 condenser. 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,<sup>1</sup> 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,<sup>3</sup> 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<sup>4,5</sup>, it is evident that we have obtained the same compound.

The dominant peaks in the mass spectrum of cyclobutadieneirontricarbonyl reported by Pettit<sup>4</sup> and by Watts<sup>5</sup> 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.<sup>6,7</sup> Successive removal of CO is found in the mass spectra of  $C_6H_8Fe(CO)_3$ .<sup>7</sup> 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  $Mn_2(CO)_{10}$ <sup>6</sup> 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

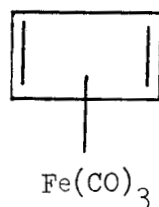
Table I. Relative abundances of the principal positive ions from cyclobutadieneiron tricarbonyl at 70 e.v.

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 Denning<sup>6</sup> and by Winters<sup>7</sup>, 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 Pettit<sup>4</sup> 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

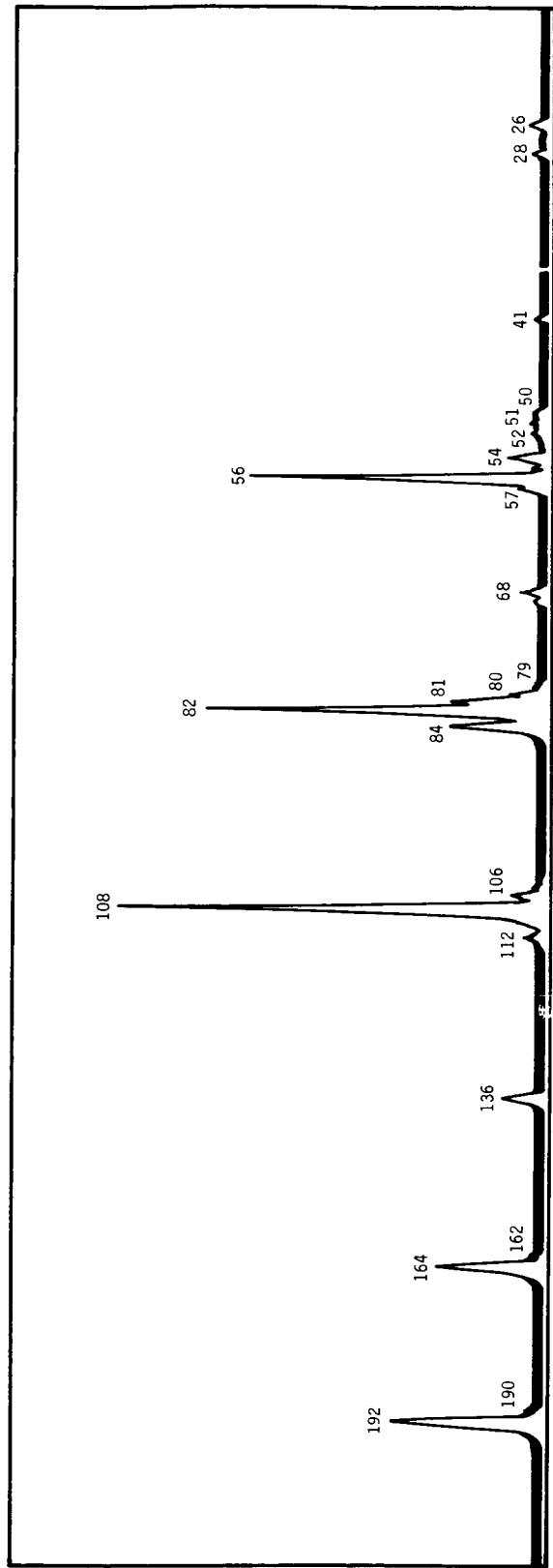


Figure 1. Mass Spectrum of Cyclobutadieneirontricarbonyl Using 70 e.v. Electrons.

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 arrangements<sup>8</sup> 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.<sup>8</sup>

## 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,<sup>9</sup> 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  $-135^{\circ}$  to  $-115^{\circ}\text{C}$  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  $-135^{\circ}\text{C}$ . 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,



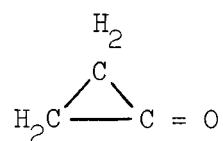
The status of this synthesis is about as described earlier wherein a series of experiments were conducted in which atomic oxygen from a resonant rf discharge was contacted with acetylene in a reactor immersed in liquid oxygen ( $90^{\circ}\text{K}$ ). This low pressure gas phase reaction was accompanied 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  $\text{CO}_2$ ,  $(\text{CHO})_2$ ,  $\text{O}_2$ ,  $\text{HCOOH}$  and  $\text{H}_2\text{O}$  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 Pimentel<sup>10</sup> had earlier shown that ketene was formed at  $20^{\circ}\text{K}$  by the reaction of photo-lytically produced ground state  $^3\text{P}$  oxygen atoms (from  $\text{N}_2\text{O}$ ) with  $\text{C}_2\text{H}_2$  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  $^1\text{D}$  oxygen atom across the triple bond of acetylene. Recent attempts to identify oxirene from room temperature experiments have failed,<sup>11,12</sup> 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  $^1\text{D}$  atom is 45 kcal above the ground state  $^3\text{P}$  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,<sup>8</sup> this laboratory is endeavoring to synthesize and isolate the free, unsubstituted, highly strained, small ring compound cyclopropanone,



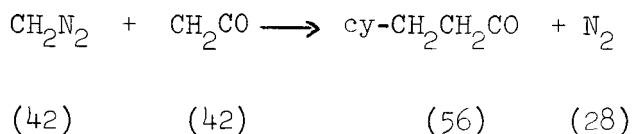
by the reaction of liquid ketene ( $\text{CH}_2\text{CO}$ ) and liquid diazomethane ( $\text{CH}_2\text{N}_2$ ) at  $-145^\circ\text{C}$ . Several modifications to earlier procedures have been made. The previous preparation of ketene had yielded a crude product of about 80% ethylene and only 20% ketene. 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  $-100^\circ\text{C}$  was also condensing a large amount of the ketene. Therefore this trap was raised to a temperature of  $-50^\circ\text{C}$ .

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  $30^\circ\text{C}$ . Then, after cooling to  $0^\circ\text{C}$ , carefully throttled gaseous nitrogen was used to blow the explosive

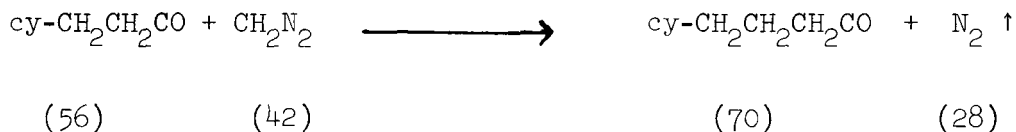
diazomethane out of its reaction mixture and carry it into a receiving flask.

Both of these reagents were purified by distilling from a trap whose temperature could be varied from  $-145^{\circ}$  to room temperature into another trap which was held at  $-196^{\circ}$ . 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  $-145^{\circ}$  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  $-50^{\circ}\text{C}$  with two separate maxima at  $m/e = 56$  at  $-130^{\circ}\text{C}$  and  $-35^{\circ}\text{C}$ . 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  $\text{CH}_2$  group into the three-membered cyclopropanone ring.

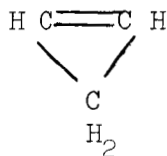
Both from the literature<sup>13</sup> and from calibration experiments in this laboratory, it is clear that  $m/e = 56$  is not present in the spectrum of cyclobutanone. Other plausible reaction products of  $m/e = 70$  and  $56$

(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

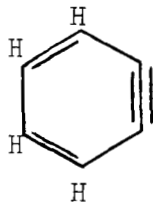
Several other compounds are of immediate interest in this research program, but progress on the study of these substances does not warrant more than a passing notation at this time.

Cyclopropene,



is an interesting molecule that is indefinitely stable at 77°K, but slowly polymerizes at dry ice temperature, -80°C.<sup>14</sup> 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<sub>2</sub> 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.<sup>8</sup> This material evidently reacts with itself near  $-113^{\circ}\text{C}$  to yield  $\text{N}_2$  and  $\text{N}_2\text{H}_4$ . Efforts are underway to prepare this interesting substance in workable amounts, say 10 - 20  $\text{cm}^3$ , and to then investigate its low temperature reactivity with several simple substances. Diimide is evidently a very powerful reducing agent.

IV. Bibliography

1. J. A. Knight, Jr., First Semi-Annual Report on Grant NsG-337 (Supplement No. 1), September 1966.
2. L. Watts, J. D. Fitzpatrick, and R. Pettit, J. Am. Chem. Soc. 87, 3253 (1965).
3. M. Avram, I. Dinulescu, M. Elian, M. Farcasiu, E. Marica, G. Mateescu and C. D. Nenitzescu, Ber. 97, 372 (1964).
4. G. F. Emerson, L. Watts and R. Pettit, J. Am. Chem. Soc. 87, 131 (1965).
5. L. Watts, Cyclobutadieneirontricarbonyl, Ph.D. thesis, University of Texas (1966).
6. R. G. Denning and R. A. D. Wentworth, J. Am. Chem. Soc. 88, 4619 (1966).
7. R. E. Winters and R. W. Kiser, J. Phys. Chem. 69, 1618, 3198 (1965).
8. H. A. McGee, Jr., Final Report on Grant NsG-337, July, 1966.
9. D. B. Bivens, Ph.D. thesis in chemical engineering, May, 1966, also D.B.B. and H. A. McGee, Jr., J. Am. Chem. Soc. in press.
10. I. Haller and G. C. Pimentel, J. Am. Chem. Soc. 84, 2855 (1962).
11. R. N. McDonald and P. A. Schwab, J. Am. Chem. Soc. 86, 4866 (1964).
12. J. K. Stille and D. S. Whitehurst, J. Am. Chem. Soc. 86, 4871 (1964).
13. H. J. Hofman, Tetrahedron Letters, No. 34, 2329 (1964).
14. K. B. Wiberg and W. J. Bartley, J. Am. Chem. Soc. 82, 6375 (1960).