

NGL 79-002-005<sup>25324</sup>

NASA CR 109552

SYNTHESIS, STABILITY AND ENERGETICS  
OF CYCLOBUTADIENE

A THESIS

Presented to

The Faculty of the Graduate Division

by

Ping Hung Li

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in the School of Chemical Engineering

CASE FILE  
COPY

Georgia Institute of Technology

October, 1969

**SYNTHESIS, STABILITY AND ENERGETICS  
OF CYCLOBUTADIENE**

**A THESIS**

**Presented to**

**The Faculty of the Graduate Division**

**by**

**Ping Hung Li**

**In Partial Fulfillment**

**of the Requirements for the Degree**

**Doctor of Philosophy in the School of Chemical Engineering**

**Georgia Institute of Technology**

**October, 1969**

**SYNTHESIS, STABILITY AND ENERGETICS  
OF CYCLOBUTADIENE**

Approved:

\_\_\_\_\_  
Chairman

\_\_\_\_\_  
Date approved by Chairman: \_\_\_\_\_

## ACKNOWLEDGMENTS

I am grateful to Dr. H. A. McGee, Jr. for the suggestion of this research problem and for his advice, encouragement, and assistance during the progress of the research work. I am thankful to Dr. J. A. Knight, Jr. for his suggestions and willing assistance in the chemical preparations, as well as in the gas chromatographic and infrared analyses carried out in this research work and for his suggestions while serving on the reading committee. I also wish to thank Dr. W. T. Ziegler for his interest and suggestions while reading this thesis.

Deep appreciation is due to the National Aeronautics and Space Administration for its support through grant NsG-337, **NGL 11-002-005** I also wish to thank Badische Anilin and Soda Fabrik A. G. for the gift of cyclooctatetrene and General Aniline and Film Corporation for furnishing the iron pentacarbonyl.

The many hours spent by Mr. G. B. Oglesby in correcting the English are deeply appreciated. I also wish to extend my thanks to Mrs. L. P. Gordon for her calculations of theoretical ionization potential and heat of formation and to Mrs. Claudine Taylor for her excellent typing.

The understanding, encouragement, and assistance of my wife, Grace, my parents, Mr. and Mrs. L. S. Li and my other relatives are gratefully acknowledged.

## TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS . . . . .	ii
LIST OF TABLES. . . . .	v
LIST OF ILLUSTRATIONS. . . . .	vii
SUMMARY. . . . .	x
Chapter	
I. INTRODUCTION . . . . .	1
Definition of the Problem	
Purpose of this Research	
Review of the Literature of Attempted Synthesis of Cyclobutadiene	
Electron Ground State of Cyclobutadiene	
Chemistry of Cyclobutadiene	
II. APPARATUS AND EXPERIMENTAL PROCEDURES . . . . .	23
Instruments	
Coaxial Furnace Inlet System	
Cryogenic Inlet System	
Low Temperature Reaction System	
Chemical Preparations	
Energy Measurements	
III. RESULTS AND DISCUSSION . . . . .	47
Reaction of Cyclobutadieneirontricarbonyl with Ceric Ion	
Dehalogenation of <u>Cis</u> -3,4-dichlorocyclobutene	
Attempted Dehalogenation of <u>Cis</u> -3,4-dichlorocyclobutene at Low Temperature	
Radio Frequency Discharge of <u>Cis</u> -3,4-dichlorocyclobutene	
Pyrolysis of Cyclobutadieneirontricarbonyl	
Copyrolysis of Cyclobutadieneirontricarbonyl and Dienophiles	
Copyrolysis of Cyclobutadieneirontricarbonyl and Oxygen	

## TABLE OF CONTENTS (Continued)

Chapter	Page
III. (Continued)	
Pyrolysis and Quenching Experiment with Cyclobutadieneirontricarboxyl	
Reaction of Dimethyl Acetylenedicarboxylate with Quenched $C_4H_4$ Produced by Pyrolysis of Cyclobutadieneirontricarboxyl	
Unsuccessful Copyrolysis with Cyclobutadieneiron- tricarboxyl	
Mechanism of the Pyrolysis of Cyclobutadieneiron- tricarboxyl	
Ionization Potential of Cyclobutadiene	
Derived Heat of Formation of Cyclobutadiene	
IV. CONCLUSIONS AND RECOMMENDATIONS. . . . .	85
APPENDICES	
A. MASS SPECTRUM AND IONIZATION POTENTIAL OF CYCLOBUTADIENEIRONTRICARBOXYL . . . . .	90
B. MISCELLANEOUS SPECTROMETRIC DATA . . . . .	95
C. DERIVATION OF HEAT OF FORMATION OF CYCLOBUTADIENE FROM ENERGETIC STUDY . . . . .	130
D. THEORETICAL IONIZATION POTENTIALS AND HEATS OF ATOMIZATION OF $C_4H_4$ ISOMERS. . . . .	137
BIBLIOGRAPHY . . . . .	141
VITA . . . . .	145

## LIST OF TABLES

Table	Page
1. Products of rf Discharge of <u>Cis</u> -3,4-dichlorocyclobutene and their Appearance Temperatures . . . . .	52
2. Mass Spectra of C <sub>4</sub> H <sub>4</sub> from rf Discharge of C <sub>4</sub> H <sub>4</sub> Cl <sub>2</sub> and C <sub>4</sub> H <sub>4</sub> Isomers at 70 eV . . . . .	54
3. Mass Spectrum of the Products at 70 eV from the Pyrolysis of Cyclobutadieneirontricarboxyl at 380 <sup>o</sup> . . . . .	57
4. Products of Copyrolysis of Cyclobutadieneirontricarboxyl with Oxygen and Their Appearance Temperatures . . . . .	64
5. Pyrolysis Products of Cyclobutadieneirontricarboxyl and their Appearance Temperatures . . . . .	68
6. Mass Spectra of C <sub>4</sub> H <sub>4</sub> Isomers and C <sub>4</sub> H <sub>4</sub> from Pyrolysis of CIT . . . . .	70
7. Ionization Potential and Heat of Formation of C <sub>4</sub> H <sub>4</sub> Isomers . . . . .	82
8. Relative Abundances of the Principal Positive Ions from Cyclobutadieneirontricarboxyl at 70 eV . . . . .	93
9. Mass Spectrum of Furan at -105 <sup>o</sup> at 70 eV from the Copyrolysis of Cyclobutadieneirontricarboxyl with Oxygen . . . . .	96
10. Relative Abundance of the Principal Positive Ions from Cyclooctatetraene (C <sub>8</sub> H <sub>8</sub> ) at 70 eV . . . . .	97
11. Relative Abundance of the Principal Positive Ions from <u>Syn</u> Cyclobutadiene Dimer at 70 eV . . . . .	99
12. Relative Abundances of the Principal Positive Ions from <u>Cis</u> -3,4-dichlorocyclobutene at 70 eV . . . . .	100
13. Mass Spectrum of the Products at 70 eV from the Copyrolysis of CIT with Methyl Propiolate at 380 <sup>o</sup> . . . . .	103

## LIST OF TABLES (Continued)

Table	Page
14. Heat of Formation of Cyclobutadiene Derived from Energetic Study. . . . .	135
15. Theoretical Ionization Potential and Heat of Atomization of $C_4H_4$ Isomers . . . . .	139



## LIST OF ILLUSTRATIONS

Figure	Page
1. Coaxial Furnace Inlet System . . . . .	25
2. Pyrex Furnace Tube . . . . .	26
3. Cold Reactor Attached to Cryogenic Inlet System A . . . . .	28
4. Radio Frequency Discharge Tube & Cryogenic Inlet System B . . . . .	31
5. Low Temperature Reaction Arrangement . . . . .	33
6. Ionization Efficiency Curves of Water and $C_4H_4$ from the Pyrolysis of CIT. . . . .	45
7. Ionization Efficiency Data for $C_4H_4$ from the Pyrolysis of CIT at $380^\circ$ (I). . . . .	79
8. Ionization Efficiency Data for $C_4H_4$ from the Pyrolysis of CIT at $380^\circ$ (II) . . . . .	80
9. Ionization Efficiency Data for Cyclobutadiene-irontricarbonyl . . . . .	92
10. Mass Spectrum of HCl and $C_2H_2$ at $-155^\circ$ from the rf Discharge of <u>Cis</u> -3,4-dichlorocyclobutene Followed by Quenching at $-196^\circ$ . . . . .	104
11. Mass Spectrum of $C_4H_4$ , $C_2H_2Cl$ and HCl at $-140^\circ$ from the rf Discharge of <u>Cis</u> -3,4-dichlorocyclobutene Followed by Quenching at $-196^\circ$ . . . . .	105
12. Mass Spectrum of $C_4H_4$ and $C_4H_2$ at $-120^\circ$ from the rf Discharge of <u>Cis</u> -3,4-dichlorocyclobutene Followed by Quenching at $-196^\circ$ . . . . .	106
13. Mass Spectrum of $C_4H_2$ , $C_2H_2Cl$ and $C_2H_2Cl_2$ at $-90^\circ$ from the rf Discharge of <u>Cis</u> -3,4-dichlorocyclobutene Followed by Quenching at $-196^\circ$ . . . . .	107

## LIST OF ILLUSTRATIONS (Continued)

Figure	Page
14. Mass Spectrum of $C_4H_3Cl$ and $C_2H_2Cl_2$ at $-80^\circ$ from the rf Discharge of <u>Cis-3,4-dichloro-</u> cyclobutene Followed by Quenching at $-196^\circ$ . . . . .	108
15. Mass Spectrum of the Products of Copyrolysis of CIT with Methyl Propiolate at $380^\circ$ . . . . .	109
16. Mass Spectrum of the Products of Copyrolysis of CIT with Dimethyl Acetylenedicarboxylate at $380^\circ$ . . . . .	110
17. Mass Spectrum of $C_4H_4O$ at $-100^\circ$ from the Copyrolysis of CIT with Oxygen Followed by Quenching to $-196^\circ$ . . . . .	111
18. Mass Spectrum of $C_4H_4O_2$ and Unpyrolyzed CIT at $-60^\circ$ from the Copyrolysis of CIT with Oxygen Followed by Quenching at $-196^\circ$ . . . . .	112
19. Mass Spectrum of $CO_2$ at $-140^\circ$ from the Pyrolysis of CIT Followed by Quenching at $-196^\circ$ . . . . .	113
20. Mass Spectrum of $C_4H_6$ and $C_4H_4$ at $-115^\circ$ from the Pyrolysis of CIT Followed by Quenching at $-196^\circ$ . . . . .	114
21. Mass Spectrum of $C_6H_6$ , $C_4H_6$ and $C_4H_4$ at $-100^\circ$ from the Pyrolysis of CIT Followed by Quenching at $-196^\circ$ . . . . .	115
22. Mass Spectrum of $C_6H_6$ at $-90^\circ$ from the Pyrolysis of CIT Followed by Quenching at $-196^\circ$ . . . . .	116
23. Mass Spectrum of $C_8H_8$ and $C_6H_6$ at $-80^\circ$ from the Pyrolysis of CIT Followed by Quenching at $-196^\circ$ . . . . .	117
24. Ionization Efficiency Data for <u>Cis-3,4-dichloro-</u> butene . . . . .	118
25. Ionization Efficiency Data for Butatriene . . . . .	119
26. Ionization Efficiency Data for Vinylacetylene . . . . .	120

## LIST OF ILLUSTRATIONS (Continued)

Figure	Page
27. Ionization Efficiency Data for Condensed $C_4H_4$ at $-100^\circ$ from Pyrolysis of CIT . . . . .	121
28. Ionization Efficiency Data for Condensed $C_8H_8$ at $-70^\circ$ from Pyrolysis of CIT . . . . .	122
29. Ionization Efficiency Data for $C_4H_4^+$ and $C_2H_2^+$ from <u>Cis</u> -3,4-dichlorocyclobutene . . . . .	123
30. Ionization Efficiency Data for $C_4H_4^+$ and $C_4H_2^+$ from <u>Cis</u> -3,4-dichlorocyclobutene . . . . .	124
31. Infrared Spectrum of the Reaction Mixture of Dimethyl Acetylenedicarboxylate and Condensed $C_4H_4$ from the Pyrolysis of CIT . . . . .	125
32. Infrared Spectrum of the Mixture of CIT and Dimethyl Acetylenedicarboxylate after $1/2$ hr of Heating at $90^\circ$ . . . . .	126
33. Infrared Spectrum of Authentic Dimethyl 1,2-Benzenedicarboxylate . . . . .	127
34. Infrared Spectrum of Cyclobutadiene- irontricarbonyl. . . . .	128
35. Infrared Spectrum of <u>Cis</u> -3,4- dichlorocyclobutene. . . . .	129

## SUMMARY

Cyclobutadiene is the simplest conjugated cyclic polyene which has still eluded the researcher in all attempts at unequivocal synthesis. 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 experimental failures of synthesis and the divergent results of theoretical calculations have whetted the curiosity of chemists concerning the problem of cyclobutadiene. Recently cyclobutadiene was reported as an intermediate from the oxidation of cyclobutadieneirontricarbonyl (CIT).<sup>19</sup> Indirect evidence showed that cyclobutadiene was isolated and exhibited a finite life time. All of the prior attempts to prepare cyclobutadiene were carried out by conventional methods and techniques.

The work reported in this thesis involved the synthesis of cyclobutadiene either by pyrolysis or by electrical discharge of suitable precursors; the proof of the existence and the determination of the energetics of this molecule was carried out using mass spectrometric techniques. Reactions of cyclobutadiene, as well as attempts to prepare this species as a stable solid or liquid phase at low temperatures by utilization of the new techniques of cryochemistry recently developed in this laboratory were carried out in the apparatus which had been designed, constructed and used successfully in earlier related studies of highly reactive molecules in this laboratory.

The oxidation reaction of CIT with ceric ion was carried out at  $0^{\circ}$ . The product of the reaction were passed through a tube kept at  $0^{\circ}$  and were then quenched at  $-180^{\circ}$  to  $-196^{\circ}$  in a cryogenic inlet arrangement attached to a mass spectrometer. Free cyclobutadiene, i. e., m/e 52, was not detected, but cyclobutadiene dimer was observed during the slow warm-up of the quenched composite solid. The dehalogenation of cis-3,4-dichlorocyclobutene with sodium amalgam at room temperature followed by immediate quenching of the products at  $-180^{\circ}$  to  $-196^{\circ}$  in the cryogenic inlet system also failed to yield evidence of cyclobutadiene although cyclobutadiene dimer was again observed. The earlier indirect evidence of the isolation of cyclobutadiene from the reaction of CIT with ceric ion at  $0^{\circ}$  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 dimer.<sup>19</sup> In this research, cyclobutadiene was both liberated from CIT and observed to react immediately with dienophiles upon pyrolysis in the injector of a gas chromatograph. In view of the conditions maintained in the reported experiment<sup>19</sup>, the formation of methyl benzoate could be due to this process instead of the reaction of isolated cyclobutadiene and methyl propiolate. This could explain the failure of the attempt at direct observation of cyclobutadiene in the reaction of CIT and ceric ion in this research.

Radio frequency discharge of cis-3,4-dichlorocyclobutene at room temperature at pressures of  $10^{-1}$  torr followed by immediate quenching at  $-196^{\circ}$  produced HCl,  $C_2H_2$ ,  $C_2HCl$ ,  $C_4H_4$ ,  $C_4H_2$ ,  $C_4H_3Cl$  and  $C_2H_2Cl_2$ . Upon comparing the mass

spectra and ionization potentials of vinylacetylene and butatriene with that of the  $C_4H_4$  produced, it was concluded that vinylacetylene, instead of cyclobutadiene, was the product of this rf discharge of CIT.

Pyrolysis of CIT was conducted in a coaxial furnace inlet system in which the furnace exhaust was only 1/8 inch from the ionizing electron beam of the mass spectrometer. With the pressures of CIT at  $10^{-2}$  to  $10^{-1}$  torr and furnace temperatures of  $350^{\circ}$  to  $400^{\circ}$ , cyclobutadiene dimer, benzene, 1,3-butadiene, vinylacetylene, acetylene, carbon monoxide and cyclobutadiene were produced. 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 detected at  $-100^{\circ}$ . The mass spectrum and ionization potential of this  $C_4H_4$  were different from that of vinylacetylene and butatriene, but the evidence for the existence of a stable cyclobutadiene at low temperatures was inconclusive because of the presence of vinylacetylene. The mechanism of the pyrolysis of CIT was examined. The formation of benzene was postulated as 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 reaction of cyclobutadiene with dienophiles was observed in the copyrolysis of CIT with methyl propiolate or with dimethyl acetylenedicarboxylate. The reaction of cyclobutadiene with oxygen, in the copyrolysis of CIT and oxygen, produced furan. This result agreed with that of flash photolysis of CIT<sup>21</sup> in the presence of oxygen but disagreed with that of the pyrolysis of photo- $\alpha$ -pyrone<sup>22</sup> in the presence of oxygen in which 2-butene 1,4-dione had been produced. The lack

of reaction of cyclobutadiene with  $\text{CH}_3^\bullet$  or  $\text{CH}_2^\bullet$  in the copyrolysis of CIT with methyl bromide or with dibromoethane suggested that cyclobutadiene produced from CIT had a singlet ground state. This conclusion was also supported by the higher ionization potential of cyclobutadiene measured in this thesis compared to the experimental ionization potential of the cyclobutadiene produced from photo- $\alpha$ -pyrone at  $800^\circ$ . The theoretically calculated ionization potential of singlet cyclobutadiene was higher than that of triplet cyclobutadiene.

The experimental ionization potential of cyclobutadiene and the experimental appearance potentials of appropriate ions from CIT permitted the direct determinations of the bond dissociation energies of cyclobutadiene,  $D(\text{C}_2\text{H}_2 - \text{C}_2\text{H}_2)$  and  $D(\text{C}_4\text{H}_2 - \text{H}_2)$ . Similarly, the bond dissociation energies can be obtained by the experimental ionization potential of cyclobutadiene and the experimental appearance potentials of appropriate ions from cis-3,4-dichlorocyclobutene. From these derived bond dissociation energies, the heats of formation of cyclobutadiene were calculated as 28.9, 33.5, 71.6 and 69.6 kcal/mole. These heats of formation of cyclobutadiene were obtained as a result of several assumptions. In the mass fragmentation of CIT and cis-3,4-dichlorocyclobutene, the  $\text{C}_4\text{H}_4^+$  was assumed to be the cyclobutadiene ion, the  $\text{C}_2\text{H}_2^+$  was acetylene ion, and  $\text{C}_4\text{H}_2^+$  was diacetylene ion. The excess energy in the measurement of the appearance potential was also assumed to be zero. These assumptions could have contributed to the large discrepancy in the values of the heat of formation of cyclobutadiene.

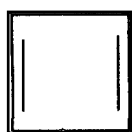
Mass spectra and ionization potentials of CIT, cis-3,4-dichlorocyclobutene and syn cyclobutadiene dimer are presented in Appendices A and B.

## CHAPTER I

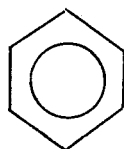
### INTRODUCTION

#### Definition of the Problem

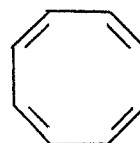
The general research program in this laboratory is concerned with the development of chemical information at cryogenic temperatures, particularly on systems that astronomers and astrophysicists feel are important in comets and in the atmospheric and surface chemistry of the Jovian planets. Each of these 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. One of the most intriguing of these compounds is cyclobutadiene (1) which is the simplest member of the fully conjugated cyclic polyenes. The next simplest member, benzene (2), was discovered in 1825. After the aromatic character of benzene was understood, it was natural for chemists to assume that other cyclic hydrocarbons which have a closed system of alternating double and single



(1)



(2)



(3)



bonds such as cyclobutadiene (1) and cyclooctatetraene (3), would also have aromatic character and exist as stable compounds. In fact, the first attempt to prepare cyclobutadiene itself was made by Willstätter<sup>1</sup> in 1905. However, in 1911 Willstätter<sup>2</sup> successfully prepared cyclooctatetraene which proved to have an olefinic rather than the expected aromatic nature. Since then, the search for the existence of cyclobutadiene or its derivatives has been the interest of many organic chemists. From previous experimental work, cyclobutadiene is believed to be a highly reactive intermediate which dimerizes immediately at room temperature. Before this thesis work, no direct observation of cyclobutadiene had been reported.

Theoretical aspects for this simple molecule have also attracted considerable interest, particularly regarding predictions of the multiplicity of its ground state. Simple Hückel molecular orbital theory predicts that cyclobutadiene which has  $4n$   $\pi$  electrons, should have a triplet ground state, and therefore, it probably would not be stable. On the contrary, a recent calculation by Dewar<sup>3</sup>, using a semiempirical self-consistent field molecular orbital (SCF MO) treatment for hydrocarbons, indicates that cyclobutadiene is a typical cyclic polyene with effectively localized single and double bonds and with a singlet ground state and a greater likelihood of stable existence.

In short, theoretical and experimental studies of the chemistry of cyclobutadiene, especially the possibility of its existence, have not demonstrated conclusive results. Clearly, much needs to be done on this problem, and experimental work is especially needed to test the theoretical predictions.

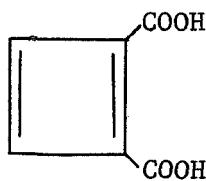
### Purpose of this Research

The prior attempts to prepare cyclobutadiene were limited to conventional methods and techniques. New approaches, such as cryochemical techniques, which can overcome the limitations of conventional methods, provide a new path to attack the cyclobutadiene problem. The purpose of this thesis is fourfold: (1) to find a method of preparing cyclobutadiene from cis-3,4-dichlorocyclobutene or cyclobutadieneirontricarbonyl so that it can be directly observed mass spectrometrically, (2) to stabilize cyclobutadiene at low temperatures by cryoquench from either new methods or from the earlier reported experimental methods which claimed to have generated cyclobutadiene, (3) to determine the energetics of cyclobutadiene from ionization efficiency measurements in the mass spectrometer, and (4) to carry out some simple reactions of cyclobutadiene either at low or high temperatures, in order to develop some chemical insight into the nature of cyclobutadiene.

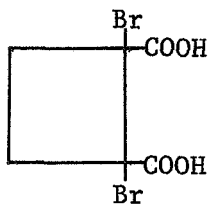
### Review of the Literature of

#### Attempted Synthesis of Cyclobutadiene

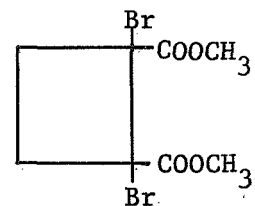
The first attempt to synthesize the members of the cyclobutadiene series appeared to have been made in 1893 by Perkin.<sup>4</sup> He tried unsuccessfully to make cyclobutadiene-1,2-dicarboxylic acid (1) by treatment of 1,2-dibromocyclobutane-1,2-dicarboxylic acid (2) with various bases. Similarly, the same treatment of the dimethyl 1,2-dibromocyclobutanedicarboxylate (3) also failed to produce the acid (1).



(1)

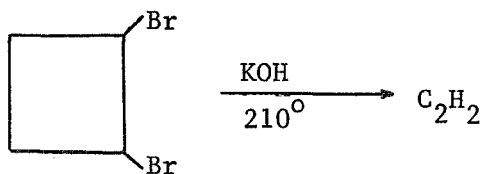


(2)



(3)

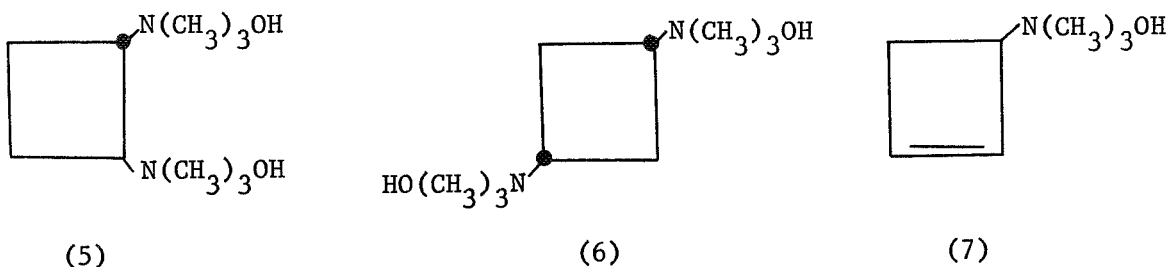
In 1905 Willstätter and Schmädell<sup>1</sup> made the first attempt to synthesize cyclobutadiene itself. Dehydrohalogenation of 1,2-dibromocyclobutane (4) with either quinoline at high temperature, potassium hydroxide at 100° to 105°, or powdered potassium hydroxide at 210° all failed to yield cyclobutadiene. In the reaction of (4) with powdered potassium hydroxide at 210°, the production of acetylene suggested that cyclobutadiene was a possible intermediate.



(4)

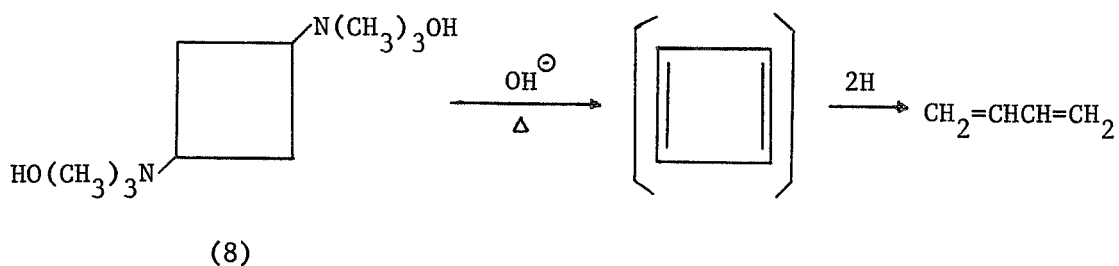
After these failures, unsuccessful attempts to synthesize cyclobutadiene were also reported at Harvard<sup>5</sup> and Münster.<sup>6</sup> The most extensive work was done by Buchman and his co-workers<sup>7</sup> at the California Institute of Technology in the years between 1940 and 1954. Their application of the Hofmann degradation to various quaternary ammonium hydroxides of the cyclobutane series failed to

yield cyclobutadiene. For example, thermal decomposition of trans-1, 2-cyclobutanebis (trimethyl-ammonium) hydroxide (5), cis-1, 3-cyclobutanebis (trimethyl-ammonium) hydroxide (6) and 2-cyclobutenyl(trimethylammonium)hydroxide (7) at temperatures varying between 250<sup>o</sup> and 420<sup>o</sup> produced no cyclobutadiene or



compound derived therefrom.

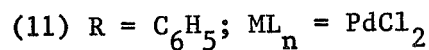
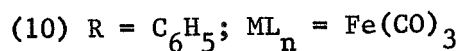
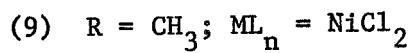
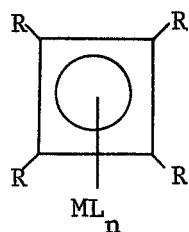
In 1957 Nenitzescu et al.,<sup>8</sup> prepared 1, 3-bis(dimethylamino) cyclobutane dimethylohydroxide (8) which decomposed into 1, 3-butadiene, and, from this, he concluded that cyclobutadiene was formed as an intermediate in the pyrolysis and



thus proceeded to two hydrogen atoms from neighboring molecules to form 1, 3-butadiene.

In 1956 Longuet-Higgins and Orgel<sup>9</sup>, on the basis of Hückel molecular orbital theory, predicted the stabilization of substituted cyclobutadiene

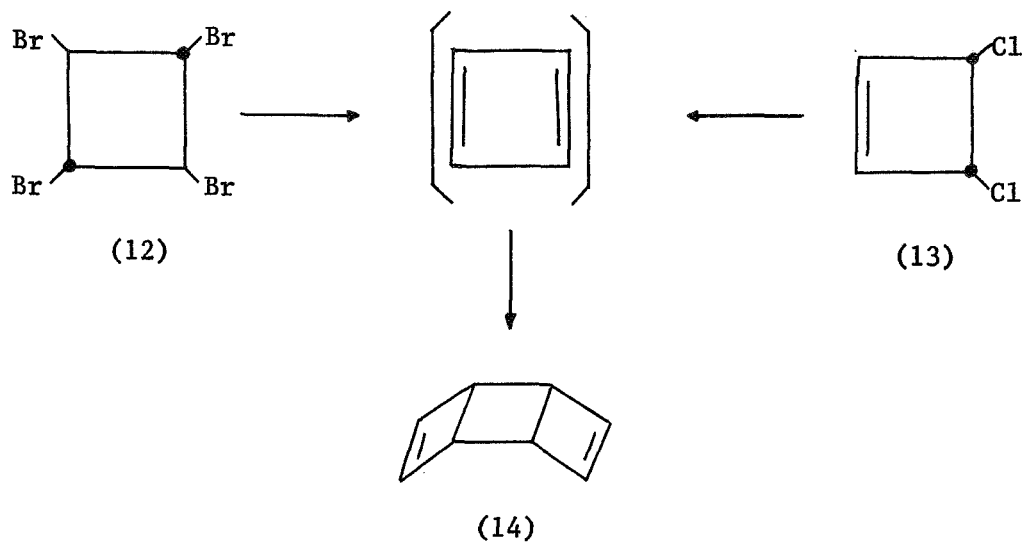
by coordination of its antibonding  $\pi$  orbitals with favorably oriented metal d orbitals. This prediction prompted another period of intensive interest in cyclobutadiene, especially substituted cyclobutadienes. Three years later, in 1959, two substituted cyclobutadiene metal complexes, tetramethylcyclobutadienenickel chloride (9)<sup>10</sup> and tetraphenylcyclobutadieneirontricarbonyl (10)<sup>11</sup> were successfully synthesized. In 1960, preparation of tetraphenylcyclobutadienepalladium chloride



(11)<sup>12</sup> was also reported.

Several attempts were made using these substituted cyclobutadiene metal complexes and other possible precursors to produce substituted cyclobutadiene which might be expected to be more stable than cyclobutadiene. The increased stability results from hyperconjugation and more importantly from the diminished tendency to polymerize arising from the fact that the cyclobutadiene is sterically hindered by substituent methyl groups.<sup>13</sup> However, no substituted cyclobutadienes have been isolated to date.

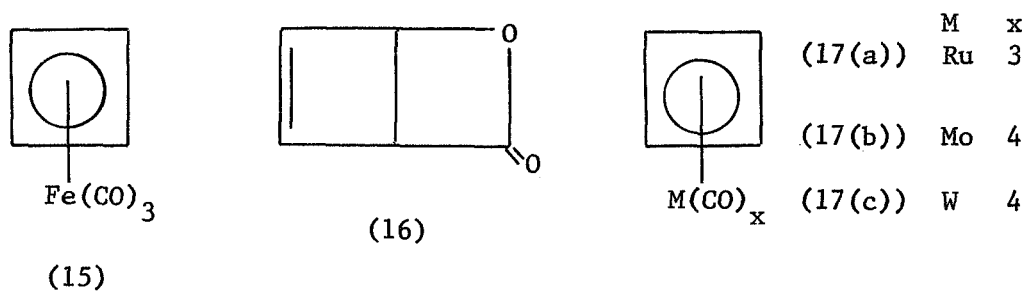
Two significant investigations concerning generation of cyclobutadiene were reported by Nenitzescu et al., in 1959 by dehalogenation of all-trans-1, 2, 3, 4-tetrabromocyclobutane (12)<sup>14</sup> and, in 1964, by dehalogenation of cis-3, 4-dichlorocyclobutene (13).<sup>15</sup> The dehalogenations were conducted at room temperature and



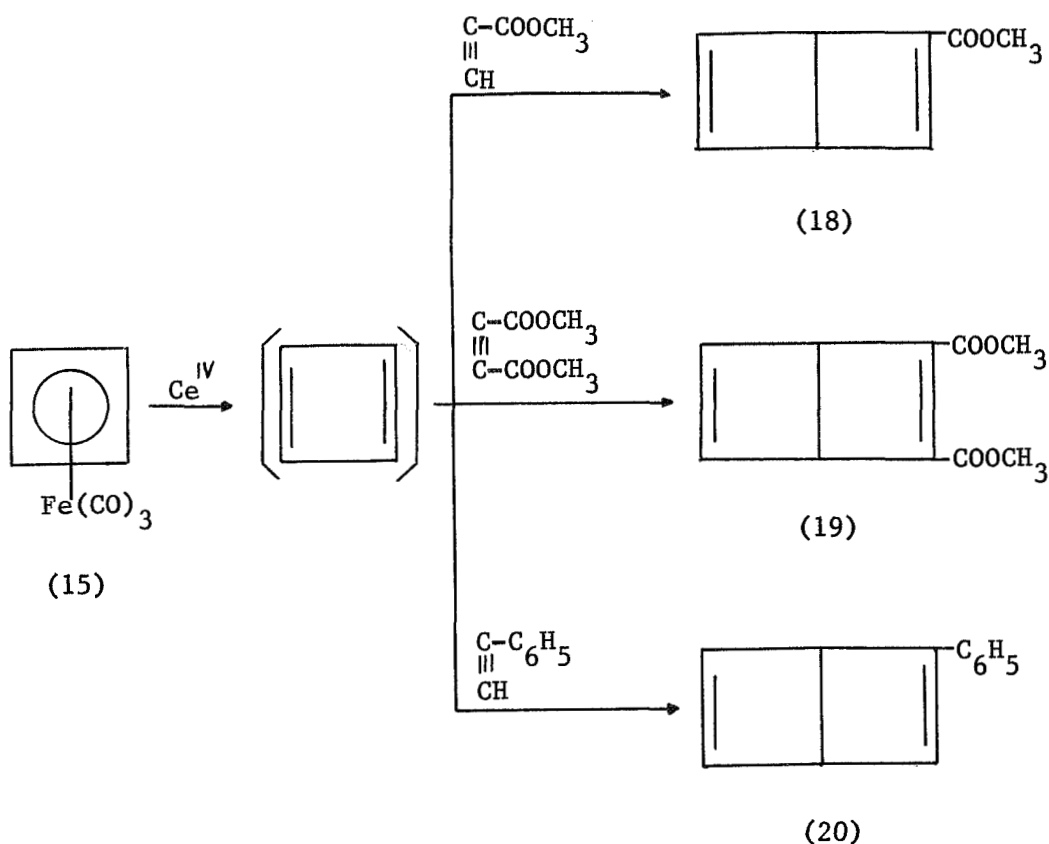
the syn dimer (14) of cyclobutadiene was produced in both experiments which suggested that cyclobutadiene was produced as an intermediate.

In 1965, Pettit et al.,<sup>16</sup> first reported the preparation of the cyclobutadiene metal complex, cyclobutadieneirontricarbonyl (CIT, 15), by the reaction of cis-3,4-dichlorocyclobutene (13) with diiron enneacarbonyl ( $\text{Fe}_2(\text{CO})_9$ ).

Rosenblum<sup>17</sup> reported that the reaction of iron pentacarbonyl or diiron enneacarbonyl with photo- $\alpha$ -pyrone (16) also produced CIT (15). Several other cyclobutadiene metal complexes (17) were also prepared by Pettit et al.<sup>18</sup>



Pettit *et al.*,<sup>19</sup> also reported the generation of cyclobutadiene by the decomposition of CIT (15) in an aqueous solution with ceric ion at 0°. When CIT was decomposed in the presence of methyl propiolate, 2-carbomethoxybicyclo[2,2,0]hexa-2,5-diene (18) (a "Dewar benzene" derivative expected from the addition of dienophile to cyclobutadiene) was formed. Similar decomposition of CIT in the presence of dimethyl acetylenedicarboxylate yielded 2,3-dicarbomethoxybicyclo[2,2,0]hexa-2,5-diene (19)<sup>19</sup> and, in the presence of phenylacetylene, 2-phenylbicyclo[2,2,0]hexa-2,5-diene (20)<sup>20</sup>.



In order to prove that free cyclobutadiene was involved in these reactions, Pettit et al.,<sup>19</sup> conducted the following experiment. CIT (15) in ether solution was added to a flask containing a stirred aqueous solution of ceric ammonium nitrate at 0°. The evolved gas was quenched in a trap at -196°. A cold ether solution of methyl propiolate was added to the condensate collected in the trap. The ether solution was then heated and analyzed by vapor phase chromatography. They reported that methyl benzoate was detected in very small amount in the product. It was postulated that free cyclobutadiene was produced by the oxidation of CIT (15) and was transferred as a gas into the second trap.

After the start of this thesis work, two direct observations of cyclobutadiene were claimed. Cyclobutadiene was reported from kinetic mass spectrometry in flash photolysed CIT (15)<sup>21</sup> as well as from flash vacuum pyrolysis of photo- $\alpha$ -pyrone (16) in which m/e 52 was produced and reported as cyclobutadiene<sup>22</sup>.

### Electron Ground State of Cyclobutadiene

Cyclobutadiene has been the object of considerable theoretical interest, and much emphasis has centered on the nature of its ground state. Both singlet and triplet ground states have been predicted<sup>23</sup>, and thus bodies of experimental data exist which allow argument from both perspectives. It is proper to briefly review these arguments at this point, since the nature of the ground state proved to be an important consideration in this thesis research.

### Triplet Ground State of Cyclobutadiene

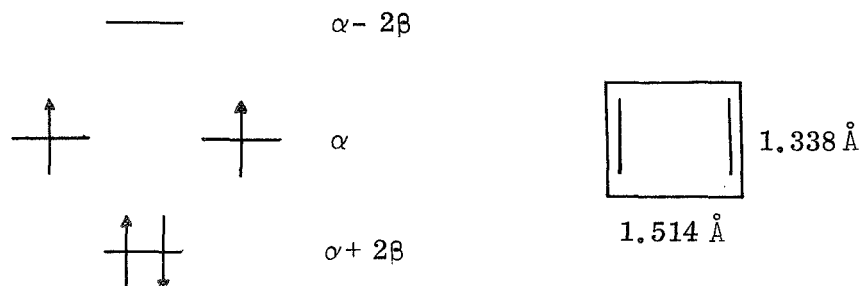
By only considering the  $\pi$  electrons in cyclobutadiene, simple Hückel



molecular orbital theory, coupled with Hund's rule, leads one to conclude that the ground state of cyclobutadiene is a triplet. Simple calculations<sup>23</sup> yield the four energy levels shown here. The total  $\pi$  binding energy of  $C_4H_4$  is  $4\alpha + 4\beta$ , which equals that of two molecules of ethylene, so that the conventional  $\pi$  delocalization energy is exactly zero.

### Singlet Ground State of Cyclobutadiene

Dewar and his associates have recently developed a semi-empirical SCF-



MO method, to calculate ground state properties of molecules.<sup>3</sup> This method yields by far the most useful and accurate predictions and correlations of any computational scheme devised. By this method, Dewar showed that triplet cyclobutadiene was square while singlet cyclobutadiene was rectangular. According to the calculation, cyclobutadiene should have a singlet ground state with a heat of formation of 830.1 kcal/mole and with the bond lengths shown above. Thus, cyclobutadiene should be a typical cyclic polyene with effectively localized single and double bonds. Singlet cyclobutadiene has a virtually zero resonance energy (0.8 kcal/mole).

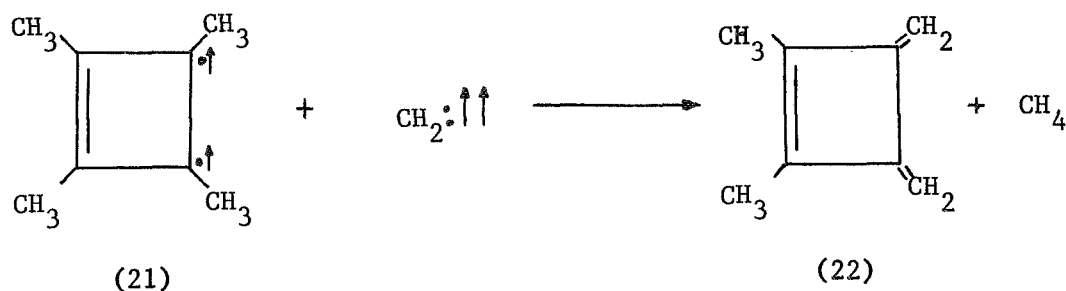
### Chemistry of Cyclobutadiene

Depending upon the approximations involved, molecular orbital theory

predicts that cyclobutadiene will have either a singlet ground state or a triplet ground state. The following review presents the chemical behavior of cyclobutadiene as reported in the literature, which provides experimental results which serve as a basis for an interpretation of the multiplicity of the ground state. Data supporting the ground state of cyclobutadiene as both singlet and triplet were found. Reported reactions of dienophiles with cyclobutadiene or substituted cyclobutadiene are also presented here.

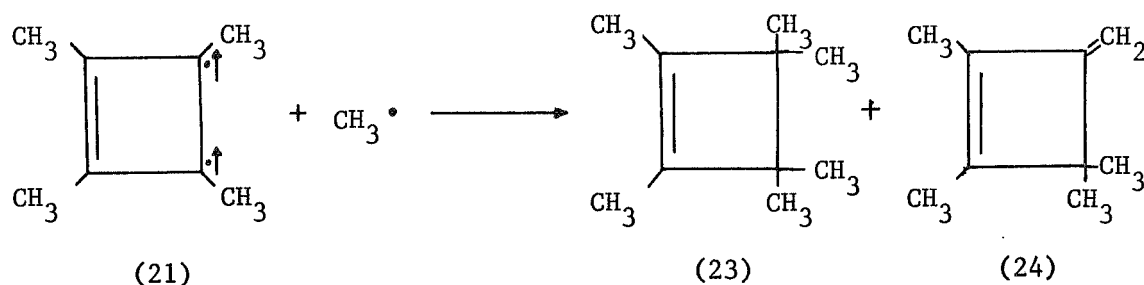
#### Triplet Diradical Character of the Cyclobutadiene

Support for a triplet diradical character of tetramethylcyclobutadiene was first demonstrated by the formation of 3,4-dimethylene-1,2-dimethylcyclobutene (22) when tetramethylcyclobutadiene (21), generated by the action of potassium vapor at about  $250^{\circ}$  with 3,4-dichloro-1,2,3,4-tetramethylcyclobutene, was reacted with triplet methylene ( $\text{CH}_2:$ ), generated *in situ* from dibromomethane.<sup>24</sup> The formation of (22) was visualized as the simultaneous transfer of two hydrogens from triplet tetramethylcyclobutadiene to triplet  $\text{CH}_2:$  (assumed to be the ground state) with conservation of spin from the two triplet species. The formation of 1,2,3,3,4,4-hexamethylcyclobutene (23) and 4-methylene-1,2,3,3-tetramethylcyclobutene

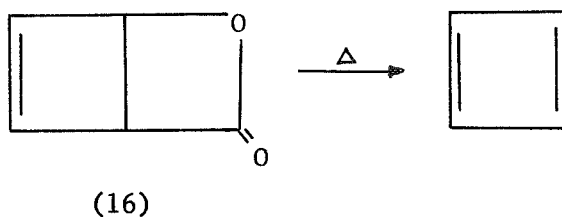


(24) among other compounds in the reaction of tetramethylcyclobutadiene (21) with methyl radicals (from methyl bromide) was also assumed to demonstrate the diradical character of (21).<sup>24</sup>

Similarly, the reaction of cyclobutadiene itself with radicals also demon-

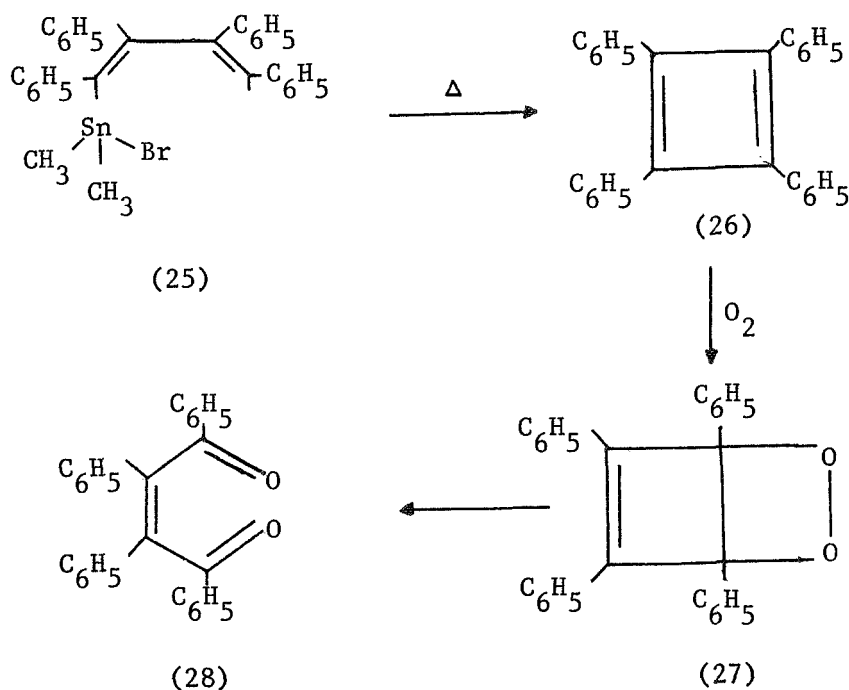


strated its diradical character.<sup>22</sup> In the mass spectrum of the pyrolysis of photo- $\alpha$ -pyrone (16) at 800<sup>o</sup>, a peak was observed at m/e 52 which corresponds to the molecular weight of cyclobutadiene. Titration with methyl radicals generated by copyrolysis of ethyl nitrite with photo- $\alpha$ -pyrone (16) at 800<sup>o</sup> led to new peaks at m/e 67 and 82 corresponding to m/e 52 plus one and two methyls respectively. Similarly, copyrolysis with allyl iodide resulted in peaks corresponding to m/e 52 plus the following combinations of allyls and iodines: one and two iodines, one and two allyls, and one allyl with one iodine. Copyrolysis of (16) with both ethyl nitrite and allyl iodide gave additional peaks corresponding to m/e 52 plus methyl



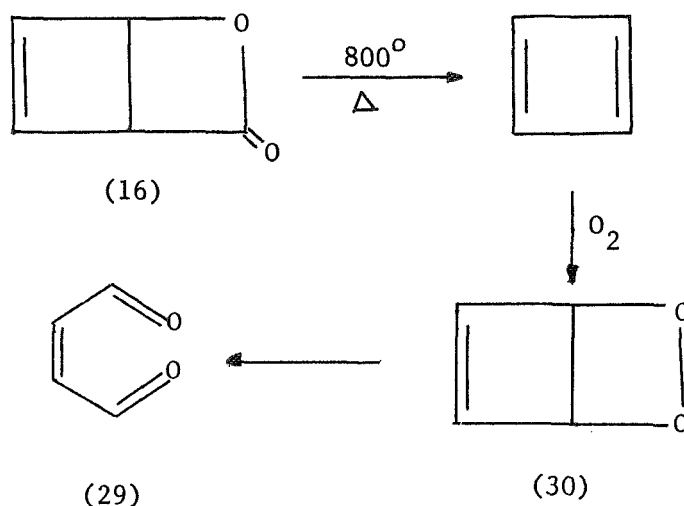
and iodine ( $m/e$  194) and methyl and allyl ( $m/e$  108).

The reaction of oxygen with substituted cyclobutadiene suggests the triplet diradical character of cyclobutadiene since oxygen itself has a triplet ground state. For example, when tetraphenylcyclobutadiene (26) was generated by the thermal decomposition of (4-bromo-1, 2, 3, 4-tetraphenyl-cis, cis-1, 3-butadienyl) dimethyltin bromide (25) in the presence of oxygen, cis-dibenzoystilbene (28) was formed, presumably by way of a four-membered peroxide intermediate (27).<sup>25</sup>



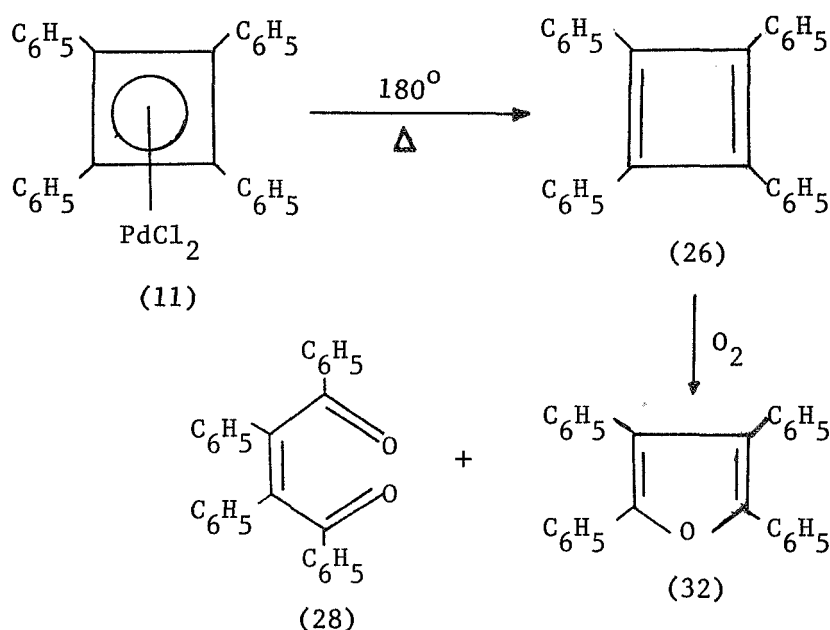
Copyrolysis of photo- $\alpha$ -pyrone (16) with oxygen at  $800^\circ$  also produced a peak at  $m/e$  84 corresponding to the molecular weight of 2-butene 1, 4-dione (29).<sup>22</sup>

Again the formation of 2-butene 1,4-dione (29) was presumed to take place by way of the four-membered peroxide intermediate (30) formed by the reaction of cyclobutadiene with oxygen.



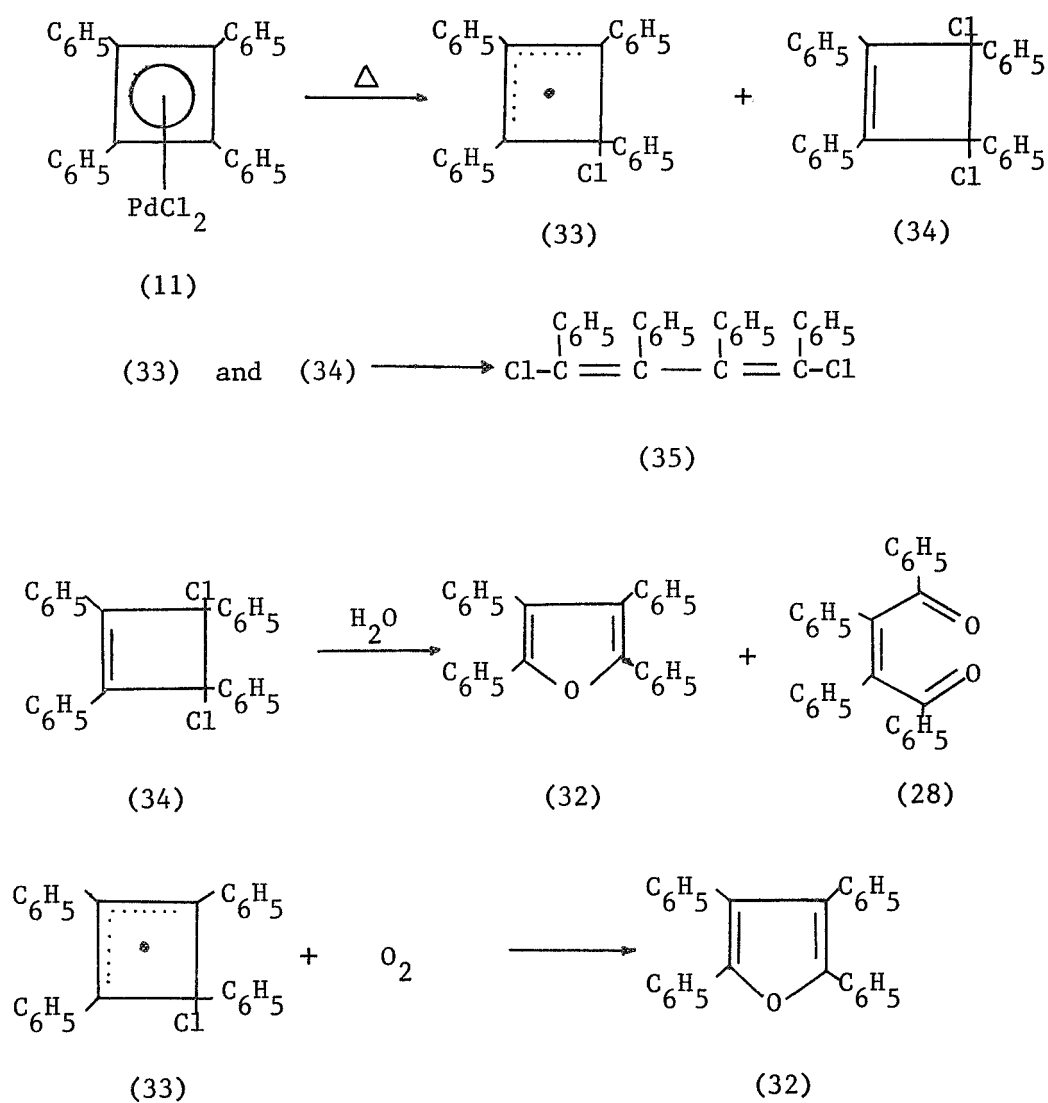
Beynon et al.,<sup>26</sup> have investigated the thermal decomposition of tetraphenylcyclobutadienepalladium chloride (11) in the mass spectrometer. The peaks at  $m/e$  426,  $[C_4(C_6H_5)_4Cl_2]^+$ ; 391,  $[C_4(C_6H_5)_4Cl]^+$ ; 356,  $[C_4(C_6H_5)_4]^+$ ; and 178,  $[C_2(C_6H_5)_2]^+$  were observed. The peak at  $m/e$  356, which corresponds to the molecular weight of tetraphenylcyclobutadiene (26) was the second largest peak. The peak at  $m/e$  356 is 85 percent of that at  $m/e$  178. In the presence of water vapor and oxygen (i. e., when the spectrum was run without prolonged evacuation of the sample), the peaks at  $m/e$  391,  $[C_4(C_6H_5)_4Cl]^+$  and  $m/e$  426,  $[C_4(C_6H_5)_4Cl_2]^+$  were replaced by peaks at  $m/e$  372, which corresponds to the molecular weight of

tetraphenylfuran (32), and  $m/e$  388, which corresponds to the molecular weight of cis-dibenzoylstilbene (28). Therefore, they concluded that tetraphenylcyclobutadiene (26) was produced in the thermal decomposition of (11) and immediately reacted with oxygen to form (32) and (28).



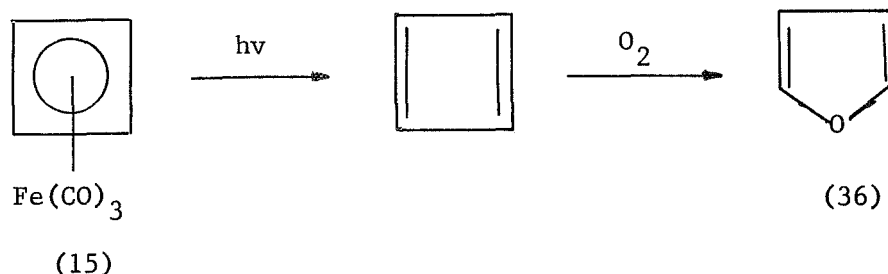
It has been questioned whether the formation of tetraphenylfuran (32) from tetraphenylcyclobutadienepalladium chloride (11) results from an actual reaction between tetraphenylcyclobutadiene and oxygen. The question arose when Blomquist and Maitlis<sup>27</sup> reported that the pyrolysis of tetraphenylcyclobutadienepalladium chloride (11) in a vacuum-sublimation apparatus generated a greenish-black sublimate from which a 26 percent yield of 1,4-dichloro-1,2,3,4-tetraphenylbutadiene (35) was isolated. Sandel and Freedman<sup>28</sup> then suggested that the primary products

of the pyrolysis of (11) could be 4-chloro-1,2,3,4-tetraphenylcyclobutenyl radical (33) (the green color) and dichlorotetraphenylcyclobutene (34) which formed (35). Sandel and Freedman<sup>28</sup> further suggested that the mass spectrum of the thermal decomposition of (11) reported by Beynon, et al.,<sup>26</sup> supported their postulation since the m/e of (33) and (34), i. e., peaks at 426 and 391, were observed. Therefore, Sandel and Freedman<sup>28</sup> concluded that the formation of tetraphenylfuran (32)



and cis-dibenzoylstilbene (28) in the presence of water and oxygen was due to the hydrolyses of dichlorotetraphenylcyclobutene (34) rather than from the oxidation of cyclobutadiene. The hydrolyses of (34), which produced (32) and (28), and the reaction of oxygen with (33), which produced (32), were both observed in the unpublished data of Freedman and his coworker.<sup>28</sup>

Photolysis of CIT (15) in the presence of oxygen produced furan (36)<sup>21</sup> but there was no evidence for the presence of 2-butene 1,4-dione (29), i. e., there was no  $m/e$  84. It was postulated that furan was formed by the reaction of cyclobutadiene with oxygen.<sup>21</sup>

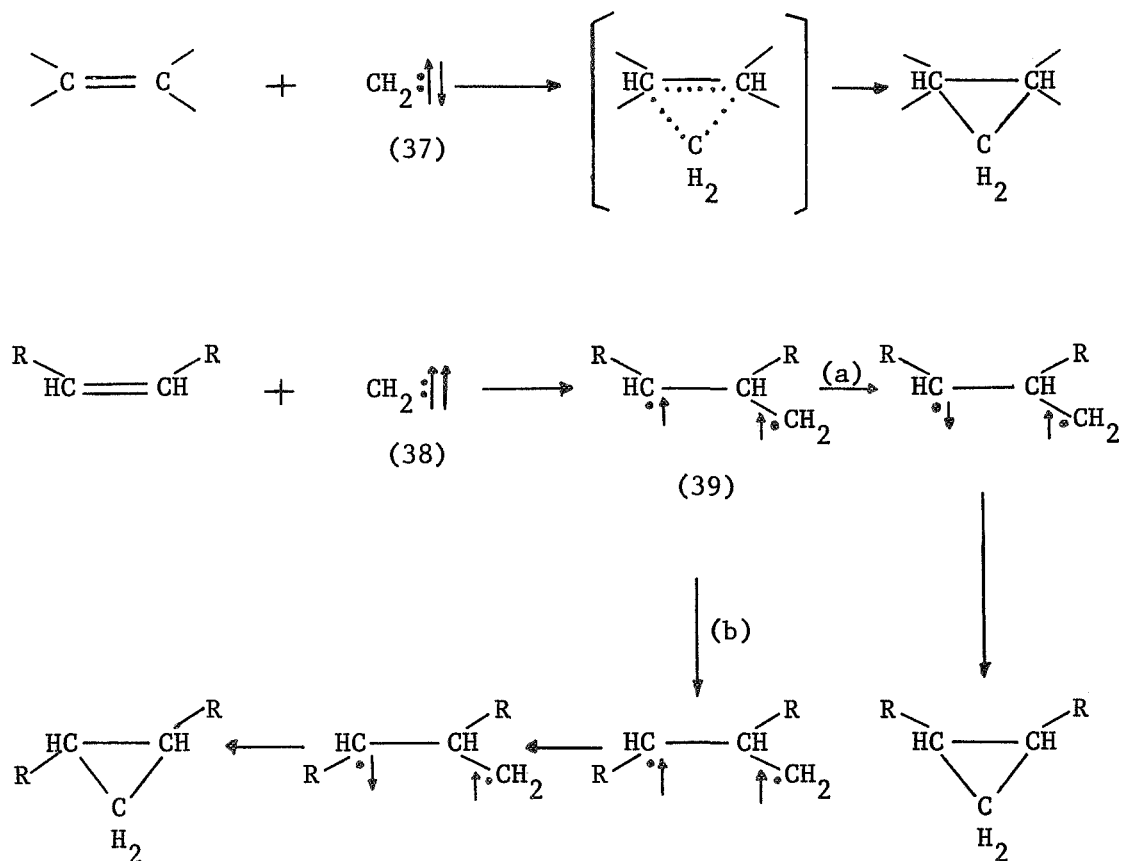


### Singlet Character of Cyclobutadiene

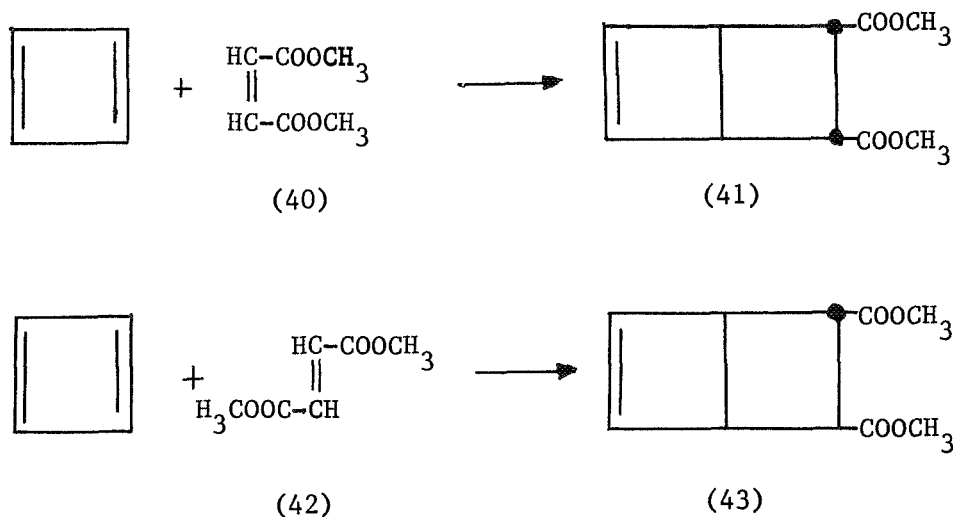
The first report suggesting the singlet character of cyclobutadiene was also based upon chemical reaction evidence. Skell<sup>29</sup> proposed a criterion to identify singlet and triplet carbene from the stereospecificity of addition reactions to carbon-carbon double bonds. He reasoned that a singlet carbene (37) might add to a double bond in a single concerted step since such a reaction could occur with spin conservation.



For a triplet carbene (38), the addition might be expected to involve two adiabatic bond-forming steps. In path (b) the rotation about the single bond in intermediate (39) is faster than spin inversion. In the path (a), spin inversion is faster so that rotation about the single bond does not occur. Skell suggested that spin inversion was slow compared to rotation in the intermediate (39) so that non-stereospecific addition reaction occurred. This hypothesis does not have any theoretical basis,<sup>30</sup> however, it correctly predicts the results of the chemical addition reaction of carbene to carbon-carbon double bonds.



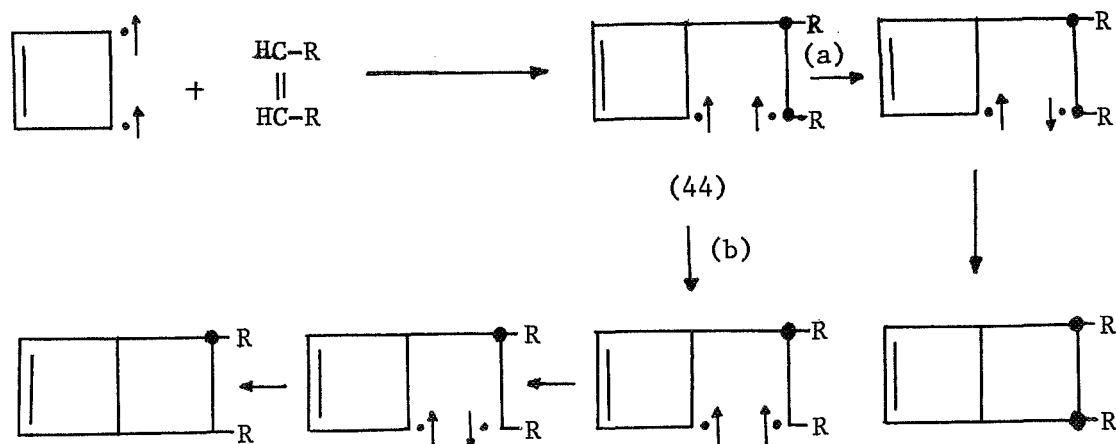
Pettit et al.,<sup>31</sup> applied this behavior of chemical additions to a study of the multiplicity of ground state cyclobutadiene. Degradation of CIT at 0° in the presence of dimethyl maleate (40) produced the endo, cis-dicarbomethoxybicyclohexane (41). On the other hand, reaction of cyclobutadiene with dimethyl fumarate (42) gave the trans-dicarbomethoxybicyclohexene (43). Pettit and his co-worker based their conclusions on the assumption that a triplet species should undergo addition reactions nonstereospecifically, while reactions of singlet species should be stereospecific. Therefore, cyclobutadiene was argued to have a singlet ground state.



The weakness of this conclusion lies in the hypothesis which, although correct for carbene, is not necessarily correct for cyclobutadiene. Suppose that in the addition reaction of triplet cyclobutadiene to a carbon-carbon double bond, the

inversion of electron spin and bond formation is faster than rotation about the single bond in the intermediate (44) (path a), then reaction of triplet cyclobutadiene should also be stereospecific<sup>57</sup> instead of nonstereospecific (path b).

In a second report, the photolysis of CIT was carried out at 77° K, both pure and in matrices of either C<sub>3</sub>F<sub>8</sub> or neopentane. By electron paramagnetic



resonance spectroscopy, only the radical Fe(CO)<sub>3</sub> was detected. Since cyclobutadiene was reported to be generated in the photolysis, Gunning and co-workers<sup>21</sup> concluded that the ground electronic state of cyclobutadiene was a singlet.

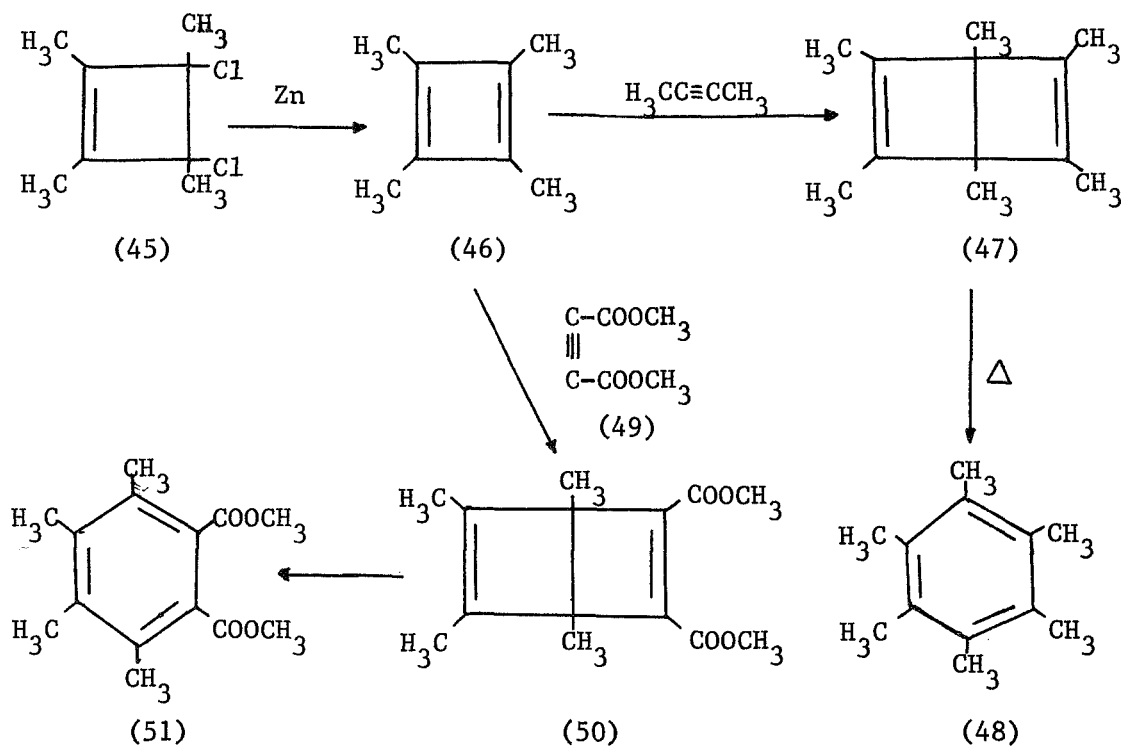
#### Reaction of Cyclobutadiene with Dienophiles

Cyclobutadiene and substituted cyclobutadiene have never been isolated. However, "Dewar benzene" and "substituted Dewar benzene" were obtained when dienophiles were present in the reaction in which cyclobutadiene and substituted cyclobutadiene were thought to be generated. It was postulated that these products were produced from the addition of dienophiles to cyclobutadiene or to substituted

cyclobutadiene. As described on page 8, when methyl propiolate or dimethyl acetylenedicarboxylate was present in the reaction of CIT with ceric ion at  $0^{\circ}$ , 2-carbomethoxybicyclo[2.2.0]hexa-2,5-diene (18) and 2,3-dicarbomethoxybicyclo[2.2.0]hexa-2,5-diene (19) were formed respectively.<sup>19</sup>

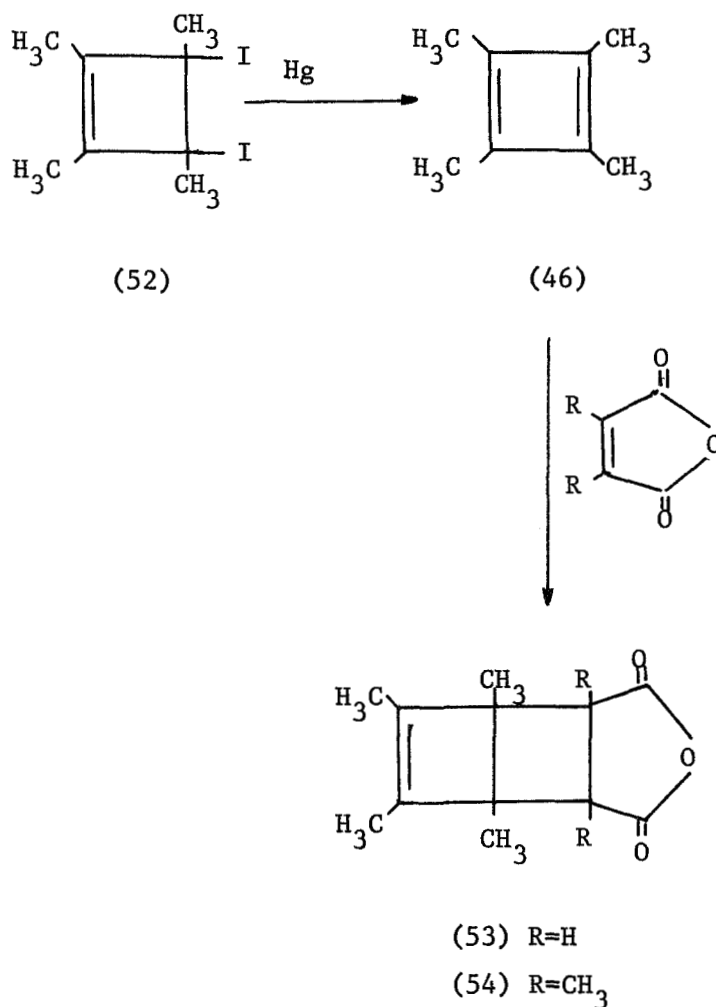
Dehalogenation of cis-3,4-dichloro-1,2,3,4-tetramethylcyclobutene (45) with zinc in the presence of 2-butyne or dimethyl acetylenedicarboxylate (49) produced hexamethylbenzene (48) and dimethyl 1,2-benzenedicarboxylate (51) respectively.<sup>35</sup> It was postulated that the tetramethylcyclobutadiene (46) was produced and bicyclic "Dewar benzene" (47) and (50) were formed in these reactions.

Similarly, dehalogenation of cis-3,4-diiodo-1,2,3,4-tetramethylcyclobutene



(52) with mercury in the presence of maleic anhydride or dimethylmaleic anhydride produced the isolable but thermally labile adducts, 1,2,3,4-tetramethylbicyclo[2.2.0]hexa-2-ene-5,6-dicarboxylic anhydride (53) and 1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2-ene-5,6-dicarboxylic anhydride (54), respectively, which attests to the intermediacy of tetramethylcyclobutadiene (46).<sup>58</sup>

Other similar reactions of dienophiles with cyclobutadiene and with substituted cyclobutadiene have been reviewed by Cava *et al.*<sup>23</sup>



## CHAPTER II

### APPARATUS AND EXPERIMENTAL PROCEDURES

#### Instruments

The following analytical instruments were used in this thesis research.

#### Mass Spectrometer

The mass spectrometer was the main analytical device used in this thesis work. It allows a determination of both the mass and the ionization potential of the parent molecules and the appearance potentials of mass fragments from these molecules. The description of the Bendix Time-of-Flight Mass Spectrometer, Model 12-107, and its auxiliary cryogenic equipments that were developed in this laboratory were presented in several earlier theses.<sup>32, 33, 34</sup>

#### Gas Chromatograph

A Perkin-Elmer Gas Chromatograph Model 800 with two different columns was used:

- A. Carbowax column -- 10' x 1/8" copper column with 10% of Carbowax 20 M on 100 mesh chromosorb P.
- B. Ucon oil column -- 10' x 1/8" copper column with 5% of ucon oil LB-550 X on 100 mesh chromosorb P.

#### N.M.R. Spectrometer

A Varian Model A-60 with tetramethylsilane as internal standard was used.

### Infrared Spectrometer

A Perkin-Elmer Spectrometer Model 221 with NaCl optics was used. Two thicknesses of the liquid sample in the NaCl cell were used: 0.1 and 0.5 mm.

### Coaxial Furnace Inlet System

The pyrolysis of CIT and the copyrolysis of CIT with other compounds were carried out in a coaxial furnace inlet system. This furnace, which was mounted inside the fast reaction chamber of the ion source header coaxially with the drift tube of the mass spectrometer was described by Wilson.<sup>34</sup> This inlet system permits the gas to travel less than 1/8 in from the furnace before being ionized by the electron beam in the mass spectrometer. The mechanical constructions have been somewhat modified and two kinds of furnaces were used in this thesis as shown in Figure 1 and Figure 2.

Pyrex and alumina tubes with 1/8 or 1/4 in o.d., depending upon the size of the o-ring seal quick-disconnect joint (1), have been used as furnaces in the configuration of Figure 1. The furnace (3) was wound with No. 28 gauge nichrome wire providing a heated length of 3 to 4 cm, it was then coated with Sauereisen cement for insulation. A chromel-alumel thermocouple wire and the power leads are passed through high vacuum electric feed-throughs soldered into the stainless steel or brass flange (2). The electrical and thermocouple wires and cement in the furnace shown in Figure 1 were exposed to the vacuum space of the ion source of the mass spectrometer. Consequently, extensive vacuum pumping was required to remove the water in cement after every new furnace was attached to the mass spectrometer. To avoid this, the Pyrex furnace shown in Figure 2 was made. The

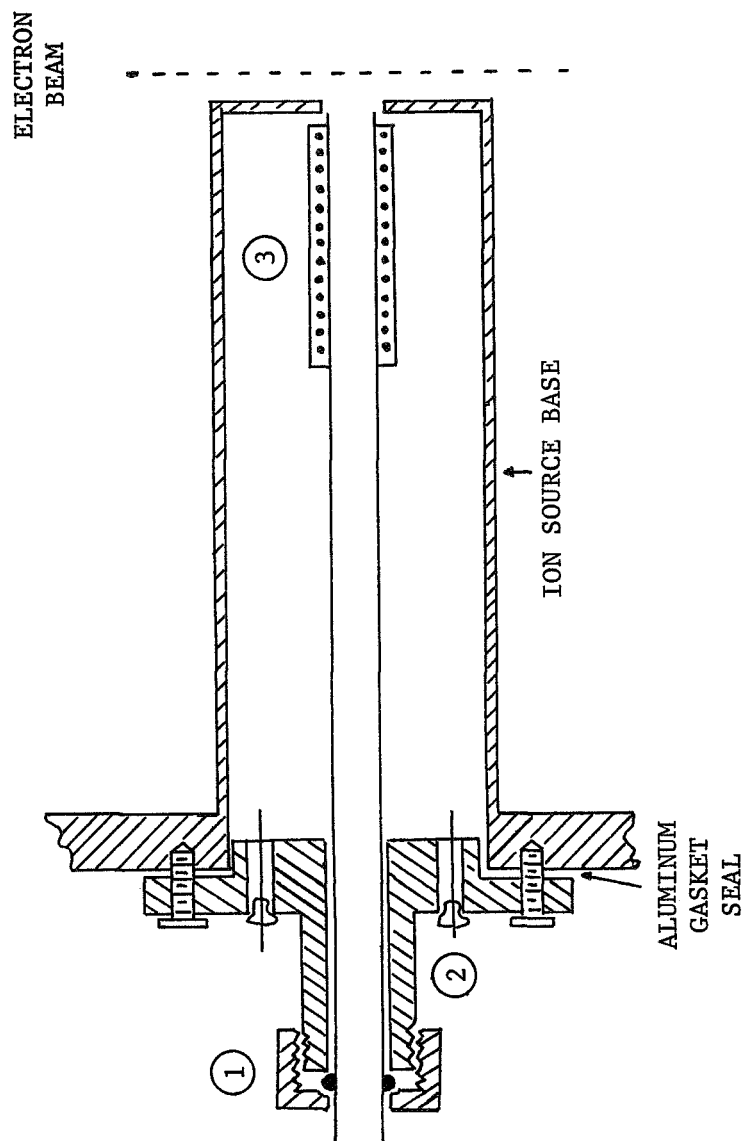


Figure 1. Coaxial Furnace Inlet System.



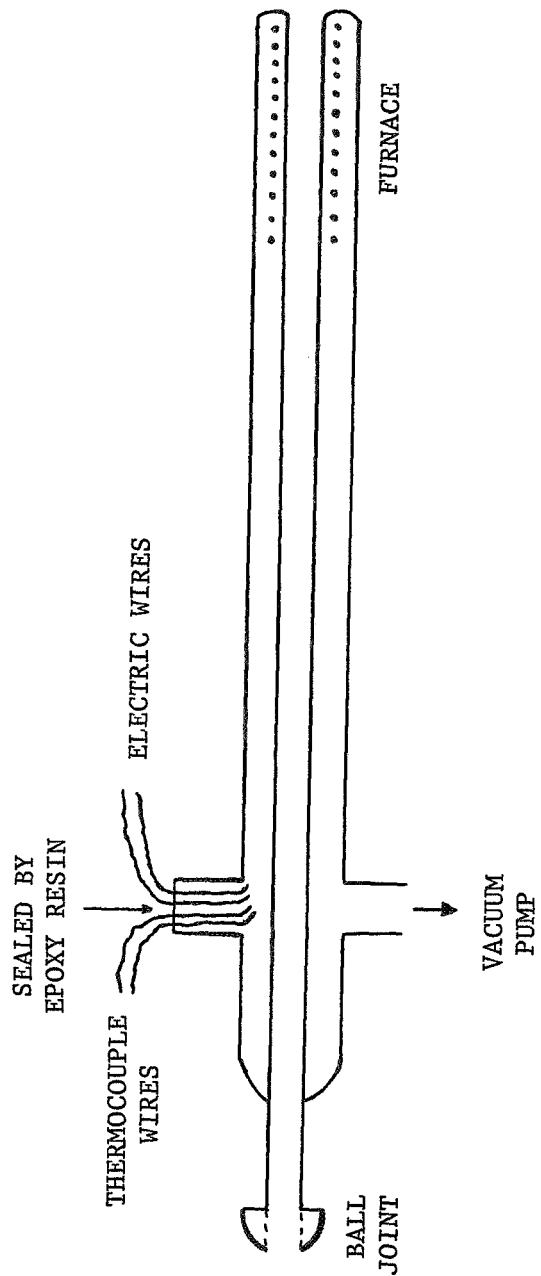


Figure 2. Pyrex Furnace Tube.

furnace was made of a 5 mm o.d. Pyrex tube with a 3.5 cm heated length. The nichrome heater, thermocouple wire, and cement were sealed inside a 1/2 inch o.d. Pyrex tube which was maintained under vacuum during the pyrolyses to insure good insulation. This Pyrex furnace can be used up to 450<sup>o</sup>.

### Cryogenic Inlet System

The cryogenic inlet system attached to the mass spectrometer allows both quenching of highly reactive chemicals and their analysis with no simultaneous warm-up. The chemicals condensed in this inlet system can be introduced into the mass spectrometer at any temperature between -196<sup>o</sup> and room temperature with no attendant warm-up before they are ionized by the electron beam in the ion source. The design considerations, mechanical description, and applications of this cryogenic inlet system have been described in detail in several theses<sup>32, 33, 34</sup> from this laboratory. The special experimental arrangements for quenching, solution reaction, pyrolysis and radio frequency discharge will be described here.

### Solution Reaction

The apparatus attached to the cryogenic inlet system A in Figure 3 was made of Pyrex glass and was designed for the reaction of ceric ammonium nitrate with CIT at temperatures near 0<sup>o</sup>. The 100 cm<sup>3</sup> reaction flask (1) was immersed in ice water, and the product of the reaction was passed through a 7 mm o.d. tube surrounded by ice water and quenched in the outer refrigerant chamber of the inlet system. The inner and outer refrigerant chambers were first cooled to -180<sup>o</sup> with liquid nitrogen. The arrangement of the inlet system was designed such that quenching would be carried out under vacuum conditions, therefore, no provision was made

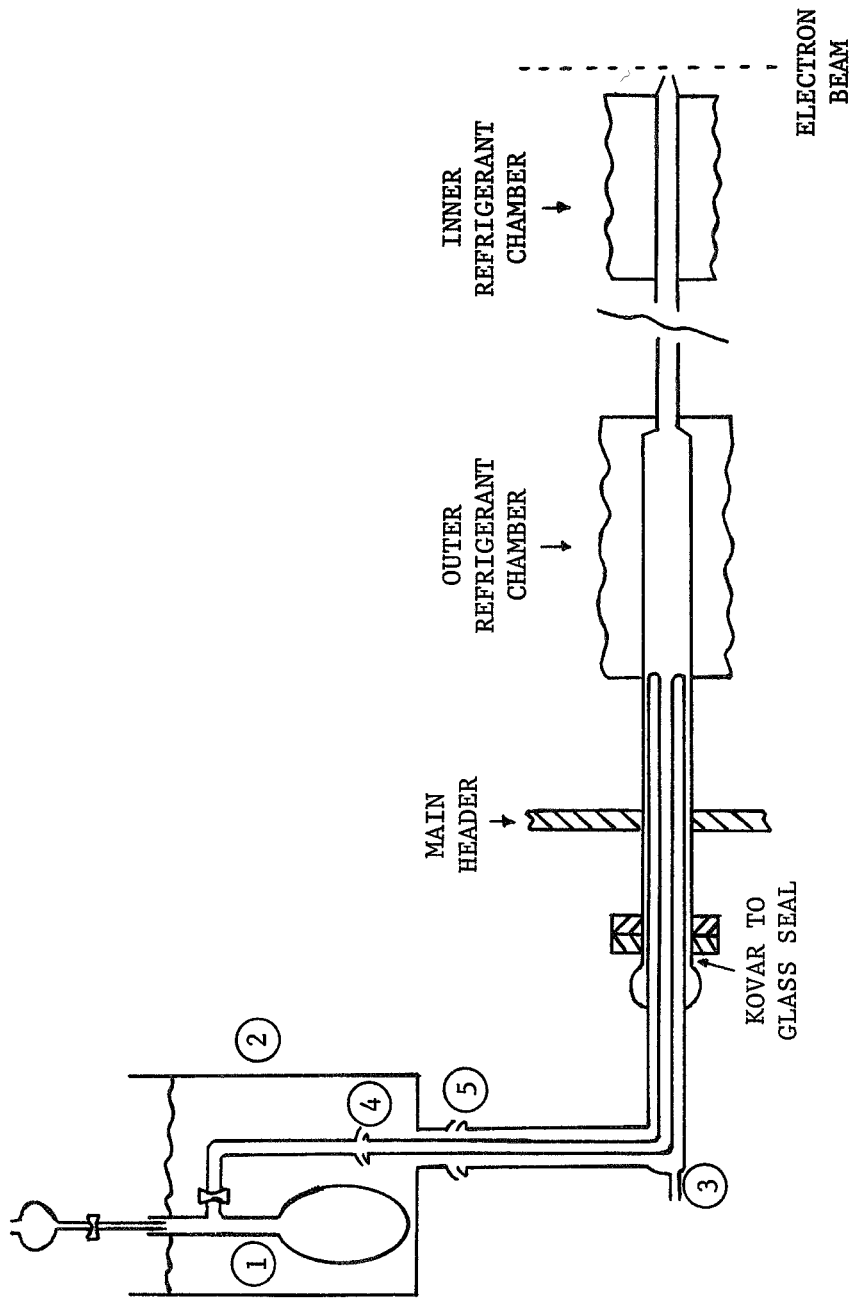


Figure 3. Cold Reactor Attached to Cryogenic Inlet System A.

for separating the quenching tube from the vacuum insulation space. In this experiment, however, it was desired to carry out the quenching at one atmosphere. This required separation of the vacuum insulation space and the quenching tube; a partial remedy was provided by a Teflon block inserted between the extension piece of quenching tube and a gate valve which separated the inlet system and mass spectrometer. The extension piece was pushed snugly against the block, but, even so, a small leak remained which allowed a heat leak through the insulation. Therefore, the refrigerant chambers could not be maintained at  $-196^{\circ}$ . Fifteen grams of ceric ammonium nitrate in 10 g of water were added to the reaction flask (1) cooled to  $0^{\circ}$  by the ice water in the jar (2). Then 1.5 g of CIT in 10 ml of diethyl ether at  $0^{\circ}$  was added to the flask (1), and the reaction mixture was well stirred. During 30 min of reaction, ice water was slowly drained from the tube exit (3) and ice water was added to the top of the jar (2) to insure the  $0^{\circ}$  thermostating of the transfer tube. At the conclusion of the reaction, all of the ice water was rapidly drained out, and the glass jar was disconnected from the ball joint (5). A socket then sealed the ball joint (4) and the quenching chambers were vacuum pumped to  $10^{-5}$  torr. The inlet system was slowly advanced into the mass spectrometer (see thesis of Malone<sup>33</sup>) such that the final position of the inlet port was at the edge of the electron beam of the ion source. The inlet system was then slowly warmed up and the mass spectrum was observed as a function of temperature.

### Pyrolysis Experiments

The pyrolysis and quenching experiment with CIT was carried out in the furnace mounted to cryogenic inlet system B which has only one refrigerant

chamber (see Figure 4). The construction of the furnace was essentially the same one as shown in Figure 2 except that the furnace was extended such that its exit was positioned inside the 11 mm i.d. monel quenching tube.

The CIT was kept between  $0^{\circ}$  and room temperature and was introduced into the furnace, which had a heated length of 3.5 cm, through a high vacuum stopcock. The inlet pressure of CIT (measured at a distance of 93 cm from the furnace) was varied between  $10^{-2}$  to  $10^{-1}$  torr. These inlet pressures were low enough to permit the inlet system extension piece to be positioned at the edge of the electron beam of the ion source and still allow the vacuum in the mass spectrometer to be maintained sufficiently low to observe the mass spectrum.

Each pyrolysis lasted two hours with furnace temperatures of  $320^{\circ}$  to  $380^{\circ}$ . The products of the pyrolysis traveled only a few mm from the furnace exhaust port before being quenched on the monel tube kept at  $-196^{\circ}$ . During controlled warm-up, the quenched products vaporized and traveled less than 8 cm with no additional warming before controlled energy electron bombardment in the ion source.

#### Radio Frequency Discharge Experiment

The pyrolysis of cis-3,4-dichlorocyclobutane at temperatures up to  $400^{\circ}$  failed to crack the molecule. Radio frequency discharge of this chloride was therefore carried out in the arrangement shown in Figure 4. The discharge coil was made of 70 turns of No. 14 gauge enameled copper wire wound on a 30 mm o.d. Pyrex tube. The discharge was produced in a 10 mm o.d. Pyrex tube and air was blown into the annular space to provide cooling for the discharge tube. The radio

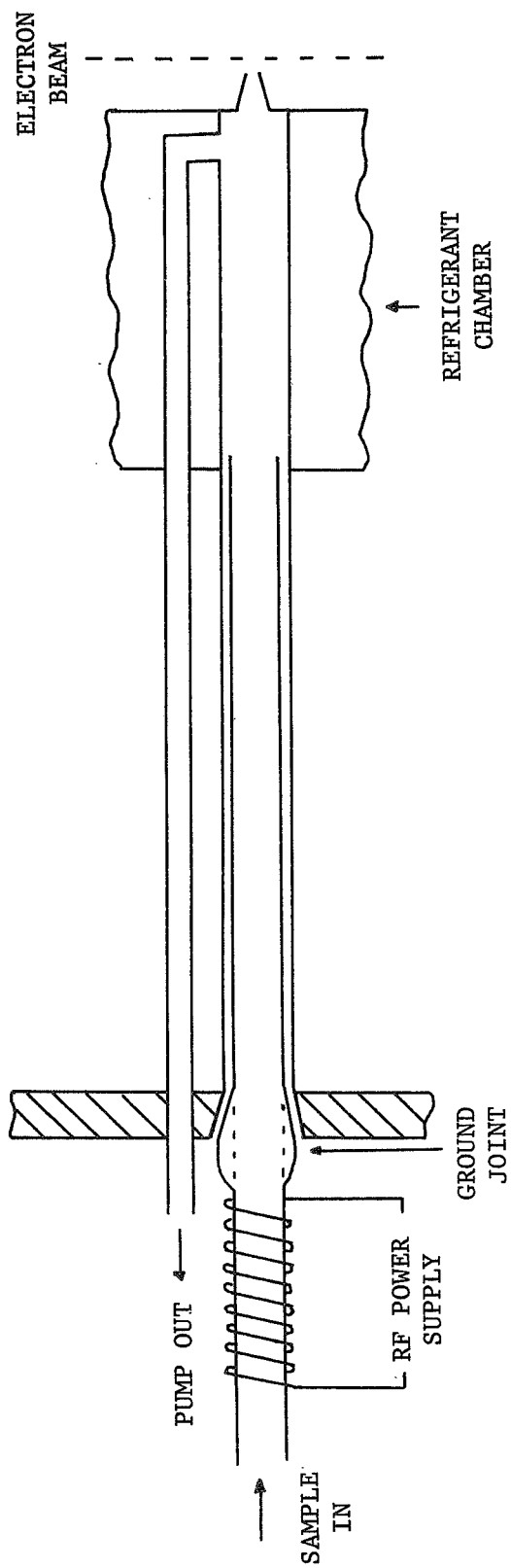


Figure 4. Radio Frequency Discharge Tube and Cryogenic Inlet System B.

transmitter and the discharge circuitry were described in detail by Bivens.<sup>51</sup>

The discharge coil was positioned close to the header of the inlet system B to minimize the distance between discharge and quenching. However, the products of the discharge still had to travel 38 cm before being quenched, and this was the principal disadvantage of this arrangement. Highly reactive species could have been decomposed or polymerized in this long transfer line.

With inlet pressures of cis-3,4-dichlorocyclobutene of  $1 \times 10^{-1}$  to  $5 \times 10^{-1}$  torr, the discharge glow was observed without introducing oxygen or argon carrier gas. When the discharge power was slowly increased, cis-3,4-dichlorocyclobutene disappeared and intense m/e 52 peaks appeared in the mass spectrum. When the discharge power was further increased, the m/e 52 peak decreased and peaks less than m/e 52 were observed.

The inlet system B was positioned inside the mass spectrometer during the radio frequency discharge in the manner previously described in the pyrolysis experiment. After 1 to 1.5 hrs of discharge and subsequent quenching at  $-196^{\circ}$ , the composite products were slowly warmed and analyzed. A brown to black film was deposited on the wall at the place of the discharge flow each time. This was probably carbon.

#### Low Temperature Reaction System

#### Reactions of Dienophiles and Condensed C<sub>4</sub>H<sub>4</sub> from Pyrolysis of CIT

The pyrolysis of CIT, quenching of the products, and the reactions of these quenched products with other compounds at low temperatures were all carried out

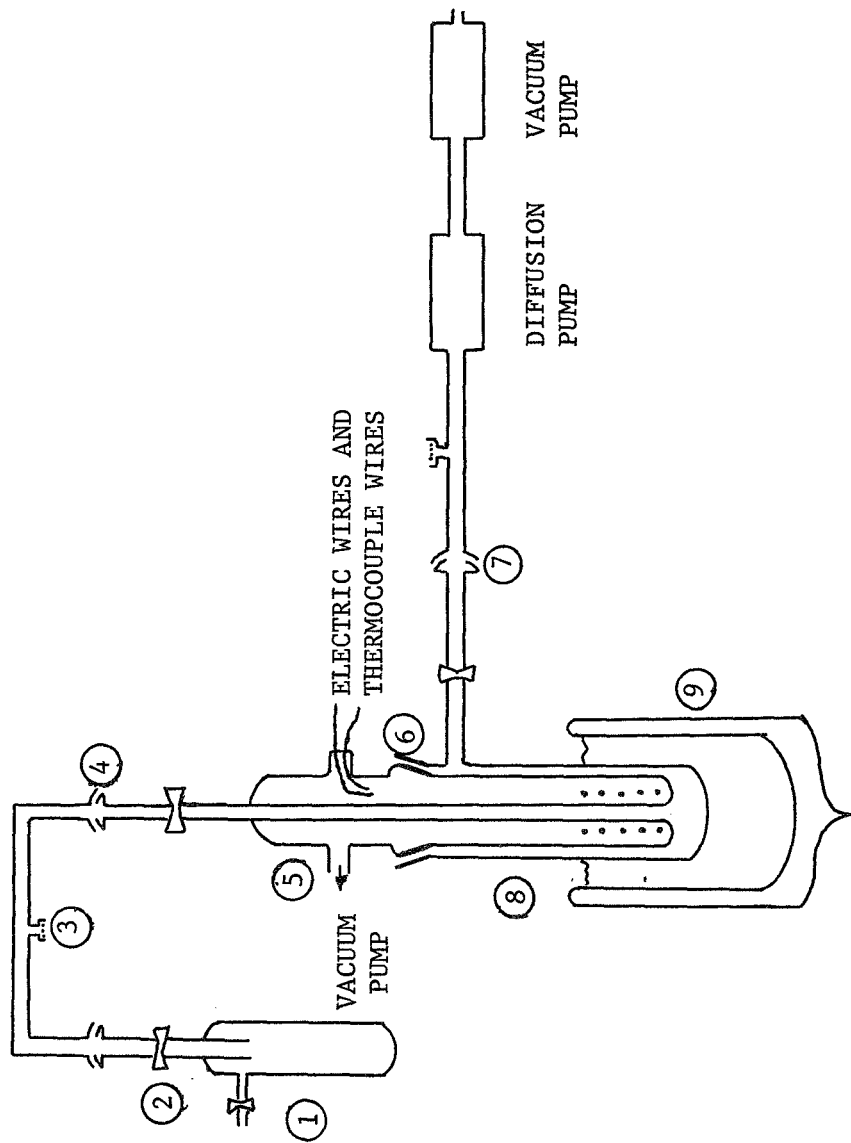


Figure 5. Low Temperature Reaction Arrangement.



in the arrangement shown in Figure 5. The CIT was kept in the tube (1) and maintained at temperatures between  $0^{\circ}$  and  $20^{\circ}$ . The flow of CIT into the furnace tube (5) was controlled by the needle valve (2) and the pressures were measured by a vacuum gauge tube (3). The furnace (5), which was essentially the same as the Pyrex furnace described previously, was connected to the quenching tube (8) by a ground glass joint (6). During the pyrolysis, the whole system was maintained at low pressures by connecting a diffusion pump and a vacuum pump through the ball joint (7); the quenching tube (8) was immersed in liquid nitrogen. This pyrolysis and quenching experiment closely resembles that carried out in the cryogenic inlet system B. After the pyrolysis, the ball joints (4) and (7) were disconnected and the quenching tube (8) was pressurized to one atmosphere by introducing nitrogen gas. The furnace (5) was then removed from the quenching tube (8). After this, compounds to be reacted with the quenched products of the pyrolysis were introduced into the quenching tube (8).

#### Attempted Dehalogenation of *Cis*-3, 4-dichlorocyclobutene with Sodium

The dehalogenation of *cis*-3, 4-dichlorocyclobutene with high surface sodium at low temperature was carried out in the following arrangement: an oil diffusion pump was connected to a Pyrex trap which was then connected to a reaction flask equipped with a magnetic stirrer. One gram of *cis*-3, 4-dichlorocyclobutene in  $50 \text{ cm}^3$  of diethyl ether was added to the flask which was immersed in a dewar of liquid nitrogen. After the solution was cooled to solid, 20 g of high surface sodium, with activated alumina as solid carrier, was added to the flask. The whole arrangement was then pumped down to 50 torr, and a dewar containing the refrigerant

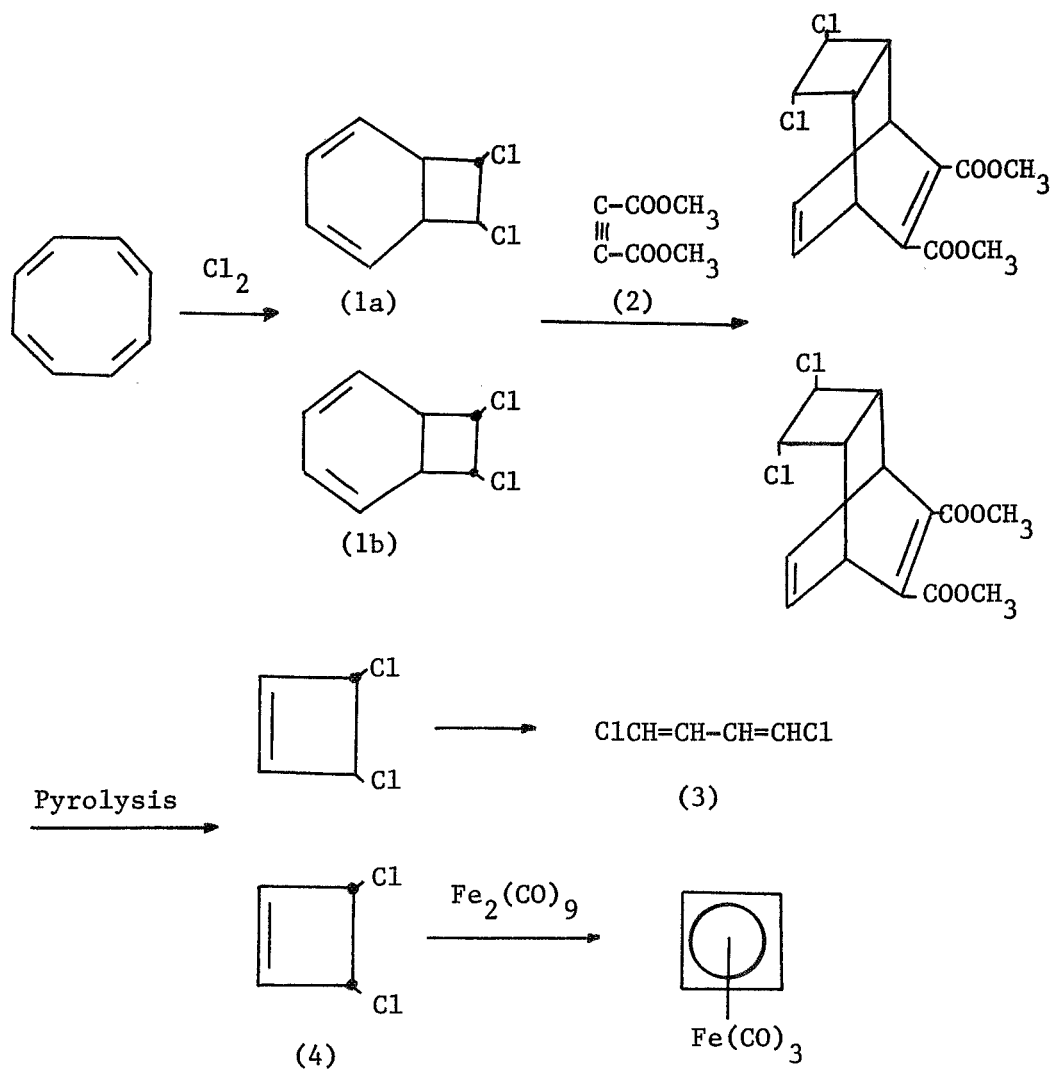
2-methyl pentane at a temperature of  $-110^{\circ}$  was substituted for the dewar of liquid nitrogen. Now, at  $-110^{\circ}$ , the flask contained an ether solution and the fine solid particles of high surface sodium. The mixture was then stirred vigorously and the evolved gas was quenched in the Pyrex trap immersed in liquid nitrogen. After two hours of reaction at  $-110^{\circ}$  with continuous pumping, the trap was removed from the arrangement and was warmed up to room temperature. The contents of the trap were analyzed mass spectrometrically. Only peaks corresponding to ether and to unreacted cis-3,4-dichlorocyclobutene were observed in the mass spectrum.

### Chemical Preparations

#### Cyclobutadieneirontricarbonyl

Cyclobutadieneirontricarbonyl was formed by the reaction of cis-3,4-dichlorocyclobutene with excess diiron enneacarbonyl.<sup>16</sup> Cis-3,4-dichlorocyclobutene was obtained by chlorination of cyclooctatetraene, followed by Diels-Alder reaction and pyrolysis. Diiron enneacarbonyl was obtained by irradiating iron pentacarbonyl.

Synthesis of Cis-3,4-dichlorocyclobutene. The synthesis procedure of cis-3,4-dichlorocyclobutene was reported by Avram et al.<sup>36</sup> Chlorination of cyclooctatetraene could be conducted either with sulfur chloride or chlorine, but chlorine was chosen here for the simplicity of its handling. However, as discussed by Avram et al.<sup>36</sup> the presence of water in the chlorine gas would cause the formation of hydrochloric acid which would then convert cis-dichloro-1,3,5-



cyclooctatetraene (1b) to the corresponding *trans* structure (1a). Without the addition of potassium carbonate immediately after the chlorination of cyclooctatetraene, Viehe *et al.*,<sup>37</sup> reported that only 1,4-dichlorobutadiene (3) was obtained. Extreme care was taken to prevent the presence of water in the reaction vessel by drying the vessels before conducting the reaction and by passing the chlorine gas through a calcium chloride tube. A typical run was carried out as follows.

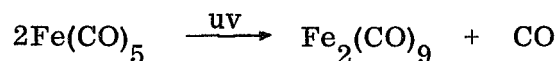
A solution of 83.2 g (0.8 mol) of 1,3,5-cyclooctatetraene (obtained from Badische Anilin and Soda Fabrik A. G. and used without further purification) in 160 cm<sup>3</sup> of carbon tetrachloride was placed in a 500 cm<sup>3</sup> three-neck flask immersed in an ice bath. Fifty-seven grams (0.8 mol) of chlorine gas (Matheson high purity grade) was passed through a one foot calcium dichloride tube and admitted into the solution with good stirring in the flask at a flow rate such that the solution temperature could be kept at 20<sup>o</sup> to 25<sup>o</sup>. The end point of the reaction was indicated by the decoloring of the solution (i. e., the yellow color of cyclooctatetraene disappeared) and the increased weight of the solution. The reaction time for a typical run was about 1 hr and 20 min.

Immediately the solution was transferred to a 500 cm<sup>3</sup> Erlenmeyer flask and was agitated vigorously with 50 g of sodium carbonate for 5 min. The solution was then filtered and the filtrate was transferred to a one liter three-neck flask. Then 100 g of dimethyl acetylenedicarboxylate (2) were added to the solution and refluxed for 3 hrs using an oil bath maintained between 80<sup>o</sup> and 90<sup>o</sup>.

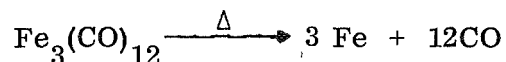
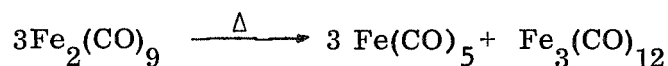
After completion of the Diels-Alder reaction, the solvent was vacuum distilled at 50<sup>o</sup> and 20 torr. The residue was then transferred to a 500 cm<sup>3</sup> distilling flask which was again immersed in an oil bath. The pyrolysis occurred at a pressure of 60 torr and at liquid temperatures of 180<sup>o</sup> to 210<sup>o</sup>. The vapor distilled over at vapor temperatures of 100<sup>o</sup> to 150<sup>o</sup>. The distillate, which consists of 1,4-dichlorobutadiene (3) and cis-3,4-dichlorocyclobutene (4), was then distilled in a Nester/Faust NFT-50 annular spinning band distillation column at a pressure of 60 torr. At vapor temperatures below 73<sup>o</sup>, the reflux ratio was set at 10 and the trans-trans-

1,4-dichlorobutadiene (3) was distilled over. At 80° the reflux ratio was decreased to 4 and about 20 g (20.5 per cent yield) of cis-3,4-dichlorocyclobutene (4) were collected. The index of refraction was 1.498 which was equal to the earlier reported value.<sup>36</sup> The mass spectrum of cis-3,4-dichlorocyclobutene (4) is shown in Table 12 of Appendix B.

Preparation of Diiron Enneacarbonyl. Diiron enneacarbonyl, Fe<sub>2</sub>(CO)<sub>9</sub> has been obtained by irradiating iron pentacarbonyl either alone or in solution.<sup>38</sup>



Since large amounts of diiron enneacarbonyl were needed, iron pentacarbonyl in glacial acetic acid solution was irradiated by sunlight instead of using an ultraviolet lamp. However, several difficulties were encountered in this irradiation by natural sunlight. (1) Weak sunlight failed to produce any precipitated golden crystal of Fe<sub>2</sub>(CO)<sub>9</sub>. (2) If the solution got too hot (as during irradiation on a summer day) a deep-green reaction mixture containing a black precipitate was produced. The deep-green color was due to Fe<sub>3</sub>(CO)<sub>12</sub> in solution and the black precipitate was metallic iron. Diiron enneacarbonyl was known to decompose on heating as follows:<sup>39</sup>



If this occurred in the preparation of Fe<sub>2</sub>(CO)<sub>9</sub>, it was best to throw away the batch, for, on two occasions, during drying the golden Fe<sub>2</sub>(CO)<sub>9</sub> containing this pyrophoric iron, self ignition occurred. (3) A white amorphous water-soluble precipitate was also produced during irradiation on hot days. This white material,

probably iron (II) acetate, could be removed from  $\text{Fe}_2(\text{CO})_9$  by simply washing with water.

If  $\text{Fe}_2(\text{CO})_9$  is to be stored for a long period of time, it is best to store it under a protective layer of water or under an inert atmosphere of nitrogen gas. These precautions were instituted when it was found that when diiron enneacarbonyl was kept in a partly emptied container without replacing the air above the solid with nitrogen, self ignition occurred after about one to two months of storage.

Typical preparation procedure was carried out as follows. A mixture of  $50 \text{ cm}^3$  of commercial iron pentacarbonyl (from K & K Laboratory or General Aniline & Film Corporation) and  $150 \text{ cm}^3$  of glacial acetic acid were charged into a  $250 \text{ cm}^3$  Erlenmeyer flask. Twenty flasks of iron pentacarbonyl were irradiated on the roof of the chemical and ceramic engineering building every run. Yellow-orange crystals of  $\text{Fe}_2(\text{CO})_9$  precipitated on the bottom and on the glass wall. Every half hour the flask was shaken in order to wash the precipitate on the wall down to the bottom. Water was sprayed around the flasks to keep it from getting too hot. After four hours, the solution was filtered to collect the  $\text{Fe}_2(\text{CO})_9$  and the solution was irradiated further. Usually after four days of irradiation, the formation of  $\text{Fe}_2(\text{CO})_9$  was slow and the solution turned black, and, it was then discarded.

The yellow-orange crystals of  $\text{Fe}_2(\text{CO})_9$  were washed with water to remove glacial acetic acid. In order to remove the metallic iron if present,  $\text{Fe}_2(\text{CO})_9$  was transferred to the water bath in which  $\text{Fe}_2(\text{CO})_9$  flakes stayed on the top of the water and were removed. Finally it was washed with ethanol and pentane or

ether to remove the water. After moderate drying by aspirating air through the moist product in Büchner funnel, the product was ready for storage.

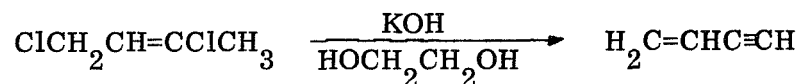
Preparation of Cyclobutadieneirontricarbonyl. Thirty five grams of cis-3,4-dichlorocyclobutene in 200 cm<sup>3</sup> of hexane were charged into a one liter three-neck flask and immersed in an oil bath. The solution was kept at 50° and provided with good stirring. Then 50 g of dry Fe<sub>2</sub>(CO)<sub>9</sub> were added to the solution. After one hour, another 50 g of Fe<sub>2</sub>(CO)<sub>9</sub> were added and then 20 g of Fe<sub>2</sub>(CO)<sub>9</sub> were added every hour. The sample of the solution was checked by mass spectrometer until the ratio of C<sub>4</sub>H<sub>4</sub>Cl<sub>2</sub> and C<sub>4</sub>H<sub>4</sub>Fe(CO)<sub>3</sub> was about 1:5. It required 12 hours of reaction and 300 g of Fe<sub>2</sub>(CO)<sub>9</sub>. The solution was filtered and washed with 200 cm<sup>3</sup> of hexane. The solvent was then vacuum distilled at 35°. The remaining solution was vacuum fractional distilled in a Nester/Faust NFT-50 annular spinning band distillation column. At a vapor temperature of 35°, yellow-orange liquid was distilled over and about 16 g (29% yield) of cyclobutadieneirontricarbonyl was obtained. The n.m.r. spectrum showed a single absorption at 6.09 which agreed with an earlier reported value.<sup>35</sup> The infra-red spectrum had fewer bands than the reported spectrum.<sup>52</sup> Watts<sup>52</sup> reported that it had bands at 874 cm<sup>-1</sup>, 912 cm<sup>-1</sup>, 1006 cm<sup>-1</sup>, 1120 cm<sup>-1</sup>, 1163 cm<sup>-1</sup>, 1202 cm<sup>-1</sup>, 1243 cm<sup>-1</sup> and 1294 cm<sup>-1</sup> which were not observed in this thesis. In one sample of C<sub>4</sub>H<sub>4</sub>Fe(CO)<sub>3</sub> these bands were observed. By checking the mass spectrum, it was found that this particular sample also contained cis-3,4-dichlorocyclobutene, and thus the more complex infrared spectrum was to be associated with impure samples. This can be easily seen from the infrared spectra of cis-3,4-dichlorocyclobutene and

CIT shown in Appendix B.

The mass spectrum of CIT is also shown in Appendix A and a parent peak at  $m/e$  192 is clearly evident.

### Vinylacetylene

Several methods for the preparation of vinylacetylene have been reported. The best method for a laboratory scale preparation is by the dehydrohalogenation of 1,3-dichloro-2-butene using potassium hydroxide in ethylene glycol.<sup>40</sup> This method has the advantages of being a one step process and having readily available starting materials.



A typical preparation of vinylacetylene was carried out as follows. One hundred grams of potassium hydroxide flakes were placed in a 500 cm<sup>3</sup> three-neck flask which was immersed in an oil bath, and 125 cm<sup>3</sup> of ethylene glycol were added. This mixture was stirred vigorously while adding 25 cm<sup>3</sup> of ethylene glycol mono-butyl ether (n-butyl cellosolve). The system was swept with a stream of nitrogen while the temperature of the oil bath was raised to 170°. Thirty grams of 1,3-dichloro-2-butene were then added dropwise from the dropping funnel. The product was passed through a one-foot tube filled with calcium dichloride, and it was then quenched in a trap immersed in liquid nitrogen. During the reaction the nitrogen gas was continuously swept over the system, the temperature of the oil bath was kept at 165° to 170° by adjusting the dropping rate and the reaction mixture was

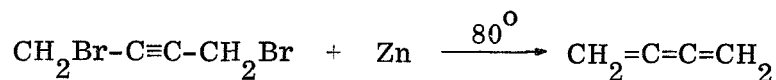


stirred vigorously. Addition of dichlorobutene was completed in less than half an hour. Heating was continued for another half hour after the addition of dichlorobutene had been complete.

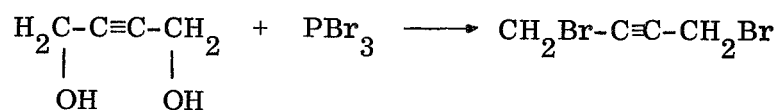
The product in the trap was warmed up and was transferred through a room temperature tube into the cryogenic inlet system B at  $-196^{\circ}$ . At  $-140^{\circ}$ ,  $m/e$  40 was observed which could be methyl acetylene (mp  $-102.7^{\circ}$  and bp  $-23.2^{\circ}$ ). The formation of a compound of molecular weight 40 had not been reported prior to this work. Continuous pumping at  $-140^{\circ}$  for two hours, the  $m/e$  40 disappeared. At  $-125^{\circ}$   $m/e$  52 was observed. The associated mass spectrum is listed in Table 2.

### Butatriene

Butatriene was first prepared by Schubert *et al.*<sup>41</sup> by the dehalogenation of 1,4-dibromo-2-butyne.



1,4-Dibromo-2-butyne was not readily available and was prepared from the reaction of 2-butyne-1,4 diol and phosphorous tribromide.



Preparation of 1,4-Dibromo-2-butyne. Fifteen grams of 2-butyne-1,4 diol and 120 cm<sup>3</sup> of benzene were placed in a 500 cm<sup>3</sup> three-neck flask. Phosphorous tribromide (51 g) was added dropwise into the flask which was immersed in a room temperature water bath. The reaction was exothermic; and the temperature of the

reaction system was kept below  $40^{\circ}$  by adjusting the dropping rate of the diol. The reaction mixture was stirred continuously for overnight. Ice water ( $100 \text{ cm}^3$ ) was then added and the mixture was extracted with ether ( $3 \times 80 \text{ cm}^3$ ). The combined extracts were washed with sodium bicarbonate solution and they were then vacuum distilled in a Nester/Faust NFT-50 annular spinning band distillation column. About 23 g of colorless oil at  $60^{\circ}/1$  torr were obtained.

Preparation of Butatriene. Both acetonitrile and diethylene glycol diethyl ether were reported to be suitable solvent in the dehalogenation reaction of 1,4-dibromo-2-butyne. Acetonitrile was chosen since in this solvent, the reaction was sufficiently fast that it was unnecessary to heat the reaction mixture in order to maintain the reaction temperature at  $80^{\circ}$ . Twenty grams of zinc and  $40 \text{ cm}^3$  of acetonitrile were placed in a  $500 \text{ cm}^3$  three-neck flask equipped with a magnetic stirrer, a dropping funnel, and a nitrogen inlet tube which extended below the surface of the reaction mixture. Fifteen grams of 1,4-dibromo-2-butyne were added dropwise at a sufficient rate to maintain the temperature of the reaction mixture between  $75^{\circ}$  and  $80^{\circ}$ . The evolved gases were swept over by the nitrogen and condensed in two series traps, first at  $-70^{\circ}$  and then at  $-196^{\circ}$ . After the addition of butyne was completed, the flow of nitrogen was continued for an hour. The condensed compound in the trap at  $-196^{\circ}$  was slowly warmed to  $90^{\circ}$  and passed through a short room temperature tube to be quenched in the cryogenic inlet system B which was kept at  $-196^{\circ}$ . At  $-100^{\circ}$ ,  $m/e$  52 was observed without any impurity. The mass spectrum was similar to the reported one<sup>41</sup> as shown in Table 2.

### High Surface Sodium

A three-neck flask equipped with a nitrogen inlet tube and a rugged sweep-type stirrer was immersed in an oil bath. About 100 g of activated alumina (80 to 200 mesh) were added into the flask and air was displaced from the flask with dry nitrogen. The oil bath was heated to 150° and 20 g of sodium, in 2 to 5 g pieces, was added into the flask while the alumina was stirred. As soon as the sodium had melted, the mixture was stirred somewhat more rapidly for about 5 minutes. The color of the mixture changed from white to dull gray as sodium spread over the alumina. The oil bath was removed from the flask. After this high surface sodium was cooled to room temperature under dry nitrogen, it was transferred to a glass container and stored under an inert atmosphere of nitrogen.

### Energy Measurements

Ionization and appearance potentials were determined from ionization efficiency curves obtained with the Bendix Time-of-Flight Mass Spectrometer, Model 12-107. The filament current was usually set at 3.0 microampere, the trap current was at 0.125 microampere, and the multiplier scale was at 5. The gas flow rates were adjusted to exhibit the ion currents between 1 x 4 and 10 x 1 microampere at 50 eV. The standard and unknown ion intensities were then adjusted to be equal by controlling one or the other of the gas flow rates. The electron energy was decreased until the ion currents of the gases were in the range of 0.01 x 4 and 0.1 x 1 microampere. The ion intensities were then plotted in a range of 2 to 4 eV on a Moseley XY recorder. The typical ionization curves were broad as shown in Figure 6. From the broad ionization efficiency curves, the thin

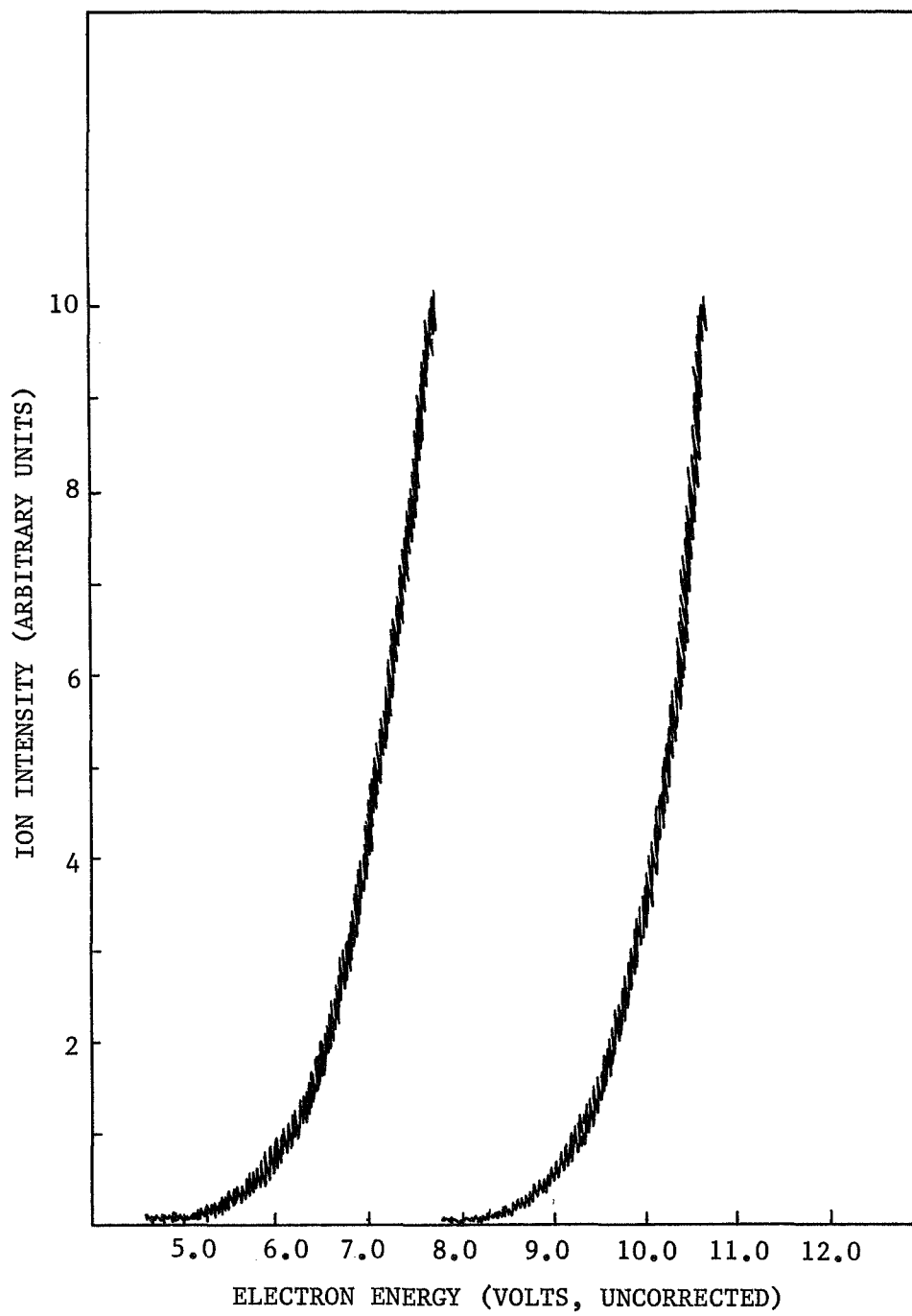


Figure 6. Ionization Efficiency Curves of Water and C<sub>4</sub>H<sub>4</sub> from the Pyrolysis of CIT.

average curves were obtained and are presented in this thesis. For the parent ions, the ionization efficiency curves for the unknown and the standard ions were parallel. The ionization efficiency curve of the fragment ion and that of the standard parent ion were frequently non-parallel.<sup>53</sup> The ionization and appearance potentials were obtained using the extrapolated voltage difference method.<sup>59</sup> The extrapolation of the voltage difference curve provided the value of the voltage difference between the unknown and known ions (see Figure 7).

## CHAPTER III

## RESULTS AND DISCUSSION

Reaction of Cyclobutadieneirontricarbonyl with Ceric Ion

Since all attempts to isolate cyclobutadiene had failed until Pettit<sup>19</sup> and his co-workers claimed that cyclobutadiene could be prepared and isolated by the straightforward reaction of cyclobutadieneirontricarbonyl (CIT) with ceric ion at 0<sup>o</sup>, it was natural that this was the first technique to produce cyclobutadiene that was explored in the present study.

CIT in ether solution at 0<sup>o</sup> was added to aqueous ceric ammonium nitrate solution at the same temperature. The evolved gases were passed through a tube kept at 0<sup>o</sup> and were then quenched at -180<sup>o</sup> to -196<sup>o</sup> in the cryogenic inlet system A as described in Chapter II. Upon slow warm-up of the quenched products, at -160<sup>o</sup>, diethyl ether (m/e 74) was observed. The parent mass of cyclobutadiene, m/e 52 was not observed upon warming the inlet system to 0<sup>o</sup>. However, m/e 104 (C<sub>8</sub>H<sub>8</sub>) and its fragments (i. e., m/e 103, 78, 77, 52, 51, 50, 39, 38 and 37) began to appear at -80<sup>o</sup>. Since in Pettit's experiment large quantities of cyclobutadiene dimer were obtained, and, the mass spectrum observed here was similar to that of authentic syn dimer of cyclobutadiene, the m/e 104 observed here was assigned to that dimer species. Cyclobutadiene apparently dimerized either in the reactor itself or during transport between the reactor and the inlet system.

There were two differences between this experiment and the original experiment by Pettit and co-workers. In this experiment the transfer line between the reactor and the quenching trap was 26 in long, while that in Pettit's experiment was much shorter, but the transfer line in this experiment was kept at 0° while that in Pettit's experiment was at room temperature. It seems unlikely that cyclobutadiene could survive in Pettit's experiment and not in this experiment. The other difference is the analysis method. Gas chromatography was used for analyzing the product of the reaction of dienophile with cyclobutadiene in Pettit's experiment while mass spectrometry was used for direct detecting of cyclobutadiene in these experiments.

#### Dehalogenation of *Cis*-3,4-dichlorocyclobutene

Since dehalogenation of *cis*-3,4-dichlorocyclobutene with sodium amalgam in ether solution was known to generate cyclobutadiene dimer, an attempt was made to freeze out the postulated cyclobutadiene intermediate by the following procedure. The reaction was carried out in the solution reactor attached to the cryogenic inlet system A. The reaction and apparatus were described in Chapter II. Nitrogen gas was bubbled through the reaction mixture and the products of the reaction were passed through a tube at room temperature and were quenched at -180° to -196° in the inlet system A. After 2.5 hours of reaction, the reactor was disconnected; the inlet system A was then slowly warmed.

Results similar to those of the reaction of CIT with ceric ion were obtained: diethyl ether was observed at -160°, m/e 104 was observed at -80°, and no m/e 52 was observed. The unreacted *cis*-3,4-dichlorocyclobutene appeared at -75°.

The quantity of m/e 104 was small compared to that of diethyl ether. In the original experiment, dehalogenation of cis-3,4-dichlorocyclobutene for 40 hours led to a 65 percent yield of syn dimer. Therefore, only a small amount of free cyclobutadiene would have been generated per unit time. If free cyclobutadiene was produced in such small amounts that if it had survived the transfer, it would have been difficult to observe the mass spectrum since diethyl ether was present in such large amounts. However, the negative results of this experiment must have been due mainly to the high reactivity of cyclobutadiene which, at room temperature, formed the syn dimer so fast that it did not have a sufficient lifetime as a free species to survive the transfer from the reactor to the quenching trap.

Attempted Dehalogenation of Cis-3,4-dichlorocyclobutene  
at Low Temperature

The dehalogenation of cis-3,4-dichlorocyclobutene at low temperature was attempted after the failure to trap cyclobutadiene in the experiment described previously.

High surface sodium was chosen, which is a film of sodium approaching colloidal dimensions spread over an inert solid of high surface area. This provided the sodium in a highly reactive form. The preparation of the high surface sodium and the procedure of the attempted dehalogenation of cis-3,4-dichlorocyclobutene at low temperature were described in Chapter II.

High surface sodium with activated alumina as a solid carrier and cis-3,4-dichlorocyclobutene in diethyl ether solution were stirred at  $-110^{\circ}$ . The temperature at  $-110^{\circ}$  was chosen because that between  $-90^{\circ}$  and  $-120^{\circ}$ , the cyclobutadiene



isomers were observed in the mass spectrometer (see next section). Therefore, free cyclobutadiene was assumed to be volatile at  $-110^{\circ}$ . The gases evolved from the reactor were quenched in a trap immersed in liquid nitrogen. To determine whether reaction occurred or not, the contents of the trap were warmed to room temperature and analyzed mass spectrometrically. Only diethyl ether and unreacted cis-3,4-dichlorocyclobutene were observed. The absence of  $m/e$  104 in the trap after it was warmed to room temperature indicated that there was no reaction between sodium and cis-3,4-dichlorocyclobutene at  $-110^{\circ}$ .

#### Radio Frequency Discharge of Cis-3,4-dichlorocyclobutene

Quenching experiments from an rf discharge of cis-3,4-dichlorocyclobutene were conducted in the cryogenic inlet system B with liquid nitrogen used as the refrigerant. The procedure and the apparatus were described in Chapter II.

Cis-3,4-dichlorocyclobutene at room temperature and at a pressure of about  $5 \times 10^{-1}$  torr was passed through an electrodeless rf discharge tube and then quenched. Before quenching, by adjusting the power of radio frequency discharge, the optimum condition was obtained when cis-3,4-dichlorocyclobutene had disappeared from the mass spectrum, and when  $m/e$  52 was at its maximum intensity.

The radio frequency discharge and subsequent quenching were conducted for a period of one to two hours. The quenched products in the cryogenic inlet system were then allowed to warm up slowly, and the effluent gases were monitored by the mass spectrometer.

The products were found to be HCl,  $C_2H_2$ ,  $C_2HCl$ ,  $C_4H_4$ ,  $C_4H_2$ ,  $C_4H_3Cl$ .

$C_2H_2Cl_2$ . As shown in Table 1, the temperature of the cryogenic inlet system at which the mass spectrum of each gas appeared and the boiling point of each gas were in sequential agreement.

The formation of HCl,  $C_4H_2$ ,  $C_2HCl$ ,  $C_2H_2Cl_2$  from the radio frequency discharge of  $C_4H_4Cl_2$  could have arisen from mere fragmentation. The structure of  $C_4H_3Cl$  could be  $ClC\equiv C-CH=CH_2$ ,  $ClCH=CHC\equiv CH$  or  $H_2C=CClC\equiv CH$ , but no attempt was made to identify the exact structure of  $C_4H_3Cl$  observed here. Its formation as any of the above structures involved not only the breaking of chemical bonds in cis-3,4-dichlorocyclobutene but also the migration of hydrogen from one carbon to another. This suggests that the radio frequency discharge of  $C_4H_4Cl_2$  was not just a straight-forward bond breakage but rather a complicated process. Hence,  $C_4H_4$  must be considered not only as cyclobutadiene but also vinylacetylene ( $CH_2=CHC\equiv CH$ ) and butatriene ( $H_2C=C=C=CH_2$ ).

These isomers of cyclobutadiene (vinylacetylene and butatriene) were prepared according to the procedures described in Chapter II. Each compound was transferred to the cryogenic inlet system to compare: (1) the vapor pressures, by observing the temperature at which each gas had the same peak height of m/e 52; (2) the mass spectrum; and (3) the ionization potential of each gas. The extension piece of the cryogenic inlet system was kept at the same distance (0.5 cm) from the edge of the electron beam in each experiment so that, except for ion cross-section differences of the molecules, the sensitivity obtained in measuring was the same. Butatriene at  $-102^\circ$ , vinylacetylene at  $-125^\circ$ , and  $C_4H_4$  from the radio frequency discharge at  $-120^\circ$  showed the same peak height of m/e 52. At  $-90^\circ$ , the ionization potential of butatriene was measured to be 9.2-9.3 eV. At  $-108^\circ$ , the

Table 1. Products of rf Discharge of Cis-3,4-dichlorocyclobutene  
and their Appearance Temperatures

<u>Compound</u>	<u>Temperature (<math>^{\circ}\text{C}</math>)</u>	<u>Boiling Point (<math>^{\circ}\text{C}</math>)</u>	<u>Relative Quantity</u>
HCl	-165	-85	large
$\text{C}_2\text{H}_2$	-155	-84 <sup>a</sup>	medium
$\text{C}_2\text{HCl}$	-150	-32	small
$\text{C}_4\text{H}_4$	-130	5 <sup>b</sup>	large
$\text{C}_4\text{H}_2$	-110	10.3	large
$\text{C}_4\text{H}_3\text{Cl}$	-95	55-57 <sup>c</sup>	small
$\text{C}_2\text{H}_2\text{Cl}_2$	-80	60.3	small

<sup>a</sup>Sublimation temperature of acetylene

<sup>b</sup>Boiling point of vinylacetylene

<sup>c</sup>Boiling point of  $\text{ClC}\equiv\text{C}-\text{CH}=\text{CH}_2$

ionization potential of vinylacetylene was measured to be 9.8-9.9 eV. At  $-110^{\circ}$ , the ionization potential of  $C_4H_4$  from the condensed products of the radio frequency discharge was measured to be 9.7-9.9 eV. From the above results,  $C_4H_4$  from the radio frequency discharge of cis-3,4-dichlorocyclobutene was closer to vinylacetylene in the characteristics of vapor pressure and ionization potential.

The mass spectra of these three  $C_4H_4$  gases are listed in Table 2. During the warm-up of the inlet system in the radio-frequency discharge experiments, diacetylene ( $C_4H_2$ ) appeared with  $C_4H_4$  at  $-120^{\circ}$ . Therefore m/e 50 was not only due to fragmentation of  $C_4H_4$  but also due to diacetylene. In the mass spectrum of diacetylene ( $C_4H_2$ ), m/e 49 was 42.8% and m/e 48 was 10.2% relative to m/e 50. Assuming the excess 21% of m/e 50 in the  $C_4H_4$  mass spectrum relative to that of vinylacetylene was due to  $C_4H_2$  molecule, then the corrected mass spectrum of  $C_4H_4$  was quite similar to that of vinylacetylene as shown in Table 2.

The fact that cyclobutadiene forms a dimer at room temperature has been discussed in Chapter I. The preceding results in this chapter confirmed that the formation of cyclobutadiene dimer at room temperature was a fast reaction. Utilizing this property of cyclobutadiene, the following experiments were conducted. The products of the radio frequency discharge of  $C_4H_4Cl_2$  were quenched in a Pyrex trap immersed in a dewar containing liquid nitrogen. In order to prevent possible polymerization or decomposition, the distance from the discharge coil to the cold surface was less than 3 inches. After one hour of discharge, a dewar containing the refrigerant 2-methyl pentane at a temperature of  $-140^{\circ}$  was substituted for the dewar of liquid nitrogen. The gases in the trap were pumped out.

Table 2. Mass Spectra of  $C_4H_4$  from rf Discharge of  
 $C_4H_4Cl_2$  and  $C_4H_4$  Isomers at 70 eV

<u>m/e</u>	<u><math>C_4H_4</math> from rf Discharge of <math>C_4H_4Cl_2</math> at <math>-120^{\circ}</math></u>	<u>Butatriene at <math>-90^{\circ}</math></u>	<u>Vinylacetylene at <math>-108^{\circ}</math></u>
52	100 (100) <sup>b</sup>	100 (100) <sup>c</sup>	100 (100) <sup>a</sup>
51	59 (59)	72 (72-78)	56 (50.2)
50	70 (49)	51 (54)	49 (41)
49	29 (19)	26 (24)	19 (13)
48	9 (9)	8 (-)	8 (2.8)
39	1 (1)	1 (-)	1 (0.85)
26	11 (11)	18 (21.2)	12 (11)

<sup>a</sup> Measured with a magnetic mass spectrometer (CEC, Model 21-101), "Selected Mass Spectral Data," API Research Project 44.

<sup>b</sup> Assume 21% of m/e 50 is due to  $C_4H_2$  molecule.

<sup>c</sup> Measured with a magnetic mass spectrometer (CEC, Model 21-103), W. M. Schubert et al., J. Am. Chem. Soc. 76, 1929 (1954).

by a mechanical vacuum pump for about one hour. A second Pyrex trap immersed in liquid nitrogen was then connected between the first trap and mechanical pump. The first trap was slowly warmed to  $-125^{\circ}$ ; the evolved gas was then quenched in the second trap. After half an hour of pumping, the second trap was allowed to stay at room temperature for one and a half hours. The mass spectra of these gases showed that they were mainly  $C_4H_4$  without any  $C_8H_8$ . After standing overnight, the  $C_4H_4$  spectra had disappeared, but still no  $C_8H_8$  was observed at room temperature.

The boiling point of vinylacetylene is  $5^{\circ}$  and it polymerizes in the presence of air at  $50^{\circ}$  within 24 hours.<sup>42</sup> Polymerization of butatriene starts at  $-30^{\circ}$ . Near  $0^{\circ}$  the polymerization reaction becomes so rapid and exothermic that a spontaneous "ignition" of the compound occurs under vacuum which produces a flash of light and deposits black char throughout the vacuum system.<sup>43</sup> In view of the close similarity of mass spectrum, temperature and ionization potential of vinylacetylene and  $C_4H_4$  produced from  $C_4H_4Cl_2$ , and of the instability of butatriene, it was concluded that vinylacetylene was the product of the radio frequency discharge of cis-3,4 dichlorocyclobutene.

#### Pyrolysis of Cyclobutadieneirontricarbonyl

As described in Chapter II, studies of the pyrolysis of CIT were conducted in a coaxial furnace inlet system in which the furnace exhaust was only 1/8 inch from the ionizing electron beam of the mass spectrometer.

Several standard wall Pyrex tubes with outside diameter from 2 mm to 7 mm were used. A 1/8-in i.d. alumina furnace was also used because it could

withstand higher temperatures. CIT was kept at different temperatures ranging from  $-50^{\circ}$  to  $0^{\circ}$ , where the vapor pressures ranged from about  $5 \times 10^{-2}$  to  $2 \times 10^{-1}$  torr (measured at a distance of 80 cm from the furnace).

At about  $280^{\circ}$ , the CIT began to decompose. The ratio of  $m/e$  52 ( $C_4H_4^+$ ) and  $m/e$  193 ( $C_4H_4Fe(CO)_3^+$ ) increased and reached a maximum value between  $350^{\circ}$  and  $400^{\circ}$ . This maximum ratio of  $m/e$  52 to  $m/e$  192 at a particular pressure varied with the furnace dimensions. With a vapor pressure of CIT of  $2 \times 10^{-1}$  torr and at  $0^{\circ}$  with a 1/8-in i.d. alumina furnace having a heated length of 3.5 cm, the maximum ratio of  $m/e$  52 and  $m/e$  192 occurred at  $380^{\circ}$ .

The dominant peaks of the pyrolysis products and their assignments are summarized in Table 3. The peak at  $m/e$  104 was assigned as  $C_8H_8$ . In view of the fast dimerization of cyclobutadiene, this  $C_8H_8$  was probably the cyclobutadiene dimer. The intense peak at  $m/e$  78 was assigned to benzene. Since  $m/e$  52 was also a fragment in the mass spectrum of  $C_8H_8$  and  $C_6H_6$ ,  $m/e$  52 could not be solely due to free  $C_4H_4$ . The mass spectrum of authentic benzene was taken at 70 eV and the intensity of  $m/e$  52 was only 19.5 percent of  $m/e$  78 ( $C_6H_6$ ). This value agreed well with the reported value of 20 percent.<sup>44</sup> In the mass spectrum of authentic cyclooctatetraene,  $m/e$  52 was 31 per cent of  $m/e$  104, and in that of authentic syn dimer of cyclobutadiene,  $m/e$  52 was 49 per cent of  $m/e$  104. In the mass spectrum of the pyrolysis products of CIT,  $m/e$  103 peak was higher than that at  $m/e$  104. In the mass spectrum of cyclooctatetraene,  $m/e$  103 peak was only 62 per cent of  $m/e$  104 while in the mass spectrum of syn dimer of cyclobutadiene  $m/e$  104 peak was only 34 per cent of  $m/e$  103. Therefore,  $m/e$  104 in

Table 3. Mass Spectrum of the Products at 70 eV from the Pyrolysis  
of Cyclobutadieneirontricarbonyl at 380<sup>o</sup>

<u>m/e</u>	<u>Assignment</u>	<u>Abundance %</u>
104	$C_8H_8^+$	2.0
103	$C_8H_7^+$	6.0
78	$C_6H_6^+$	40.7
56	$Fe^+$	18.2
54	$C_4H_6^+$	6.5
53	$C_4H_5^+$	4.5
52	$C_4H_4^+$	17.1
51	$C_4H_3^+$	22.7
50	$C_4H_2^+$	20.5
44	$CO_2^+$	21.6
39	$C_3H_3^+$	21.6
28	$CO^+$	100.0
27	$C_2H_3^+$	25.0
26	$C_2H_2^+$	21.6
16	$O^+$	36.4



the mass spectrum of the pyrolysis products of CIT was assigned to the syn dimer of cyclobutadiene. From this, one was able to calculate that the contribution of m/e 52 from m/e 104 in the mass spectrum of the pyrolysis products of CIT was less than 1 per cent. The relative ratio of m/e 78 and m/e 104 was 4.5:1 in the mass spectrum of syn dimer of cyclobutadiene. The m/e 78 due to  $C_6H_6$  in the mass spectrum of the pyrolysis products of CIT was therefore 31.7 per cent ( $40.7 - 2 \times 4.5 = 31.7$ ). Hence, the total contribution of m/e 52 from  $C_8H_8$  and  $C_6H_6$  was 7.3 per cent ( $1 + 31.7 \times 0.2 = 7.3$ ). Since the total m/e 52 abundance was 17.1%, the remaining 9.8% must have been due to free  $C_4H_4$ . A rough appearance potential measurement of  $C_4H_4^+$  was much less than 15.6 eV, which was the appearance potential of  $C_4H_4^+$  from  $C_6H_6$ . Therefore, from the pyrolysis data, m/e 52 was concluded to be at least partially due to free  $C_4H_4$ . The mass spectrum from the pyrolysis products of CIT did not allow a determination of whether the remaining 9.8 per cent of m/e 52 was due to cyclobutadiene or to one, or both, of its known isomers.

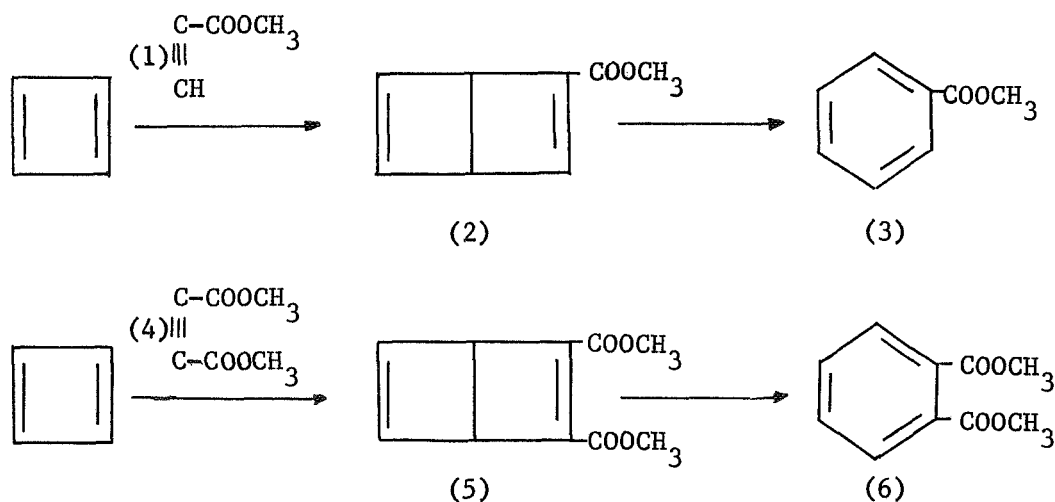
Gunning<sup>21</sup> has also observed free cyclobutadiene from the photolysis of CIT. Dominant peaks of the photolysis products in the mass spectrometer were m/e 26 ( $C_2H_2^+$ ), m/e 52 ( $C_4H_4^+$ ), m/e 78 ( $C_6H_6^+$ ), m/e 104 ( $C_8H_8^+$ ), m/e 140 ( $Fe(CO)_3^+$ ), and m/e 28 ( $CO^+$ ). However, in the pyrolysis of CIT carried out in this thesis work, there was no observation of m/e 140 ( $Fe(CO)_3^+$ ), but there was a peak at m/e 44 ( $CO_2^+$ ). This could be due to the decomposition of  $Fe(CO)_3^+$  and the reaction of oxygen and CO at the high temperatures attained in the pyrolysis of CIT.

Recent reports of the pyrolysis of photo- $\alpha$ -pyrone<sup>22</sup> in which cyclobutadiene

was generated also indicated, among others, mass peaks at  $m/e$  104, 78, and 26.

### Copolyrolysis of Cyclobutadieneirontricarboxyl and Dienophiles

The study of the chemistry of cyclobutadiene has shown that cyclobutadiene and substituted cyclobutadiene easily reacted with dienophiles as discussed in Chapter I. Reaction of cyclobutadiene with methyl propiolate (1) afforded a "Dewar benzene" derivative (2) which isomerized to the corresponding benzene compound (3) upon heating to  $90^{\circ}$ . A similar reaction of cyclobutadiene with dimethyl acetylenedicarboxylate (4) yielded dimethyl 1,2-benzenedicarboxylate (6).<sup>19</sup>



Copolyrolysis of CIT and carboxylic esters were carried out in the coaxial furnace inlet system. At the same conditions of pyrolysis of CIT which produced the highest intensity of  $C_4H_4$ , and with the inlet vapor pressure ratio of methyl propiolate and CIT of 2.5:1 (500 torr: 200 torr), an ion peak at  $m/e$  136 (i.e., methyl benzoate) was observed (Figure 15). When the introduction of methyl propiolate was stopped, the  $m/e$  136 peak disappeared and the mass spectrum was

again solely due to the products of the pyrolysis of CIT. When methyl propiolate was introduced into the furnace again, the m/e 136 again appeared and the m/e 52 ( $C_4H_4$ ), 78 ( $C_6H_6$ ), 104 ( $C_8H_8$ ) decreased. The fragmentation mass spectrum of m/e 136 was similar to that of methyl benzoate as listed in Table 13. The prominent peaks of the mass spectrum of methyl benzoate, m/e 136, 105, 77 all appeared in the mass spectrum of the copyrolysis of CIT and methyl propiolate although the peak height ratios were not exactly the same. Therefore, the observed m/e 136 in the copyrolysis could be due either to 2-carbomethoxybicyclo[2,20]hexa-2,5-diene (2) or to the mixture of (2) and methyl benzoate.

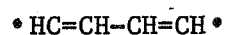
Similar copyrolysis of CIT and dimethyl acetylenedicarboxylate also produced the expected ion peak at m/e 194 (i. e., dimethyl 1,2-benzenedicarboxylate). The mass spectrum of copyrolysis had m/e 194, 163, 92 which were the prominent peaks of authentic dimethyl 1,2-benzenedicarboxylate. Again the mass peak height ratios were not exactly the same as that of authentic dimethyl 1,2-benzenedicarboxylate (6). Therefore, the observed m/e 194 in the copyrolysis could have been due either to 2,3-dicarbomethoxybicyclo[2,2,0]hexa-2,5-diene (5) or to the mixture of compounds (5) and (6).

Since cyclobutadiene and substituted cyclobutadienes (i. e., tetramethylcyclobutadiene and tetraphenylcyclobutadiene) have never been isolated, one might question whether the dienophiles reacted with cyclobutadiene and substituted cyclobutadiene or with their precursors in these reactions. As was seen in Chapter I, "Dewar benzene" and "substituted Dewar benzene" compounds were obtained when dienophiles were present in the reactions in which cyclobutadiene and substituted

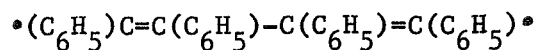
cyclobutadiene were thought to be generated, regardless of the precursors. This would seem to indicate that dienophiles did not react with the precursors of cyclobutadiene and substituted cyclobutadiene. In this thesis research, the mass spectrum of CIT was not observed in the copyrolysis of CIT with dienophiles. This provided further evidence that "Dewar benzene" was not the product of the reaction of dienophile with CIT.

Now, one might question whether dienophile reacted with cyclobutadiene or with butadienyl radical (7) to form "Dewar benzene." When dimethyl acetylenedicarboxylate (4) was present in the pyrolysis of (4-bromo-1,2,3,4-tetraphenyl-cis, cis-1,3-butadienyl)-dimethyltin bromide (8), dimethyl tetraphenylphthalate (10) was obtained.<sup>25</sup> It has been postulated that tetraphenylcyclobutadiene (9a) was generated and underwent immediate reaction with the dienophile (4).<sup>25</sup> Recently, a kinetic investigation by Sandel and Freedman<sup>28</sup> confirmed the existence of an intermediate in the pyrolysis of (8), and employed a label-scrambling scheme to establish that the intermediate was a four-carbon cycle with two chemically equivalent adjacent ring bonds. Furthermore, their epr studies showed that no radical due to the substituted butadienyl radical (9b) was observed. Therefore, they concluded that tetraphenylcyclobutadiene (9a) rather than the radical (9b) was produced in the pyrolysis of (8). Recent calculations<sup>67</sup> have shown that the conversion of cyclobutadiene to butadienyl radical (7) was predicted to be very strongly endothermic (by 47 kcal/mole); this indicated that cyclobutadiene was more stable than butadienyl radical (7). These two studies strongly suggested that dienophiles reacted with cyclobutadiene rather than with the butadienyl

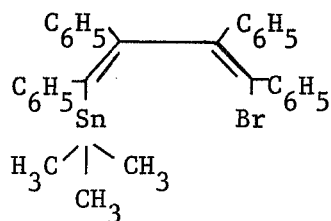
radical (7). Therefore, it must be concluded that free cyclobutadiene was produced in the pyrolysis of CIT.



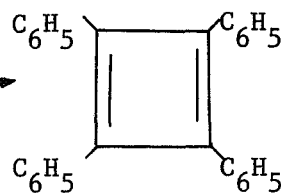
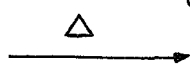
(7)



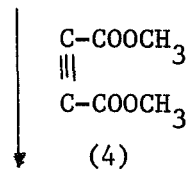
(9b)



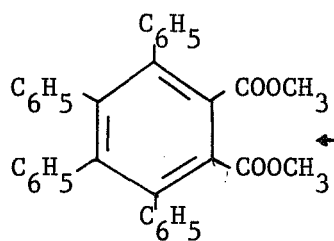
(8)



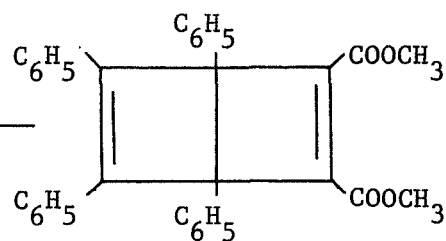
(9a)



(4)



(10)



### Copyrolysis of Cyclobutadieneirontricarboxyl and Oxygen

From the reaction of oxygen and cyclobutadiene, it has been previously assumed that the ground state of cyclobutadiene was a triplet because oxygen had

a triplet ground state<sup>22, 25</sup>. However, different products of the reaction has been reported as discussed in Chapter I. In this thesis research, the copyrolysis of oxygen and CIT was conducted in the furnace attached to the inlet system B.

Since cis-3,4-dichlorocyclobutene reacted with diiron enneacarbonyl to form CIT, a small amount of cis-3,4-dichlorocyclobutene was present in the sample of CIT. This cis-3,4-dichlorocyclobutene was removed by vacuum pumping for several hours before copyrolysis to eliminate the possibility of the type of hydrolysis postulated by Freedman<sup>25</sup> as discussed in Chapter I. The mass spectrum of CIT showed no impurity. This eliminated the possibility of the hydrolysis of cis-3,4-dichlorocyclobutene to form furan.

With the pressure ratio of oxygen and cyclobutadieneirontricarbonyl at 2.5:1 (500 torr:200 torr) and the temperature at 380<sup>o</sup> to 390<sup>o</sup>, m/e 68 in large amounts and m/e 84 in a smaller amount were observed.

Copyrolysis and quenching were then carried out to obtain clearer results. Pure oxygen gas was condensed as a liquid in a trap at -196<sup>o</sup> to eliminate its impurities. With the pressure ratio of oxygen and CIT at about 2.5:1 (500:200 torr), and with the furnace temperature at 390<sup>o</sup>, the products were quenched at -196<sup>o</sup> in the inlet system B. After 1.5 hours of copyrolysis, the products were slowly warmed. The products and the temperatures at which they appeared are shown in Table 4.

All the usual products of pyrolysis of CIT were observed. However, except for CO<sub>2</sub>, the products were reduced substantially in quantity. Carbon dioxide increased substantially, which must have been due to the introduction of excess

Table 4. Products of Copyrolysis of Cyclobutadieneirontricarbonyl  
with Oxygen and their Appearance Temperatures

<u>Compound</u>	<u>Temperature (<math>^{\circ}</math>C)</u>	<u>Relative Quantity</u>
CO	-196	medium
$C_2H_2$	-155	small
CO <sub>2</sub>	-145	large
$C_4H_6$	-120	small
$C_4H_4O$	-110	large
$C_4H_4$	-105	small
$C_6H_6$	- 90	small
$C_8H_8$	- 80	small
$C_4H_4O_2$	- 80	small

oxygen and then subsequent oxidation of CO at the high temperature.

An intense mass peak at  $m/e$  68 ( $C_4H_4O$ ) began to appear at  $-110^\circ$ . The mass spectrum associated with  $m/e$  68 was similar to the reported mass spectrum of furan, as shown in Figure 17 and Table 9. At  $-80^\circ$ , not only  $m/e$  84 ( $C_4H_4O_2$ ) was observed in very small amounts (see Figure 18), but also unpyrolyzed CIT ( $m/e$  192), which had a mass fragment at  $m/e$  84 ( $Fe^{56}CO$ ). The peak heights of  $m/e$  84 and  $m/e$  192 were equal in the mass spectrum of the quenched products of the coprolysis of CIT with oxygen at  $-80^\circ$ . Since the ratio of  $m/e$  84 to  $m/e$  192 in the mass spectrum of CIT was only 70.5%, the excess 29.5% of  $m/e$  84 was assumed to be due to free  $C_4H_4O_2$ . Gunning and his co-workers<sup>21</sup> reported that the photolysis of oxygen and CIT yielded only furan. Hedaya and his co-workers<sup>22</sup> on the contrary, reported that coprolysis of photo- $\alpha$ -pyrone with oxygen yielded only  $C_4H_4O_2$ . Gunning<sup>21</sup> also used electron paramagnetic resonance to search for a radical in the photolysis of CIT at  $77^\circ K$  with negative results. He concluded that cyclobutadiene had a singlet ground state. Both furan and  $C_4H_4O_2$  were the products of the reaction between oxygen and cyclobutadiene, therefore it would appear that the different products were due to the different natures of the ground state of cyclobutadiene produced in two experiments. If this assumption is correct, then the reaction of oxygen with a singlet ground state of cyclobutadiene produces furan and the reaction of oxygen with a triplet ground state of cyclobutadiene produces  $C_4H_4O_2$ . Therefore, the pyrolysis of CIT produced more cyclobutadiene in the singlet ground state than in the triplet state.



Pyrolysis and Quenching Experiment with  
Cyclobutadieneirontricarboxyl

From the above results of the pyrolysis of CIT alone and, from its copyrolysis with other compounds, it was concluded that cyclobutadiene was produced in the gas phase. Pyrolysis and quenching of CIT were carried out in order to investigate the low temperature stability of cyclobutadiene.

Seven pyrolysis experiments were carried out in the inlet system B. Each pyrolysis lasted two hours with inlet pressures of CIT from  $5 \times 10^{-2}$  to  $5 \times 10^{-1}$  torr (measured with a thermocouple gauge at a distance of 93 cm from the furnace) and with furnace temperatures of  $320^{\circ}$  to  $380^{\circ}$ .

During pyrolysis and quenching with simultaneous observation of the mass spectrum, the ratio of  $m/e$  28 and  $m/e$  32 was seen to be 20:1 instead of the usual ratio of 4:1 from the air background. The  $m/e$  28 was assigned to CO. Carbon monoxide is a liquid at  $-196^{\circ}$  under its own vapor pressure of 400 torr. However, with this vapor pressure, CO would be expected to volatilize under the vacuum conditions ( $10^{-6}$  torr) maintained in the quenching tube. This could explain the failure to quench CO, and, subsequently, its appearance in the mass spectrum.

The pyrolysis products of cyclobutadieneirontricarboxyl and their appearance temperatures are shown in Table 5.

At  $-120^{\circ}$ ,  $m/e$  54 was observed and was assigned to  $C_4H_6$ . There are several possible structures of  $C_4H_6$ : 1,2-butadiene, 1,3-butadiene, 1-butyne, 2-butyne, and cyclobutene. The percentage of  $m/e$  53 relative to  $m/e$  54 is 44.5 per cent for 1,2-butadiene, 43 percent for 1-butyne, 44.8 percent for 2-butyne

and 69.2 percent for 1,3-butadiene.<sup>65</sup> A mass spectrum of cyclobutene was not available in the literature. The percentage of m/e 53 relative to m/e 54 that was observed here was calculated to be 69 to 71 percent at  $-120^{\circ}$ . At  $-105^{\circ}$ , the peak at m/e 52 ( $C_4H_4$ ) was larger than that at m/e 54. Between  $-110^{\circ}$  and  $-100^{\circ}$  the m/e 54, 53, 52, 51, 50, 49, 39, 27, 26 were predominant peaks. To calculate the percentage contribution of m/e 54 and m/e 52 to each of the mass peaks less than 52, two linear equations were set up at two different constant temperatures by assuming that m/e 54 contributed 12.3 percent of its peak height to m/e 52 (which is the ratio of m/e 52 and m/e 54 in the mass spectrum of 1,3-butadiene). The equations were of the form

$$A_n X + B_n (1 - A_n \times 0.123) Y = C_n \quad n = 1, 2$$

where X was the percentage of m/e 39 relative to m/e 54 due to m/e 54 and Y was the percentage of m/e 39 relative to m/e 52 due to m/e 52.  $A_n$ ,  $B_n$ ,  $C_n$  were the peak heights of m/e 54, 52, 39 at  $T_n$ . Solving the equations, the m/e 39 due to m/e 54 was between 115 percent and 120 percent of m/e 54. The percentage of m/e 39 relative to m/e 54 was reported<sup>65</sup> as 43.6 percent for 1,2-butadiene, 76.3 percent for 1-butyne, 25.7 percent for 2-butyne, and 116.5 percent for 1,3-butadiene. From a comparison of the calculated and reported values of the percentages of m/e 53 and m/e 39 relative to m/e 54, the mass peak at 54 was assigned to 1,3-butadiene.

Since 1,3-butadiene had a peak at m/e 52 in its mass spectrum, it would be best if 1,3-butadiene could be pumped out in order to more accurately assign the mass fragments. Continuous pumping for 6 hours with the temperature between  $-115^{\circ}$  and  $-110^{\circ}$  failed to completely remove  $C_4H_6$ . The mass spectrum of  $C_4H_4$

Table 5. Pyrolysis Products of Cyclobutadieneirontricarbonyl  
and their Appearance Temperatures

<u>Compound</u>	<u>Temperature (<math>^{\circ}</math>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

at  $-105^{\circ}$ , shown in Table 6, was obtained by subtracting the mass spectrum of 1,3-butadiene from the observed total mass spectrum. The mass spectrum of  $C_4H_4$  at  $-105^{\circ}$  was different from that of butatriene and vinylacetylene as shown in Table 6.

The ionization potential of  $C_4H_4$  at  $-105^{\circ}$  was measured as 9.5 to 9.6 eV, which was between the measured values of butatriene (9.2-9.3 eV) and vinylacetylene (9.8-9.9 eV). The ionization potentials of  $m/e$  78 ( $C_6H_6$ ) and  $m/e$  104 ( $C_8H_8$ ) were also determined from the low temperature evolved gases. The IP of  $C_8H_8$  measured in this experiment was 9.0 to 9.1 eV, and since an earlier value of cyclooctatetraene was reported to be 8.6 eV<sup>45</sup>, the  $m/e$  104 observed here was postulated as cyclobutadiene dimer. The associated mass spectrum and ionization potential at  $m/e$  78 were in agreement with that of benzene.

These results showed that the mass spectra and IP of authentic butatriene and vinylacetylene differed from those of the  $C_4H_4$  produced from the pyrolysis of CIT. To determine whether the  $C_4H_4$  observed here was a mixture of  $C_4H_4$  isomers, pyrolysis and quenching were carried out in an apparatus outside the inlet system B. The quenched products were warmed to room temperature and allowed to stand for 1 hour. The mass spectrum was then taken;  $m/e$  52 was observed in small amounts. It was difficult to interpret the results since both  $m/e$  52 ( $C_4H_4$ ) and  $m/e$  104 ( $C_8H_8$ ) were formed in the warmed product. If  $m/e$  52 had not been observed, it would have been possible to assume that  $m/e$  52 was cyclobutadiene and had undergone dimerization to  $C_8H_8$ . From the chemistry of cyclobutadiene already known, it was apparent that cyclobutadiene could not exist at room

Table 6. Mass Spectra of  $C_4H_4$  Isomers and  $C_4H_4$   
from Pyrolysis of CIT

<u>m/e</u>	<u><math>C_4H_4</math> from Pyrolysis of cyclobutadieneiron- tricarbonyl at 100°</u>	<u>Butatriene at -90°</u>	<u>Vinylacetylene at -108°</u>
52	100%	100% (100%) <sup>a</sup>	100% (100%) <sup>b</sup>
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)

<sup>a</sup> 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). An additional peak at m/e 53 of 14.7-22.2 percent is evidently produced by reaction during inlet.

<sup>b</sup> Measured with a magnetic mass spectrometer (CEC, Model 21-101), "Selected Mass Spectral Data," API Research Project 44.

temperature. On the other hand, since butatriene was reported to polymerize at  $-30^{\circ}$ <sup>43</sup>, the m/e 52 observed here at room temperature must have been due to vinylacetylene.

An attempt was made to deactivate cyclobutadiene in the pyrolysis by introducing helium along with the CIT into the furnace. Several experiments were made with ratios of helium to CIT of 1:1, 2:1, and 3:1. No significant change in the quantity of the products was observed.

To prove the existence of cyclobutadiene in the quenched product, chemical reaction with the isolated product was carried out. The results are presented in the next section.

#### Reaction of Dimethyl Acetylenedicarboxylate with Quenched C<sub>4</sub>H<sub>4</sub>

##### Produced by Pyrolysis of Cyclobutadieneirontricarbonyl

The apparatus for this experiment was a 22 mm o.d. Pyrex quenching tube into which a 10 mm o.d. furnace Pyrex tube had been fastened by a ground joint (see Figure 5). A side arm tube in the Pyrex quenching tube was connected to a diffusion pump. During the pyrolysis of CIT, the Pyrex quenching tube was vacuum pumped and it was immersed in liquid nitrogen. This pyrolysis and quenching experiment closely resembled that carried out in the cryogenic inlet system B.

With the inlet pressure of CIT at  $5 \times 10^{-1}$  torr, the pyrolysis was carried out for 4 hrs at the temperatures between  $350^{\circ}$  and  $380^{\circ}$ . At the end of the pyrolysis, the high vacuum in the quenching tube was broken. Dimethyl acetylenedicarboxylate in diethyl ether solution at  $-90^{\circ}$  was added to the quenched product

at  $-196^{\circ}$ . The mixture was transferred to a Dewar kept at  $-90^{\circ}$  and was slowly warmed to room temperature in a period of 1/2 to 1 hrs. The mixture was then heated to  $90^{\circ}$  for 1/2 hour to convert the expected 2,3-dicarbomethoxybicyclo [2,2,0]hexa-2,4-diene into dimethyl 1,2-benzenedicarboxylate and this was divided into two portions. In view of the high boiling point ( $195^{\circ}$  to  $198^{\circ}$ ) of dimethyl 1,2-benzenedicarboxylate and the excess dimethyl acetylenedicarboxylate in the reaction mixture, gas chromatographic analysis was used in the analysis of one of the portions.

Dimethyl 1,2-benzenedicarboxylate was detected in each gas chromatographic analysis using two different columns. Since some unpyrolyzed CIT was also present in the reaction mixture that had been heated to  $90^{\circ}$  for 1/2 hr, dimethyl 1,2-benzenedicarboxylate could have been due to the reaction of dimethyl acetylenedicarboxylate with CIT instead of with cyclobutadiene. When dimethyl acetylenedicarboxylate was added to an equal amount of CIT and then heated for 1/2 hr at  $90^{\circ}$ ; dimethyl 1,2-benzenedicarboxylate was detected in this mixture in the gas chromatogram. Since the boiling point of dimethyl 1,2-benzenedicarboxylate was  $195^{\circ}$  to  $198^{\circ}$ , the temperature of the injector of the gas chromatograph was set at  $200^{\circ}$  to  $230^{\circ}$ . The CIT could have been decomposed to produce cyclobutadiene in the injector. Then dimethyl 1,2-benzenedicarboxylate was formed by the immediate reaction of cyclobutadiene with dimethyl acetylenedicarboxylate. With this consideration, only CIT and an equal amount of dimethyl acetylenedicarboxylate were mixed together at room temperature and were injected into the gas chromatograph; again, small amounts of dimethyl 1,2-benzenedicarboxylate were detected. To

avoid the effects of the high temperatures inherent in the gas chromatograph, infrared analysis was used. Dimethyl acetylenedicarboxylate was added to an equal amount of CIT, heated for 1/2 hr at 90° and then cooled to room temperature. The ir spectrum of this mixture showed no bands due to dimethyl 1,2-benzenedicarboxylate (See Figure 32 and Figure 33). From these results, it was concluded that dimethyl acetylenedicarboxylate did not react with the CIT. Therefore, it was assumed that cyclobutadiene was produced by the decomposition of CIT in the injector of the gas chromatograph and immediately underwent reaction with dimethyl acetylenedicarboxylate.

It appeared that the unpyrolyzed CIT would have to be removed if gas chromatography were to be used in the search for evidence of the reaction between quenched  $C_4H_4$ , produced by the pyrolysis of CIT, and dimethyl acetylenedicarboxylate. An attempt was made to remove the unpyrolyzed CIT from the second portion of this reaction mixture by vacuum pumping for several hours. The pumping was continued until only a negligible amount of CIT was present in the mass spectrum. Examination of the pumped portion by gas chromatography still showed a small amount of CIT together with a small amount of dimethyl 1,2-benzenedicarboxylate. Since gas chromatography was not a suitable method of analysis in this case, infrared spectroscopy was employed. The infrared spectrum of this reaction mixture showed no bands due to dimethyl 1,2-benzenedicarboxylate (Figure 31). From this, it would seem that the quenched  $C_4H_4$ , produced by the pyrolysis of CIT, did not react with dimethyl acetylenedicarboxylate at low temperatures. This could be explained by the fact that the diethyl ether solution of dimethyl acetylene-



dicarboxylate separated into a solid phase and a liquid phase when the solution was cooled to  $-20^{\circ}$ . It was unlikely that the reaction between quenched  $C_4H_4$  and dimethyl acetylenedicarboxylate, a solid phase at temperatures below  $-20^{\circ}$ , would have occurred. If reaction only occurred above  $-20^{\circ}$ , cyclobutadiene would probably have already formed the dimer before being warmed to  $-20^{\circ}$  so that, again, no dimethyl 1,2-benzenedicarboxylate would have been formed.

It is appropriate here to comment on an earlier report<sup>19</sup> in which it was postulated that cyclobutadiene had been isolated. During the experiment, a pressure of 100 torr was maintained in the system in order to transfer the cyclobutadiene, formed at  $0^{\circ}$  by the reaction of ceric ammonium nitrate in the diethyl ether solution of CIT, into the trap at  $-196^{\circ}$ . Since diethyl ether exerted a vapor pressure of more than 100 torr at  $0^{\circ}$ , CIT could have been easily swept over with the diethyl ether into the trap at  $-196^{\circ}$ . If this did occur, the similar finding of methyl benzoate by gas chromatography in the earlier experiment<sup>19</sup> would not necessarily have been due to the reaction of isolated cyclobutadiene with methyl propiolate.

#### Unsuccessful Copyrolysis with Cyclobutadieneirontricarbonyl

After encountering difficulty in the reaction between dimethyl acetylenedicarboxylate and the quenched products produced by the pyrolysis of CIT at low temperatures, it was felt that a solution to the problem would be provided if a chemical could be found which would be a liquid below  $-60^{\circ}$  and which could also react with cyclobutadiene at low temperatures. Ethyl acetylene was chosen because it melted at  $-122.5^{\circ}$  and boiled at  $8.1^{\circ}$ . If ethyl acetylene could react with cyclobutadiene to form ethyl benzene in copyrolysis with CIT, then ethyl acetylene

could be used to detect cyclobutadiene by adding to the quenched products of the pyrolysis of CIT at  $-100^{\circ}$ . One would expect that, as the mixture was slowly warmed, a reaction would take place between ethyl acetylene and cyclobutadiene at some temperature above  $-100^{\circ}$ . However, copyrolysis of ethyl acetylene and CIT at temperatures between  $350^{\circ}$  and  $400^{\circ}$  failed to yield any mass peak corresponding to ethyl benzene. Therefore this low temperature experiment was abandoned.

From the formation of 3,4-dimethylene-1,2-dimethylcyclobutene in the reaction of triplet methylene and tetramethylcyclobutadiene at  $240^{\circ}$ , as was discussed in Chapter I, Skell<sup>24</sup> concluded that tetramethylcyclobutadiene had a triplet ground state. Copyrolysis of CIT with dibromomethane, which produced triplet methylene in Skell's experiment, failed to yield any mass peak corresponding to 3,4-dimethylenecyclobutene at the temperatures between  $350^{\circ}$  and  $400^{\circ}$ .

Further support of the triplet tetramethylcyclobutadiene reported by Skell<sup>24</sup> was furnished by the formation of 1,2,3,3,4,4-hexamethylcyclobutene in the reaction of tetramethylcyclobutadiene and methyl radical (from methyl bromide) at  $240^{\circ}$  as discussed in Chapter II. Hedaya<sup>22</sup> also reported that appearance of  $m/e$  82 ( $C_4H_4(CH_3)_2$ ) and 67 ( $C_4H_4CH_3$ ) in the mass spectrum of the copyrolysis of ethyl nitrite and photo- $\alpha$ -pyrone at  $800^{\circ}$  was due to the reaction of cyclobutadiene and methyl radical. Copyrolysis of CIT and methyl bromide at the temperatures between  $350^{\circ}$  and  $400^{\circ}$  failed to yield any peak in the mass spectrum that could be assigned to 3,4-dimethylcyclobutene. The copyrolysis of CIT and NO also failed to produce any evidence of 3,4-dinitrosocyclobutene.

The copyrolysis of CIT with the following dienophiles: tetracyanoethylene, diethyl maleate, diethyl fumarate and ethylene, did not produce any compound expected from the reaction of these dienophiles and cyclobutadiene.

The failure of the copyrolysis of CIT with  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_3\text{Br}$  and  $\text{NO}$  seemed to suggest that cyclobutadiene produced from the pyrolysis of CIT was not a triplet diradical. Since the reaction of methylene and tetracyclobutadiene had been conducted at  $240^\circ$ , the temperature of  $400^\circ$  in this copyrolysis should certainly have been high enough to insure the reaction of cyclobutadiene and methylene. However, there was still the possibility that at the condition of this copyrolysis, the short contact time was not long enough to permit the formation of methylene and the subsequent reaction of methylene and cyclobutadiene. The failure of the copyrolysis of CIT and the several dienophiles could also be explained by this argument.

#### Mechanism of the Pyrolysis of Cyclobutadieneirontricarbonyl

From the result of the copyrolysis of CIT with each of the following compounds: dimethyl propiolate, dimethyl acetylenedicarboxylate and oxygen, it was concluded that cyclobutadiene was produced as a gas from the pyrolysis of CIT. However, vinylacetylene, benzene, and acetylene were also found in the isolated quenched products of the pyrolysis. The formation of benzene and vinylacetylene in the pyrolysis of CIT could have been due to the pyrolysis of the acetylene. It has been previously reported that vinylacetylene and benzene, along with hydrogen, methane, ethane, ethylene, methylacetylene and diacetylene, had been produced in the pyrolysis of acetylene at the temperatures of  $500^\circ$  to  $1000^\circ$ <sup>46</sup>. Using the same furnace in the inlet system B and with temperatures of  $380^\circ$  to  $390^\circ$ , pure acetylene,

at pressures of  $2.5 \times 10^{-1}$ ,  $5 \times 10^{-1}$  and 1 torr, was pyrolyzed in three runs and quenched to  $-196^{\circ}$ . Neither vinylacetylene nor benzene was observed. Therefore, the benzene and vinylacetylene formed in the pyrolysis of CIT were not due to the reaction of acetylene present in the pyrolysis. This conclusion was also supported by the absence of methane, ethane, ethylene, methylacetylene and diacetylene, which were other known products of the pyrolysis of acetylene. Since the benzene could not have been produced by the pyrolysis of acetylene, it could have resulted from the reaction of cyclobutadiene with acetylene to form Dewar benzene, with the latter undergoing thermal rearrangement to benzene.

It was not clear whether the acetylene was produced by the decomposition of cyclobutadiene or CIT. Willstätter<sup>1</sup> had noted that dehalogenation of 1,2-dibromocyclobutane with potassium hydroxide at  $210^{\circ}$  produced acetylene which was postulated as the product of the fissioning of cyclobutadiene. From the estimated heat of formation of cyclobutadiene<sup>3</sup> (830.1 kcal/mole) and the known heat of formation of 2 moles of acetylene (778.9 kcal), the dissociation of singlet cyclobutadiene into acetylene was calculated to be endothermic by no less than 51.2 kcal/mole. The heat of formation of cyclobutadiene, calculated by Gordon in this laboratory, was 812.33 and 836.25 kcal/mole (see Appendix D). Therefore, the dissociation of cyclobutadiene to acetylene was endothermic by 33.43 and 57.35 kcal/mole. There was some question as to whether or not molecules having bonds with dissociation energies of between 30 and 60 kcal/mole would survive at the conditions of the pyrolysis ( $380^{\circ}$ ). This problem was not investigated in this work.

The formation of 1,3-butadiene had been noted in several cases in an attempt

to prepare cyclobutadiene by pyrolytic reactions.<sup>8</sup> It was suggested that, in all of these reactions, cyclobutadiene was formed and underwent subsequent hydrogen abstraction to form cyclobutene, and that the latter underwent thermal cleavage to produce butadiene. However, this interpretation seemed to assume a greater instability for cyclobutene than was actually the case. If cyclobutadiene had been formed, then it certainly would have been observed in this thesis, since the pyrolysis products were quenched immediately.

#### Ionization Potential of Cyclobutadiene

The measured ionization potential (IP) of  $C_4H_4$  in the pyrolysis of CIT at  $380^{\circ}$  without quenching was between 9.3 and 9.4 eV. As shown in Fig. 7, the measured IP of  $C_4H_4$  was 9.36 eV with water as a standard. This 9.36 eV is in good agreement with the 9.33 eV value using toluene as a calibration gas as shown in Fig. 8. However, in the pyrolysis and quenching experiment of CIT, the IP of the quenched  $C_4H_4$  was found to be between 9.5 and 9.6 eV.

The theoretical values of the IP of butatriene and vinylacetylene calculated by a semiempirical SCF approach using Dewar and Klopman methods were 0.2 to 0.3 eV lower than the experimental values (Table 7). The electron impact method for obtaining these experimental values had been found to give results which were usually about 0.1 to 0.5 eV higher than the values obtained from photoelectron spectroscopy or photoionization methods. When this difference was considered, the agreement was improved between the theoretical and measured values. Therefore, the theoretical electron impact IP of cyclobutadiene should have been 9.0 to 9.1 eV which was in close agreement with the measured value, 9.3 to 9.4 eV.

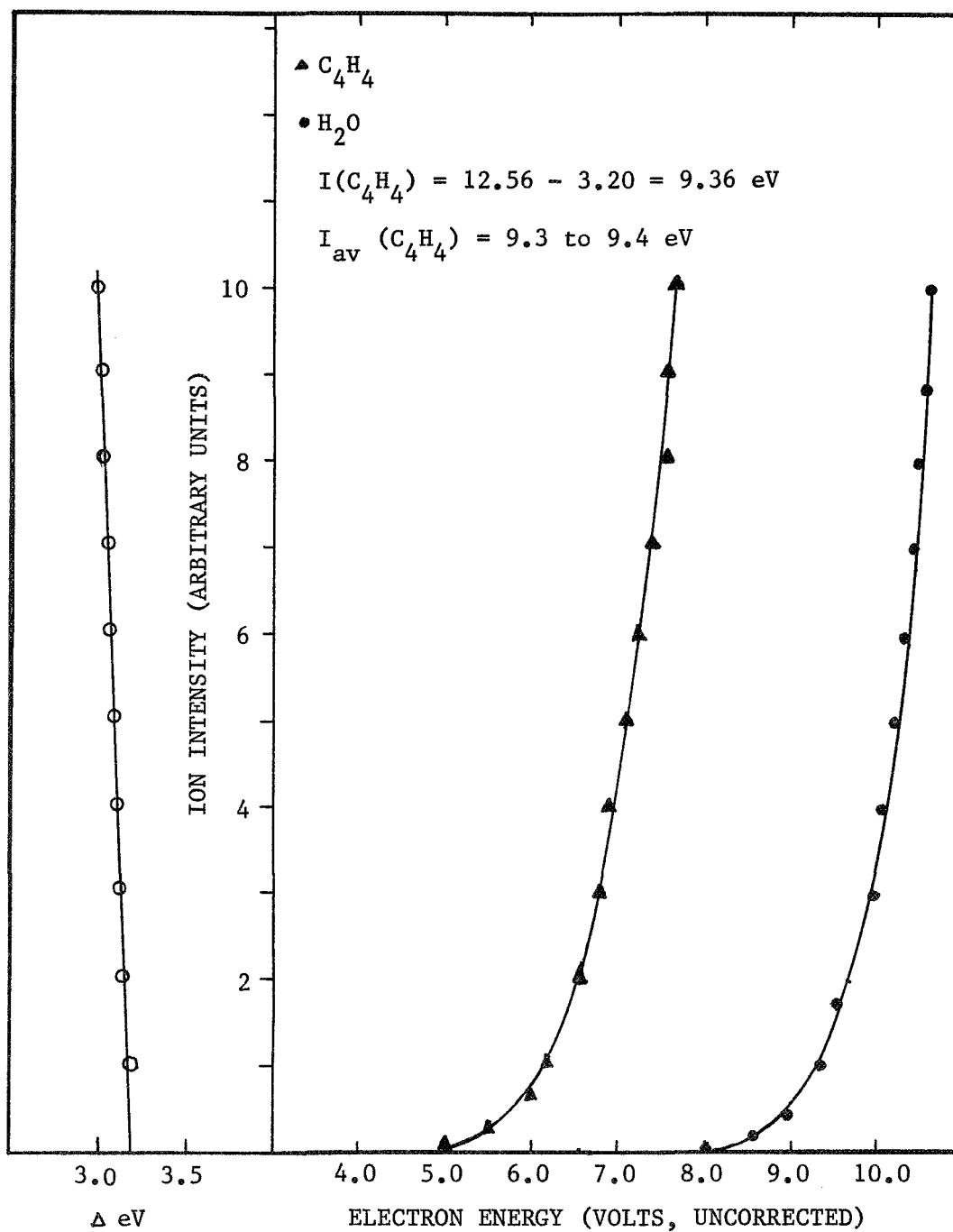


Figure 7. Ionization Efficiency Data for  $C_4H_4$  from the Pyrolysis of CIT at  $380^\circ$  (1).

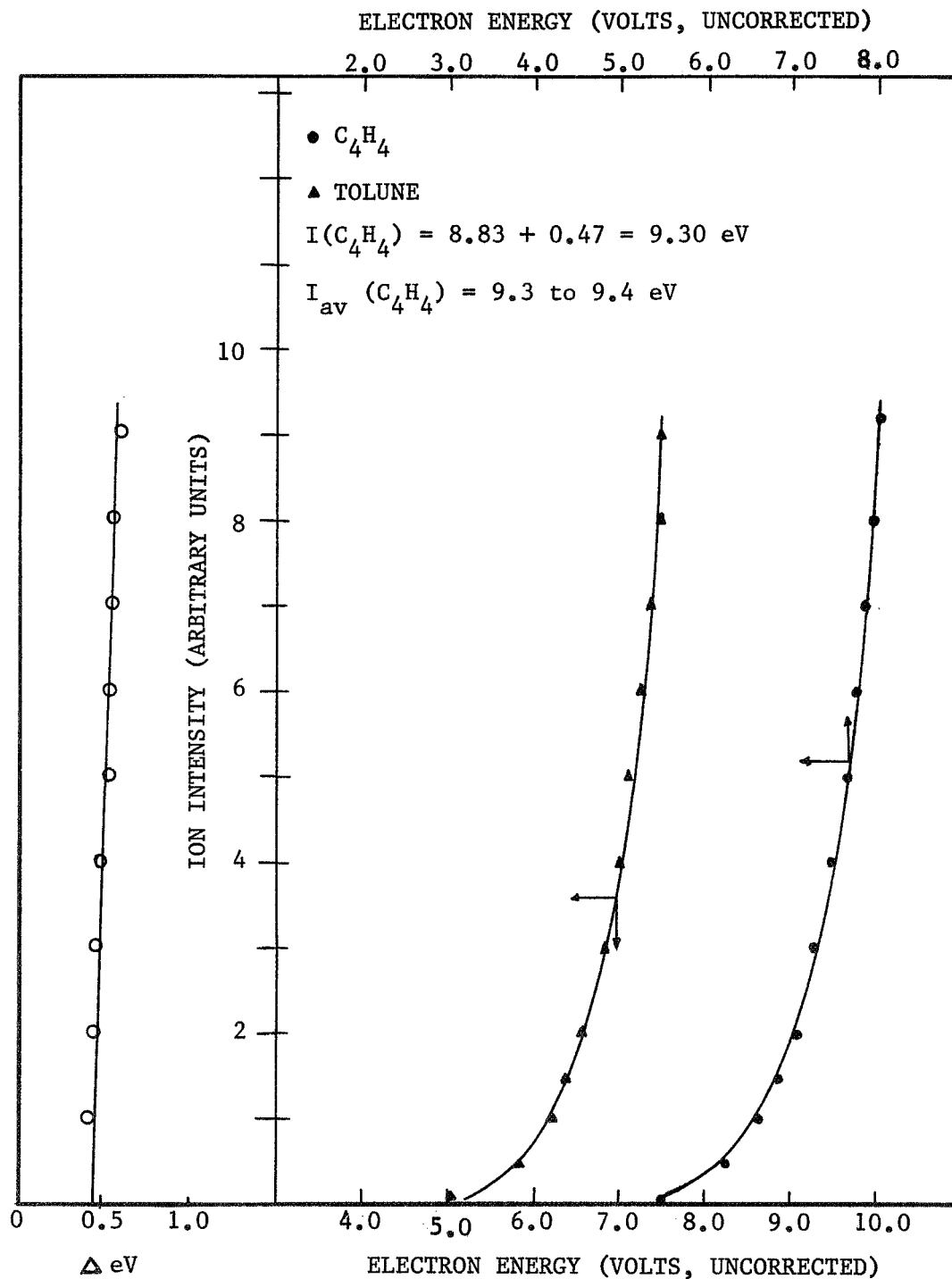


Figure 8. Ionization Efficiency Data for C<sub>4</sub>H<sub>4</sub> from the Pyrolysis of CIT at 380<sup>o</sup> (II).

Cyclobutadiene and vinylacetylene were the products of the pyrolysis of CIT. In the measurement of the IP, the ionization efficiency curve in the range of 2 to 4 eV was usually needed to obtain a value. The difference in theoretical IP of cyclobutadiene and vinylacetylene was less than 1 eV. The ionization efficiency curve of this  $C_4H_4$  mixture was not only contributed by cyclobutadiene but also by vinylacetylene. Therefore, the measured IP of the  $C_4H_4$  was somewhat between that of cyclobutadiene and vinylacetylene depending upon the quantity and ion cross-section of these molecules. If the theoretical electron impact IP of cyclobutadiene were correct, the presence of vinylacetylene could explain the higher measured IP of  $C_4H_4$  (9.3 to 9.4 eV) in the coaxial inlet system at  $380^\circ$  without quenching. The IP of the quenched  $C_4H_4$  measured in the cryogenic inlet system at  $-100^\circ$  was higher than the value measured in the coaxial inlet system because the percentage of cyclobutadiene in the  $C_4H_4$  mixture in the coaxial inlet system was higher. This was a reasonable assumption since, during the quenching process, some cyclobutadiene did not survive.

The only other value of the measured IP of cyclobutadiene was 8.2 to 8.6 eV which was also determined by the electron impact method. This cyclobutadiene had been produced by the pyrolysis of photo- $\alpha$ -pyrone at  $800^\circ$ . From reaction with other compounds, this cyclobutadiene seemed to have a triplet character as discussed in Chapter I. The theoretical IP of triplet cyclobutadiene was calculated by Gordon to be 8.43 eV (Table 7). The close agreement of the theoretical and observed IP provided further evidence that cyclobutadiene produced in the pyrolysis of photo- $\alpha$ -pyrone was a triplet. By the same argument, the higher ionization



Table 7. Ionization Potential and Heat of Formation

of C<sub>4</sub>H<sub>4</sub> Isomers

<u>Compound</u>	<u>IONIZATION POTENTIAL, eV</u>			
	<u>Experimental</u>		<u>Theoretical</u>	
	<u>This Thesis</u>	<u>Other</u>	<u>Klopman<sup>a</sup></u>	<u>MINDO<sup>a</sup></u>
Cyclobutadiene, Singlet	9.3-9.4		8.83	8.56
Cyclobutadiene, Triplet		8.2-8.6 <sup>b</sup>	8.43	
Vinylacetylene	9.8-9.9	9.9 <sup>c</sup>	9.60	
Butatriene	9.2-9.3	9.4 <sup>b</sup>	8.99	9.16
<u>Compound</u>	<u>HEAT OF FORMATION, kcal/mole</u>			
	<u>Experimental</u>		<u>Theoretical</u>	
	<u>Derived in this thesis</u>	<u>Other</u>	<u>Klopman<sup>a</sup></u>	<u>MINDO<sup>a</sup></u>
Cyclobutadiene, Singlet	28.9, 33.5 71.9, 69.6		51.9	79.7
Vinylacetylene		77.3 <sup>d</sup>	32.7	
Butatriene			89.9	83.5

<sup>a</sup> Calculated by L. P. Gordon, Georgia Institute of Technology

<sup>b</sup> E. Hedaya et al., J. Am. Chem. Soc. 91, 1875 (1969)

<sup>c</sup> F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y. (1957) pp. 261

<sup>d</sup> E. I. du Pont de Nemours and Company personal communication

potential observed for the cyclobutadiene produced by the pyrolysis of CIT in this thesis provided further evidence that cyclobutadiene from CIT was a singlet.

#### Derived Heat of Formation of Cyclobutadiene

The derivations of the bond dissociation energies  $D(C_2H_2 - C_2H_2)$  and  $D(C_4H_2 - H_2)$ , and of the heat of formation of cyclobutadiene from the energy measurement on CIT and cis-3,4-dichlorocyclobutene are presented in Appendix C. The measured values required were the ionization potentials of cyclobutadiene, diacetylene and acetylene, and the difference in the appearance potentials of the fragment ions from CIT or from cis-3,4-dichlorocyclobutene. The difference in the appearance potentials of  $C_4H_4^+$  and  $C_2H_2^+$ ,  $[A(C_2H_2^+) - A(C_4H_4^+)]$ , from CIT was measured to be 5.50 eV. This value was in reasonably close agreement with the value of 5.30 eV, the measured  $[A(C_2H_2^+) - A(C_4H_4^+)]$  from cis-3,4-dichlorocyclobutene. From these values, the bond dissociation energy of cyclobutadiene,  $D(C_2H_2 - C_2H_2)$ , was calculated to be 3.45 and 3.25 eV. The heat of formation of cyclobutadiene was then calculated to be 28.9 and 33.5 kcal/mole.

Similarly, the bond dissociation energy of cyclobutadiene,  $D(C_4H_2 - H_2)$ , and the heat of formation of cyclobutadiene were obtained from the measured values of the difference in the appearance potentials of  $C_4H_4^+$  and  $C_4H_2^+$ ,  $[A(C_4H_2^+) - A(C_4H_4^+)]$ , either from CIT or cis-3,4-dichlorocyclobutene. The measured  $[A(C_4H_2^+) - A(C_4H_4^+)]$  from CIT was 2.7 eV and from cis-3,4-dichlorocyclobutene was 2.8 eV. The bond dissociation energy of cyclobutadiene,  $D(C_4H_2 - H_2)$ , was calculated to be 1.85 eV and 1.95 eV. From these values, the heat of formation was calculated to be 71.9 and 69.6 kcal/mole. These values are much different

from the values derived from the measured  $[A(C_2H_2^+) - A(C_4H_4^+)]$  from CIT and cis-3,4-dichlorocyclobutene.

From the electron impact of CIT or cis-3,4-dichlorocyclobutene, these heats of formation of cyclobutadiene were obtained as a result of several assumptions. In the mass fragments of CIT and cis-3,4-dichlorocyclobutene, the  $C_4H_4^+$  was assumed to be cyclobutadiene ion, the  $C_2H_2^+$  acetylene ion, and  $C_4H_2^+$  diacetylene ion. The excess energy in the measurement of the appearance potential was also assumed to be zero. These assumptions could have contributed to the large discrepancy in the values of the heat of formation of cyclobutadiene.

The heats of atomization of cyclobutadiene obtained from theoretical calculations are listed in Table 14 in Appendix C. From the conversion of the heats of atomization, the theoretical heats of formation of cyclobutadiene were obtained and were listed in Table 7. The theoretical heats of formation of cyclobutadiene (51.9 and 79.7 kcal/mole) were close to the derived heats of formation, 71.6 and 69.6 kcal/mole, obtained from the measured  $[A(C_4H_2^+) - A(C_4H_4^+)]$ .

## CHAPTER IV

## CONCLUSIONS AND RECOMMENDATIONS

The work described in the preceding chapters has led to the following conclusions:

(1) The failure to isolate cyclobutadiene in the reaction of CIT with ceric ion at  $0^{\circ}$  and the subsequent discovery that, in the injector of the gas chromatograph, cyclobutadiene was produced from CIT and reacted immediately with a dienophile, strongly suggested that cyclobutadiene was not actually isolated from the reaction of CIT with ceric ion at  $0^{\circ}$  in the previous report.<sup>19</sup>

(2) Radio frequency discharge of cis-3,4-dichlorocyclobutene could not be utilized to produce cyclobutadiene; rather, vinylacetylene, an isomer of cyclobutadiene, was produced along with HCl,  $C_2H_2$ ,  $C_2HCl$ ,  $C_4H_2$ ,  $C_4H_3Cl$ , and  $C_2H_2Cl_2$ .

(3) Cyclobutadiene could be produced and directly observed in the pyrolysis of CIT at temperatures of  $350^{\circ}$  to  $400^{\circ}$  at low pressures. The products of the pyrolysis included carbon monoxide, acetylene, 1,3-butadiene, benzene, cyclobutadiene and cyclobutadiene dimer.

(4) Cyclobutadiene, produced in the copyrolysis of CIT with dienophiles at  $350^{\circ}$  to  $400^{\circ}$ , reacted immediately with the dienophiles in a way similar to that of cyclobutadiene produced by other earlier methods.

(5) The formation of furan instead of 2-butene 1,4-dione in the reaction of cyclobutadiene and oxygen, the absence of reaction between cyclobutadiene and free

radicals, and a measured ionization potential of cyclobutadiene higher than that of a cyclobutadiene which seemed to have a triplet character<sup>22</sup>, all strongly suggest that singlet cyclobutadiene was produced from the pyrolysis of CIT.

(6) The formation of benzene and vinylacetylene in the pyrolysis of CIT did not arise from the further high temperature reaction of the initial product acetylene suggesting that benzene was formed from the reaction of cyclobutadiene and acetylene.

(7) The ionization potential of cyclobutadiene was measured to be between 9.3 and 9.4 eV. Heats of formation of cyclobutadiene were calculated to be 28.9, 33.5, 71.9 and 69.6 kcal/mole depending upon the method used. The considerable difference among these results may be interpreted as arising from difficulties inherent in the electron impact method of energy determination.

(8) In the pyrolysis of CIT followed by a rapid quench, the evidence strongly suggested that cyclobutadiene was quenched. However, the presence of vinylacetylene in the quenched composite prevented a definite conclusion.

Several extensions of the present work may be proposed.

(1) In this thesis, comparisons of mass spectra, ionization potentials, and temperatures of appearance of the mass spectra were used to support the postulated existence of cyclobutadiene at low temperatures. These methods showed defect when vinylacetylene, an isomer of cyclobutadiene, was also present. Low temperature spectroscopic methods, such as nmr, infrared, or uv could provide more positive results.

(2) The nature of the ground state of cyclobutadiene is interesting enough

for further investigation. Since cyclobutadiene produced from the pyrolysis of photo- $\alpha$ -pyrone at 800<sup>o</sup> exhibited the triplet character and no isomers of cyclobutadiene were present in that pyrolysis, attempts to quench this cyclobutadiene should be carried out in the cryogenic inlet system. This can be done simply by replacing the Pyrex furnace tube with a quartz tube. Without the presence of matrices, triplet cyclobutadiene diradical should not survive quenching.

(3) Electron paramagnetic resonance spectroscopy would be the best way to investigate the multiplicity of the ground state. After the nature of the ground state of cyclobutadiene is determined, one may better judge the application to cyclobutadiene chemistry of chemical reaction methods applied in carbene chemistry such as with the triplet carbenes which show selectivity reminiscent of that of the typical free radical along with nonsterospecific addition to carbon-carbon double bonds.

(4) If the cyclobutadiene which is produced from the pyrolysis of CIT and rapidly quenched is not found to exist at low temperatures by the above proposed spectroscopic study, the flash photolysis of CIT at -196<sup>o</sup> coupled with use of the cryogenic inlet system is probably the next best step to investigate the possible existence of stable cyclobutadiene at low temperatures.

(5) The direct observation of the isolated substituted cyclobutadiene, such as tetramethylcyclobutadiene and tetraphenylcyclobutadiene, has never been reported. Mass spectroscopic study of the pyrolysis of tetraphenylcyclobutadienepalladium chloride at 185<sup>o</sup> has indicated the existence of tetraphenylcyclobutadiene in the gas phase. Tetraphenylcyclobutadiene was the intermediate in the thermal

decomposition of (4-bromo-1, 2, 3, 4-tetraphenyl-cis, cis-1, 3-butadienyl) dimethyltin bromide at 150<sup>o</sup>. These experiments could be adapted to the cryogenic inlet system to investigate the existence of stable substituted cyclobutadiene at low temperatures.

**APPENDICES**



## APPENDIX A

MASS SPECTRUM AND IONIZATION POTENTIAL OF  
CYCLOBUTADIENEIRONTRICARBONYL

Metal carbonyls and their derivatives have been the subjects of recent mass spectrometric studies<sup>47, 48</sup> to determine molecular formulas, fragmentation mechanisms, ion energetics, and to test theories of mass spectra.

This appendix presents the mass spectrum and ionization potential of CIT for the purpose of comparing with other substituted metal carbonyls.

As listed in Table 8, the typical stepwise losses of carbon monoxide from the parent molecule of these carbonyl compounds was also observed in CIT. Like other metal carbonyls, the parent ion was not the most abundant ion. The  $C_4H_4Fe^+$  ion was the most prevalent ion in  $C_4H_4Fe(CO)_3$  while  $C_5H_4Mo^+$  was the most prevalent ion in  $C_5H_5Mo(CO)_2NO$ .

The intensities of the metal carbonyl ions of the type  $Fe(CO)_x^+$  are also interesting. The  $Fe(CO)^+$  and  $Fe(CO)_2^+$  were found to have a low abundance and there was no  $Fe(CO)_3^+$  in the mass spectrum of either  $C_4H_4Fe(CO)_3$  or  $C_6H_8Fe(CO)_3$ . On the contrary,  $Fe(CO)_3^+$ ,  $Fe(CO)_2^+$  and  $Fe(CO)^+$  were observed in a large abundance in the mass spectrum of  $C_6F_8Fe(CO)_3$ . These differences in the intensities of  $Fe(CO)_x^+$  in the mass spectra of  $C_6H_8Fe(CO)_3$  and  $C_6F_8Fe(CO)_3$  suggested that the hydrocarbon-iron bond was greater than the fluorocarbon-iron bond as was proposed by Winters.<sup>47</sup>

Another point of interest is the presence of metalhydrocarbon ions containing smaller hydrocarbon fragments than the original ligand. For example,  $C_3H_3Mo^+$  was 95% of  $C_5H_5Mo^+$  in the mass spectrum of  $C_5H_5(Mo(CO)_2NO)$  while  $C_2H_2Fe^+$  was 80% of  $C_4H_4Fe^+$  in the mass spectrum of  $C_4H_4Fe(CO)_3$ . The  $C_3H_3Fe^+$  ion was also observed in the mass spectrum of ferrocene.<sup>49</sup>

The ionization potential of CIT was measured to be 8.2-8.3 eV which was close to recent reported value of 8.04 eV by photoelectron spectroscopy.<sup>50</sup> The difference between the results is reasonable since electron impact values usually exceed the photoelectron spectroscopic values.

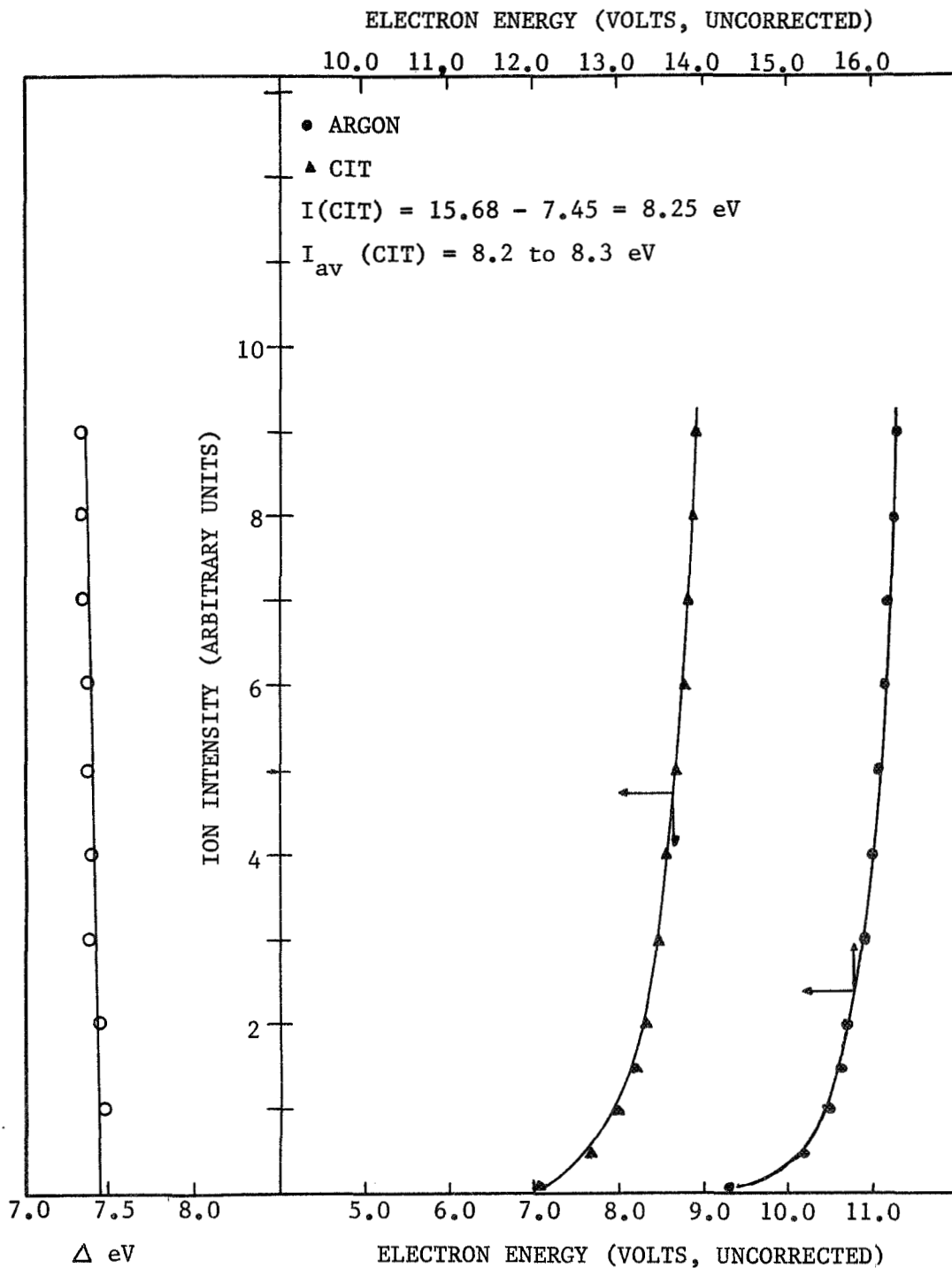


Figure 9. Ionization Efficiency Data for Cyclobutadieneirontricarbonyl.

Table 8. Relative Abundances of the Principal Positive Ions  
from Cyclobutadieneiron Tricarbonyl at 70 eV

<u>m/e</u>	<u>Ion</u>	<u>Relative Abundance</u>
192	$C_4H_4Fe^{56}(CO)_3^+$	34.0
190	$C_4H_4Fe^{54}(CO)_3^+$	3.0
164	$C_4H_4Fe^{56}(CO)_2^+$	25.0
162	$C_4H_4Fe^{54}(CO)_2^+$	3.0
136	$C_4H_4Fe^{56}CO^+$	11.0
134	$C_4H_4Fe^{54}CO^+$	1.0
112	$Fe^{56}(CO)_2^+$	4.0
108	$C_4H_4Fe^{56+}$	100.0
106	$C_4H_4Fe^{54+}$	9.0
84	$Fe^{56}CO^+$	24.0
82	$Fe^{54}CO^+$	81.0
	$Fe^{56}C_2H_2^+$	
81	$Fe^{56}C_2H^+$	19.0

Table 8 (Continued). Relative Abundances of the Principal Positive Ions  
from Cyclobutadieneiron Tricarbonyl at 70 eV

<u>m/e</u>	Ion	<u>Relative Abundance</u>
80	$\text{Fe}^{54}\text{C}_2\text{H}_2^+$	6.0
79	$\text{Fe}^{54}\text{C}_2\text{H}^+$	1.0
68	$\text{FeC}^+$	4.0
57	$\text{Fe}^{57+}$	3.0
56	$\text{Fe}^{56+}$	43.0
54	$\text{Fe}^{54+}$	6.0
52	$\text{C}_4\text{H}_4^+$	2.0
51	$\text{C}_4\text{H}_3^+$	2.0
50	$\text{C}_4\text{H}_2^+$	2.0
26	$\text{C}_2\text{H}_2^+$	2.0

## APPENDIX B

## MISCELLANEOUS SPECTROMETRIC DATA

Mass spectra of several molecules are presented in this appendix. Some of these mass spectra have not been reported previously while others have been found in the literature. The reported mass spectra were usually measured with a magnetic mass spectrometer and the reported values are listed here for comparison with the Time-of-Flight mass spectrometer.

Mass spectra of the products of the rf discharge of cis-3,4-dichlorocyclobutene are shown in Figure 10 through Figure 14. Mass spectra of the products of the copyrolysis of CIT with methyl propiolate and with dimethyl acetylenedicarboxylate are shown in Figure 15 and Figure 16. Mass spectra of the products of the copyrolysis of CIT with oxygen followed by quenching to  $-196^{\circ}$  are shown in Figure 17 and Figure 18. Mass spectra of the products of the pyrolysis of CIT followed by quenching to  $-196^{\circ}$  are shown in Figure 19 through Figure 23.

Ionization efficiency curves for the determination of ionization potentials and appearance potential are shown in Figure 24 to 30.

Several infrared spectra are also included.

Table 9. Mass Spectrum of Furan at  $-105^{\circ}$  at 70 eV from the Copyrolysis  
of Cyclobutadieneirontricarboxyl with Oxygen

<u>m/e</u>	<u>This Research</u>	<u>Literature</u>	
68	64.5	62.1 <sup>a</sup>	71.0 <sup>b</sup>
40	22.0	11.5	13.2
39	100.0	100.0	100.0
38	18.5	16.5	17.9
37	12.0	10.5	11.2
29	15.5	15.8	16.1

<sup>a</sup>CEC Model 21-102, "Selected Mass Spectral Data," API Research Project 44,  
Serial no. 545.

<sup>b</sup>CEC Model 21-102, "Selected Mass Spectral Data," API Research Project 44,  
Serial no. 508.

Table 10. Relative Abundance of the Principal Positive Ions  
from Cyclooctatetraene (C<sub>8</sub>H<sub>8</sub>) at 70 eV

<u>m/e</u>	<u>Ion</u>	<u>Relative Abundance</u>	
		<u>This Research</u>	<u>Literature</u> <sup>a</sup>
104	C <sub>8</sub> H <sub>8</sub> <sup>+</sup>	100.0	100.0
103	C <sub>8</sub> H <sub>7</sub> <sup>+</sup>	62.0	60.9
102	C <sub>8</sub> H <sub>6</sub> <sup>+</sup>	19.0	10.5
78	C <sub>6</sub> H <sub>6</sub> <sup>+</sup>	84.0	82.5
77	C <sub>6</sub> H <sub>5</sub> <sup>+</sup>	31.0	35.0
76	C <sub>6</sub> H <sub>4</sub> <sup>+</sup>	12.0	6.6
75	C <sub>6</sub> H <sub>3</sub> <sup>+</sup>	10.0	5.0
74	C <sub>6</sub> H <sub>2</sub> <sup>+</sup>	16.0	7.60
73	C <sub>6</sub> H <sup>+</sup>	5.0	1.60
65	C <sub>5</sub> H <sub>5</sub> <sup>+</sup>	8.0	3.9
64	C <sub>5</sub> H <sub>4</sub> <sup>+</sup>	5.0	1.5
63	C <sub>5</sub> H <sub>3</sub> <sup>+</sup>	22.0	11.4



Table 10 (Continued). Relative Abundance of the Principal Positive Ions  
from Cyclooctatetraene ( $C_8H_8$ ) at 70 eV

<u>m/e</u>	<u>Ion</u>	<u>Relative Abundance</u>	
		<u>This Research</u>	<u>Literature</u> <sup>a</sup>
62	$C_5H_2^+$	11.0	4.8
61	$C_5H^+$	9.0	2.5
52	$C_4H_4^+$	31.0	21.0
51	$C_4H_3^+$	57.0	45.9
50	$C_4H_2^+$	49.0	27.8
40	$C_4H^+$	8.0	3.7
39	$C_3H_3^+$	50.0	30.8
38	$C_3H_2^+$	23.0	9.3
37	$C_3H^+$	13.0	5.6
27	$C_2H_3^+$	25.0	12.6
26	$C_2H_2^+$	24.0	7.6

<sup>a</sup> Measured with CEC, Model 21-101, "Selected Mass Spectral Data, API  
Research Project 44, Serial No. 690

Table 11. Relative Abundance of the Principal Positive Ions  
from Syn Cyclobutadiene Dimer at 70 eV

<u>m/e</u>	<u>Ion</u>	<u>Relative Abundance</u>
104	$C_8H_8^+$	22.0
103	$C_8H_7^+$	65.0
78	$C_6H_6^+$	100.0
77	$C_6H_5^+$	25.0
52	$C_4H_4^+$	11.0
51	$C_4H_3^+$	65.0
50	$C_4H_2^+$	22.0
39	$C_3H_3^+$	35.0
38	$C_3H_2^+$	10.0
37	$C_3H^+$	7.0

Table 12. Relative Abundances of the Principal Positive Ions  
 from Cis-3,4-dichlorocyclobutene at 70 eV

<u>m/e</u>	<u>Ion</u>	<u>Relative Abundance</u>
126	$C_4H_4Cl_2^{37+}$	5.0
124	$C_4H_4Cl^{37}Cl^{35+}$	21.0
122	$C_4H_4Cl_2^{35+}$	31.0
100	$C_2H_2Cl_2^{37+}$	1.0
98	$C_2H_2Cl^{37}Cl^{35+}$	5.0
96	$C_2H_2Cl_2^{35+}$	6.0
89	$C_4H_4Cl^{37+}$	33.0
88	$C_4H_3Cl^{37+}$	14.0
87	$C_4H_4Cl^{35+}$ , $C_4H_2Cl^{37+}$	88.0
86	$C_4H_3Cl^{35+}$ ,	8.0
85	$C_4H_2Cl^{35+}$	7.0
75	$C_3H_2Cl^{37+}$	3.0
73	$C_3H_2Cl^{35+}$	9.0

Table 12 (Continued). Relative Abundances of the Principal Positive Ions  
from Cis-3,4-dichlorocyclobutene at 70 eV

<u>m/e</u>	<u>Ion</u>	<u>Relative Abundance</u>
64	$C_2H_3Cl^{37+}$	2.0
63	$C_2H_2Cl^{37+}$	6.0
62	$C_2HCl^{37+}$ , $C_2H_3Cl^{35+}$	7.0
61	$C_2H_2Cl^{35+}$	14.0
60	$C_2HCl^{35+}$	7.0
52	$C_4H_4^+$	21.0
51	$C_4H_3^+$	100.0
50	$C_4H_2^+$	43.0
49	$C_4H^+$	16.0
48	$C_4^+$	7.0
39	$C_3H_3^+$	9.0
38	$C_3H_2^+$	10.0

Table 12 (Continued). Relative Abundances of the Principal Positive Ions  
from Cis-3,4-dichlorocyclobutene at 70 eV

---

<u>m/e</u>	<u>Ion</u>	<u>Relative Abundance</u>
37	$\text{Cl}^{37+}, \text{C}_3\text{H}^+$	16.0
36	$\text{C}_3^+$	7.0
35	$\text{Cl}^{35+}$	14.0
26	$\text{C}_2\text{H}_2^+$	36.0
25	$\text{C}_2\text{H}^+$	12.0

---

---

Table 13. Mass Spectrum of the Products at 70 eV from the Copyrolysis  
of CIT with Methyl Propiolate at 380<sup>0</sup>

<u>m/e</u>	<u>Ion</u>	<u>Relative Abundance</u>	
		<u>This Research</u>	<u>Literature<sup>a</sup></u>
136	$C_8H_8O_2^+$	32.0	32.15
105	$C_7H_5O^+$	100.0	100.00
78	$C_6H_6^+$	68.0 <sup>b</sup>	4.95
77	$C_6H_5^+$	83.0	65.45

<sup>a</sup>CEC Model 21-103C, "Selected Mass Spectral Data," API Research Project 44, Serial no. 1752

<sup>b</sup>Due to benzene which is prominent product of CIT pyrolysis

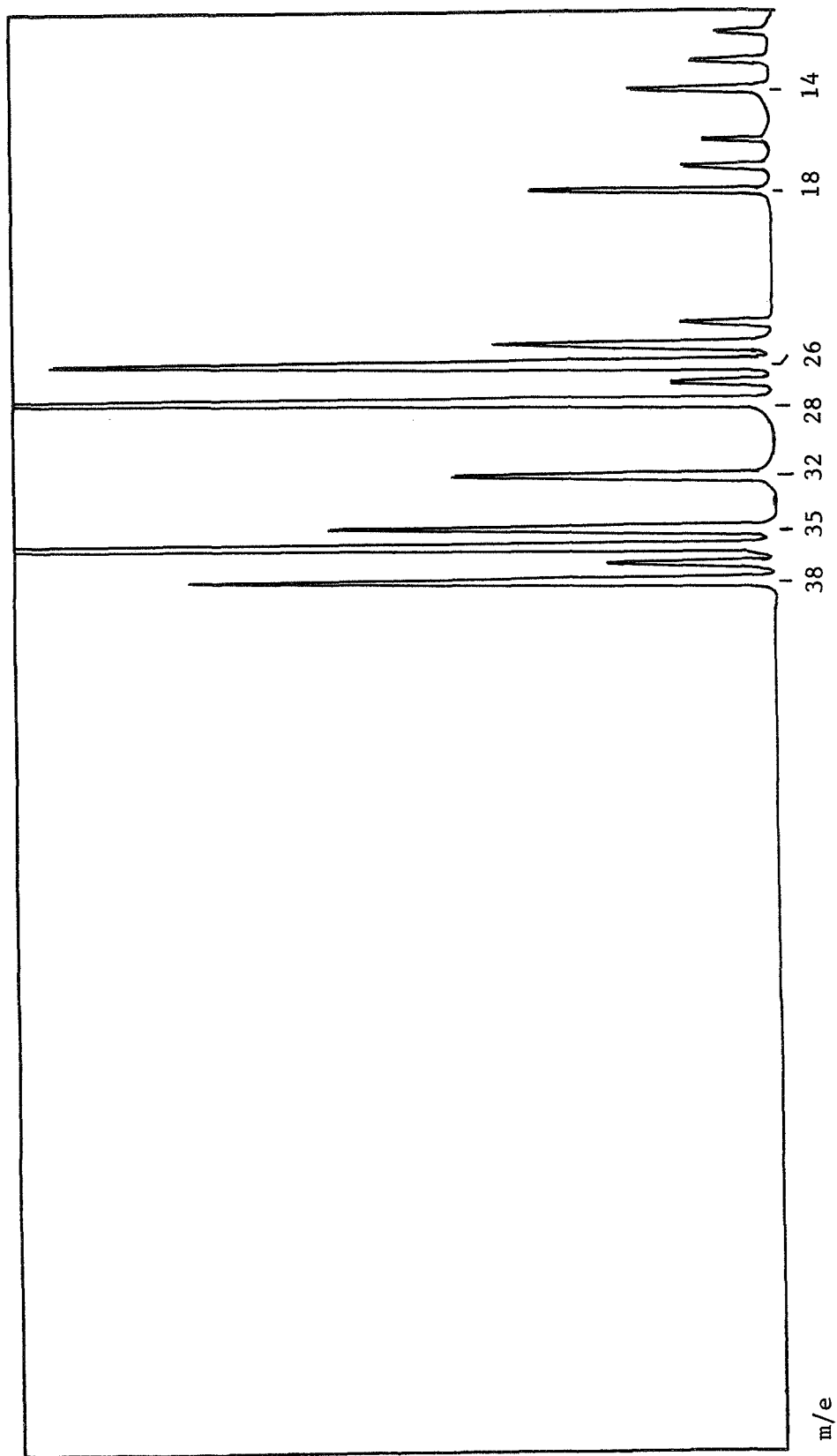


Figure 10. Mass Spectrum of HCl and  $C_2H_2$  at  $-155^\circ$  from the rf Discharge of Cis-3, 4-dichlorocyclobutene Followed by Quenching at  $-196^\circ$ .

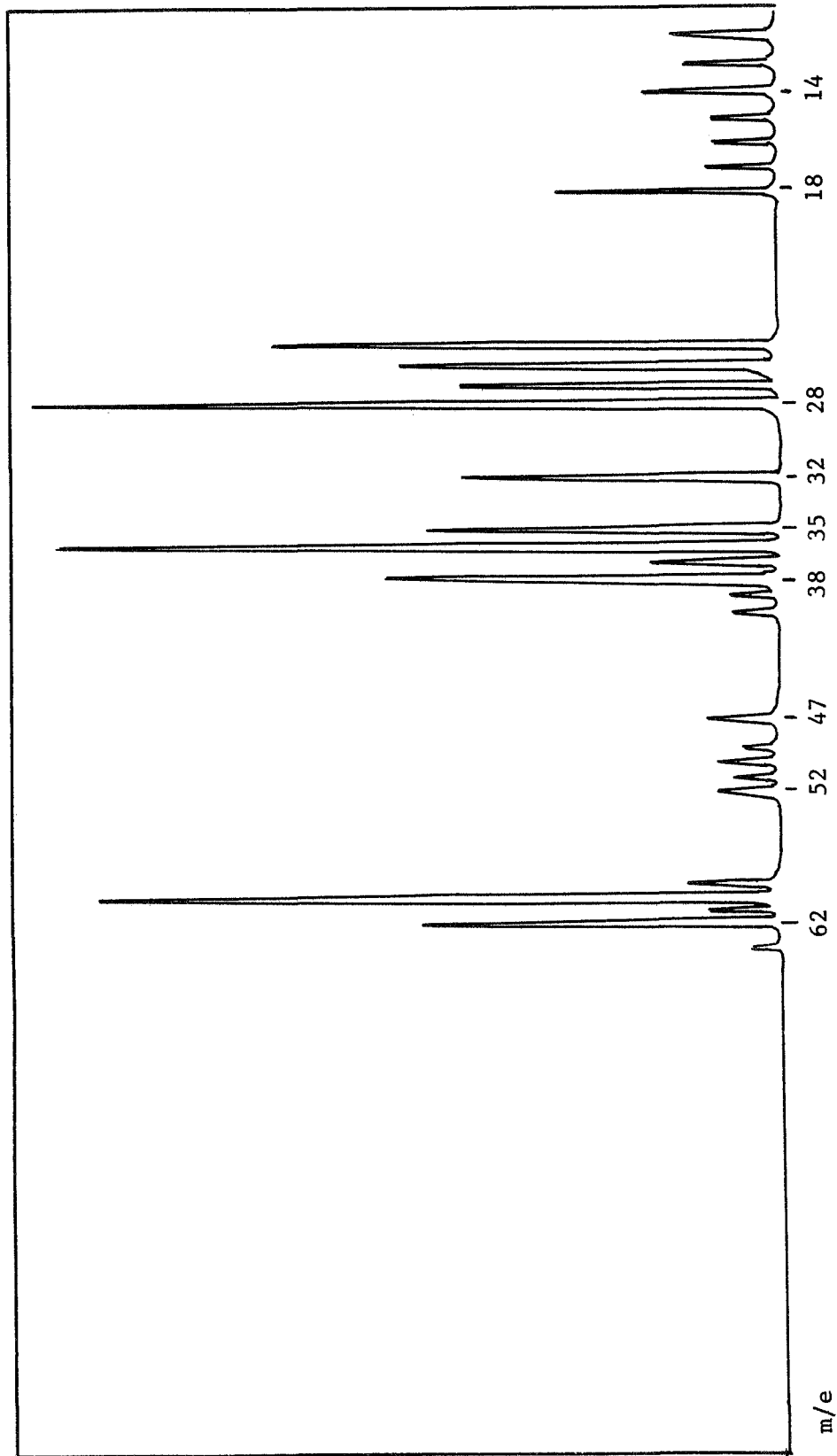


Figure 11. Mass Spectrum of  $C_4H_4$ ,  $C_2H_2Cl$  and  $HCl$  at  $-140^\circ$  from the rf Discharge of Cis-3,4-dichlorocyclobutene Followed by Quenching at  $-196^\circ$ .



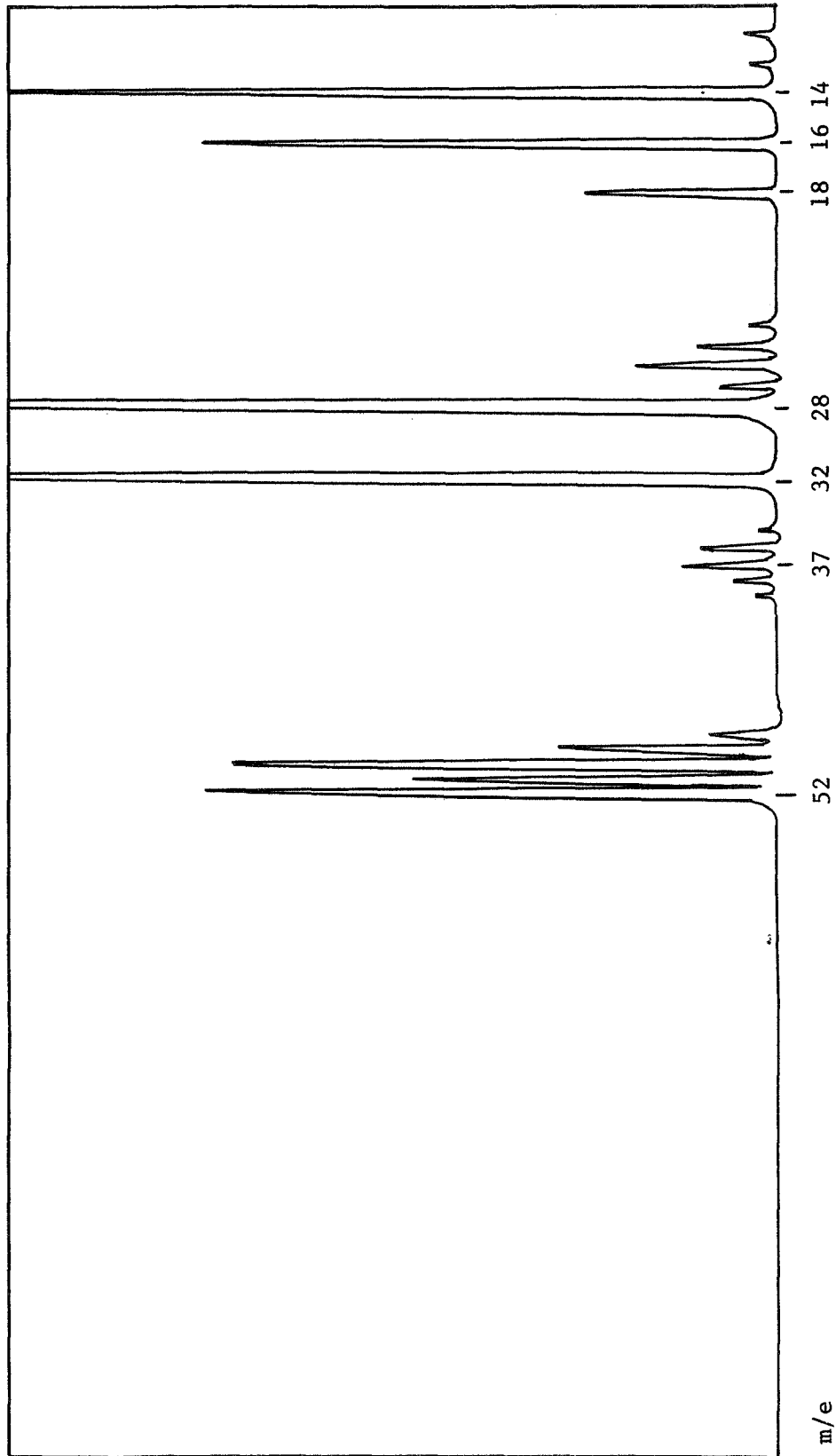


Figure 12. Mass Spectrum of  $C_4H_4$  and  $C_4H_2$  at  $-120^\circ$  from the rf Discharge of

Cis-3,4-dichlorocyclobutene Followed by Quenching at  $-196^\circ$ .

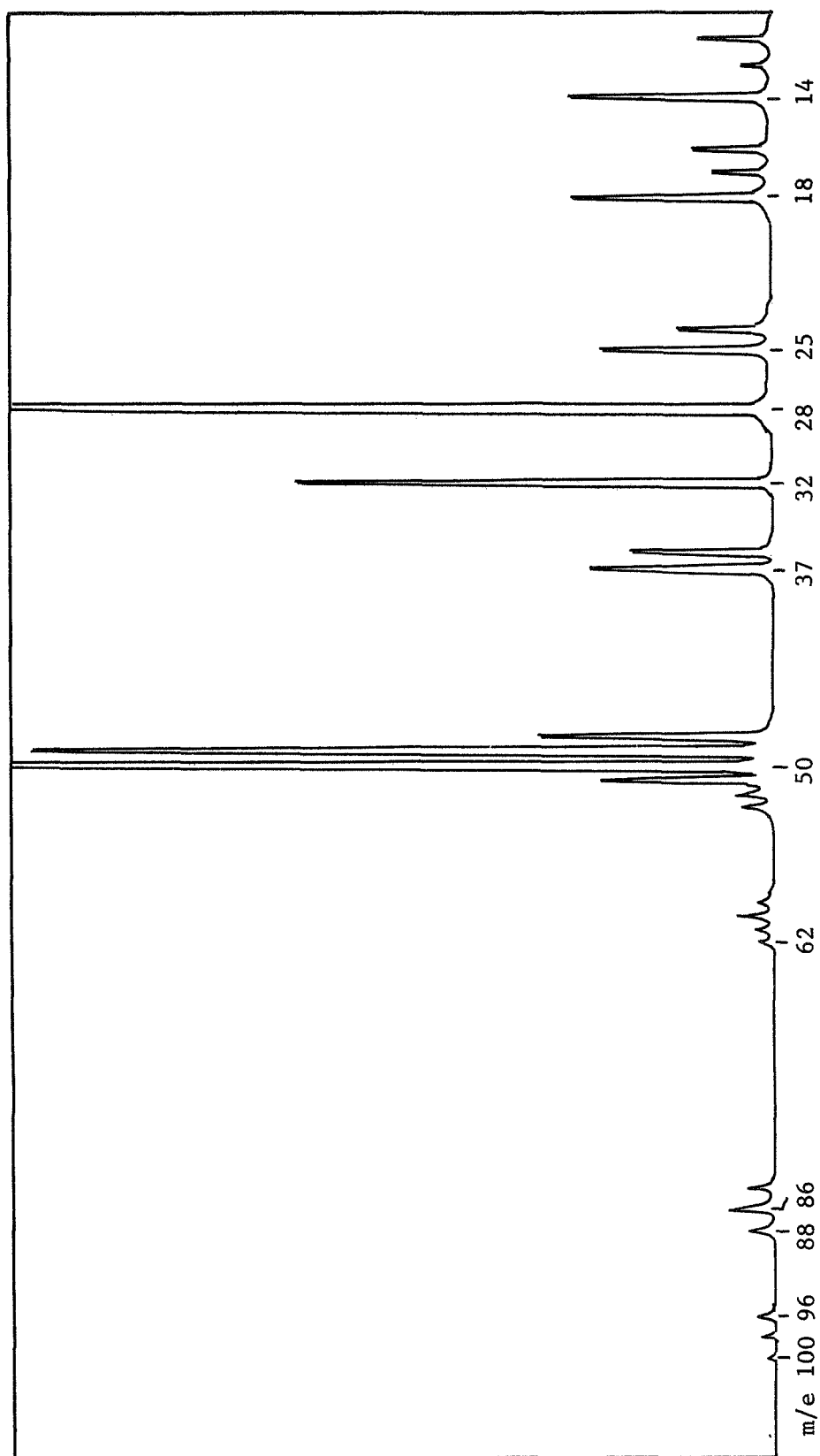


Figure 13. Mass Spectrum of  $C_4H_2$ ,  $C_4H_3Cl$  and  $C_2H_2Cl_2$  at  $-90^\circ$  from the rf Discharge of Cis-3,4-dichlorocyclobutene Followed by Quenching at  $-196^\circ$ .

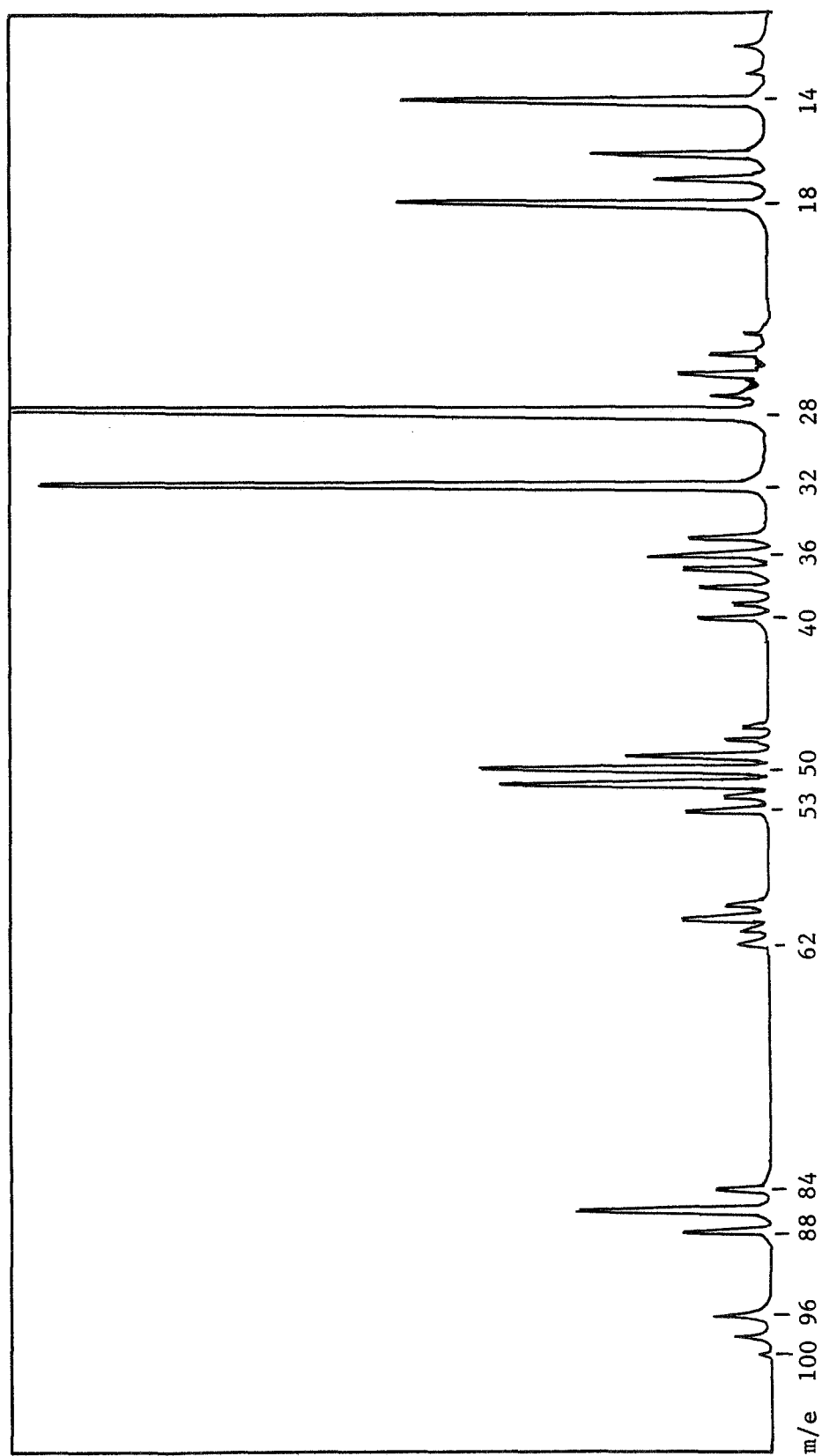


Figure 14. Mass Spectrum of  $C_4H_3Cl$  and  $C_2H_2Cl_2$  at  $-80^\circ$  from the rf Discharge of

Cis-3,4-dichlorocyclobutene Followed by Quenching at  $-196^\circ$ .

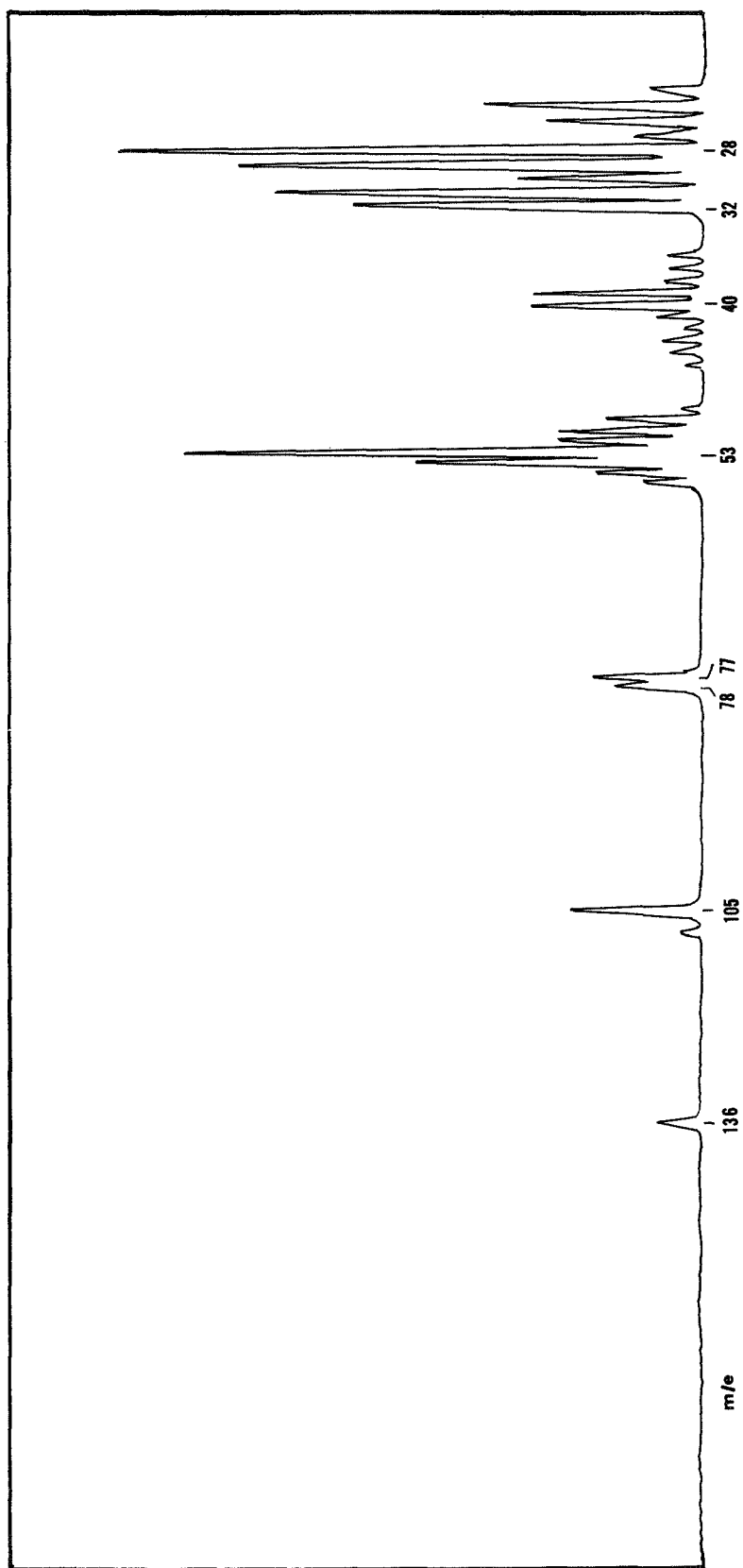


Figure 15. Mass Spectrum of the Products of Copolymerization of CIT  
with Methyl Propiolate at 380°.

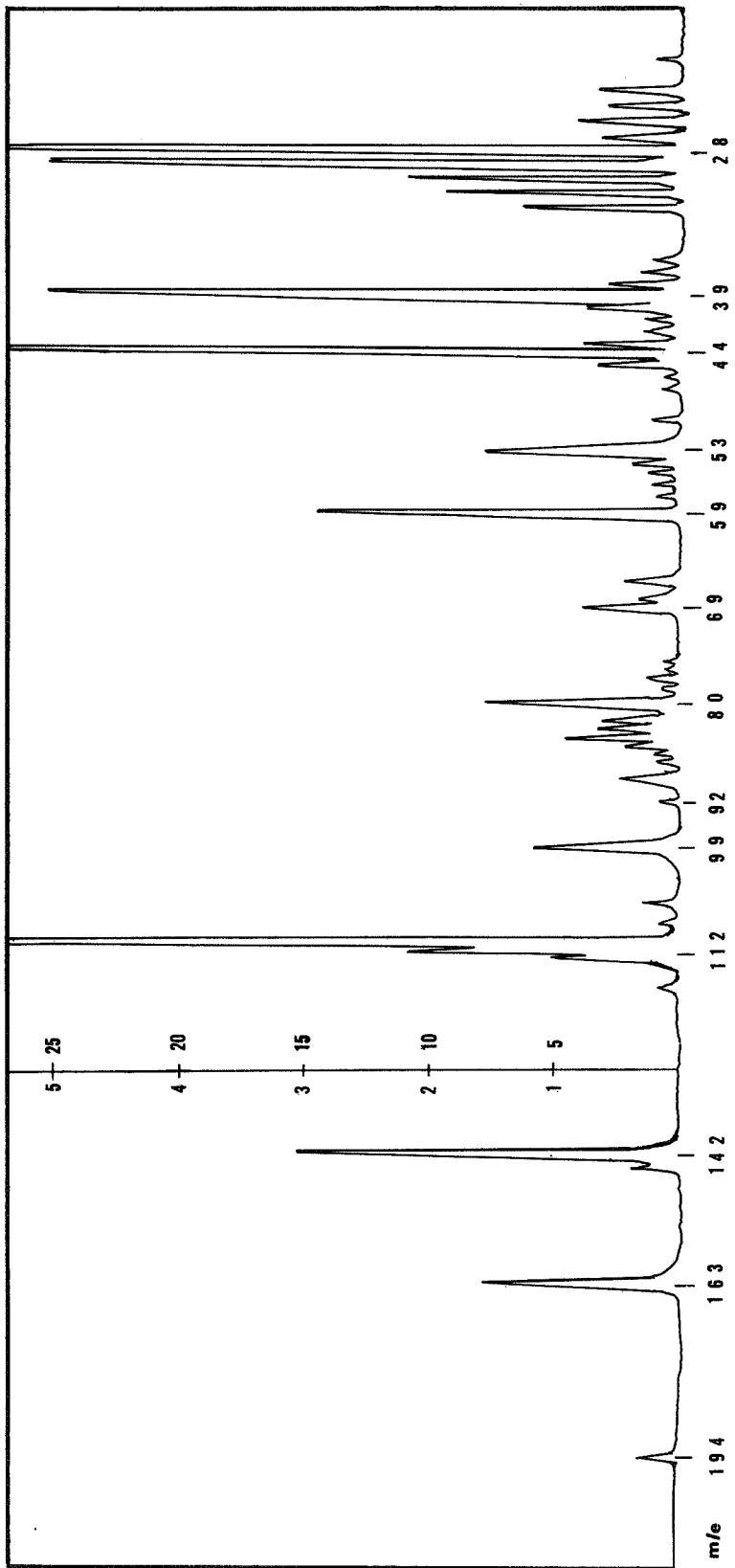


Figure 16. Mass Spectrum of the Products of Copolymerization of CIT with  
Dimethyl Acetylenedicarboxylate at 380°

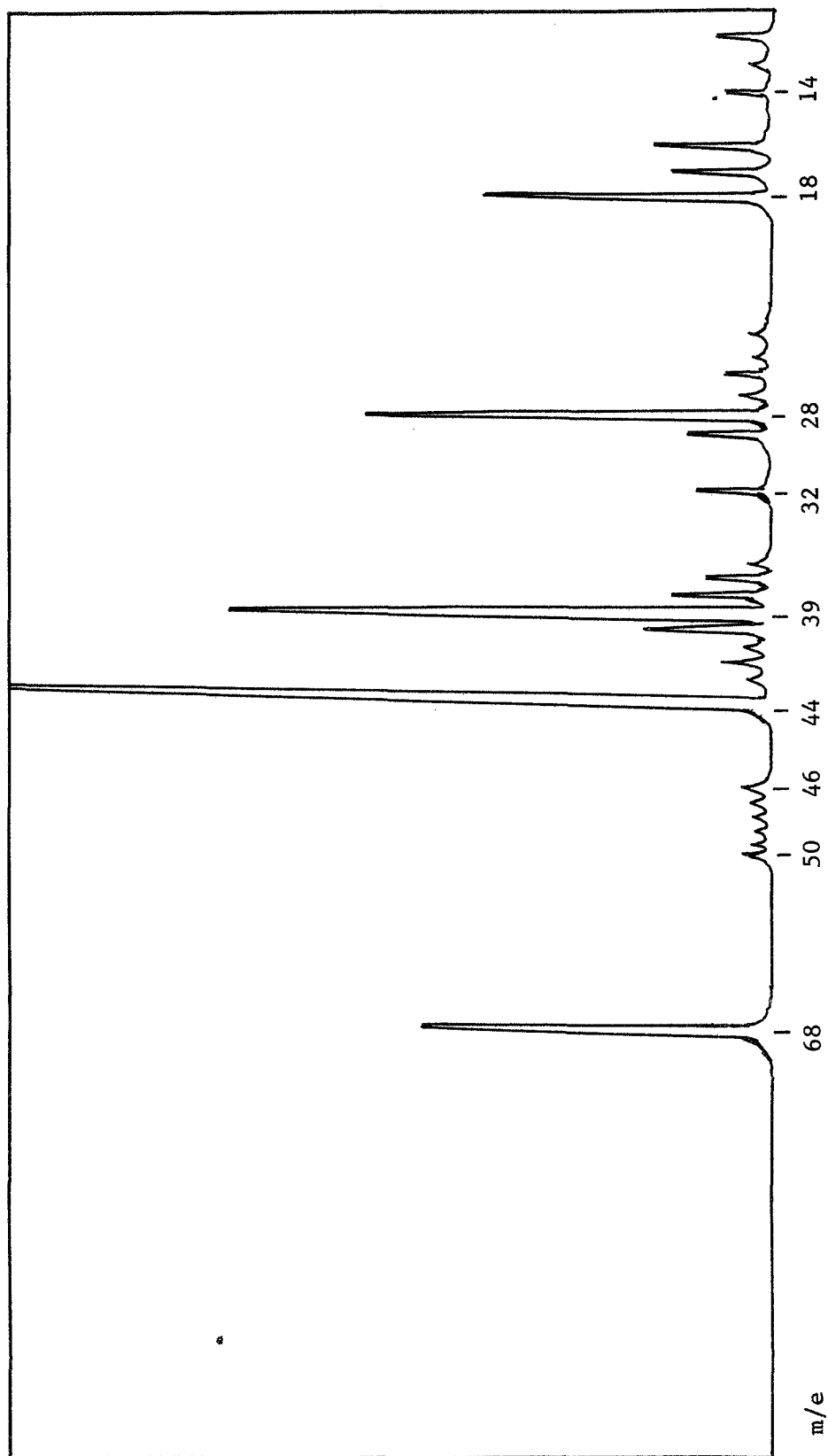


Figure 17. Mass Spectrum of  $C_4H_4O$  at  $-100^\circ$  from the Copolyolysis of CIT with Oxygen Followed by Quenching to  $-196^\circ$ .

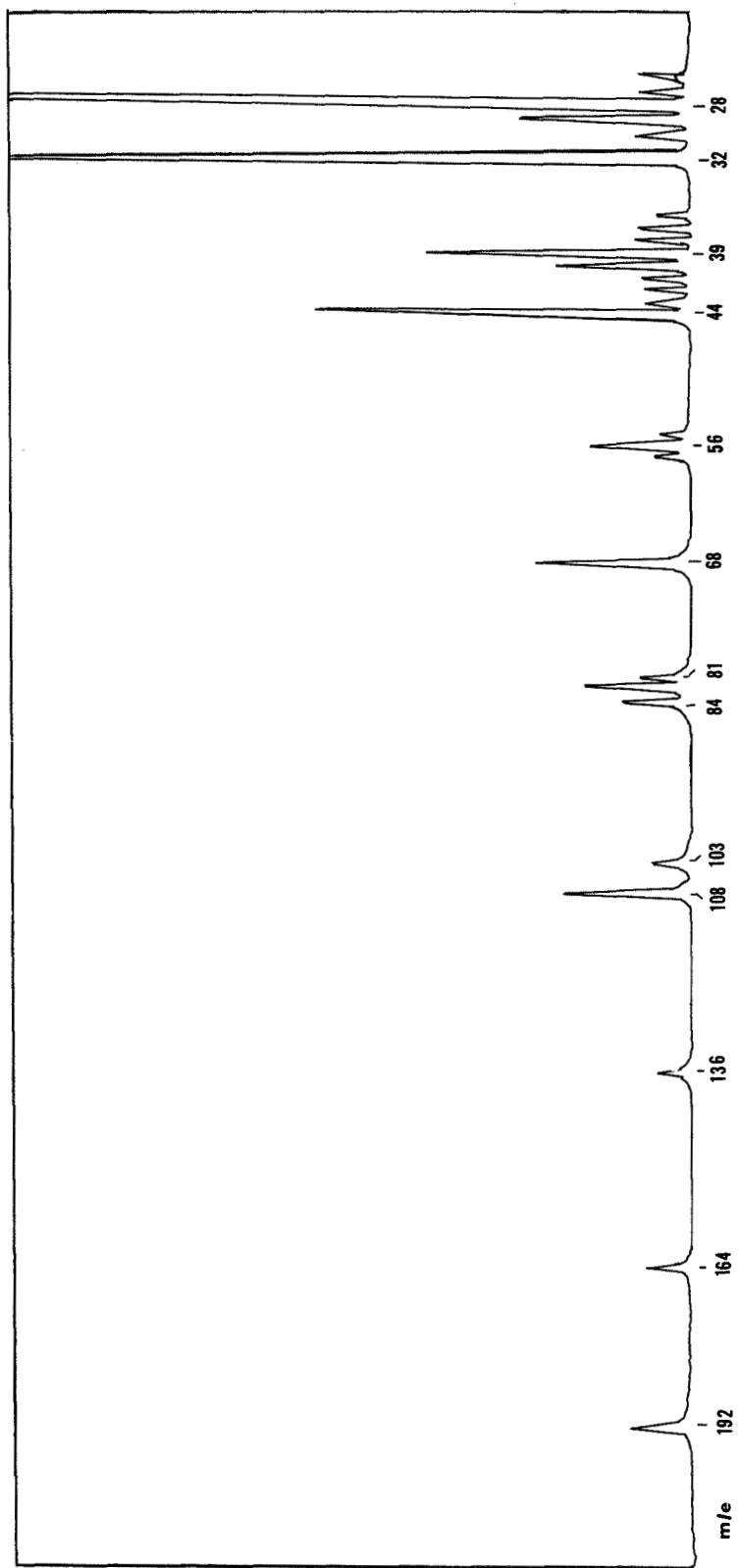


Figure 18. Mass Spectrum of  $C_4H_4O_2$  and Unpyrolyzed CIT at  $-60^\circ$  from the

Copyrolysis of CIT with Oxygen followed by Quenching at  $-196^\circ$ .

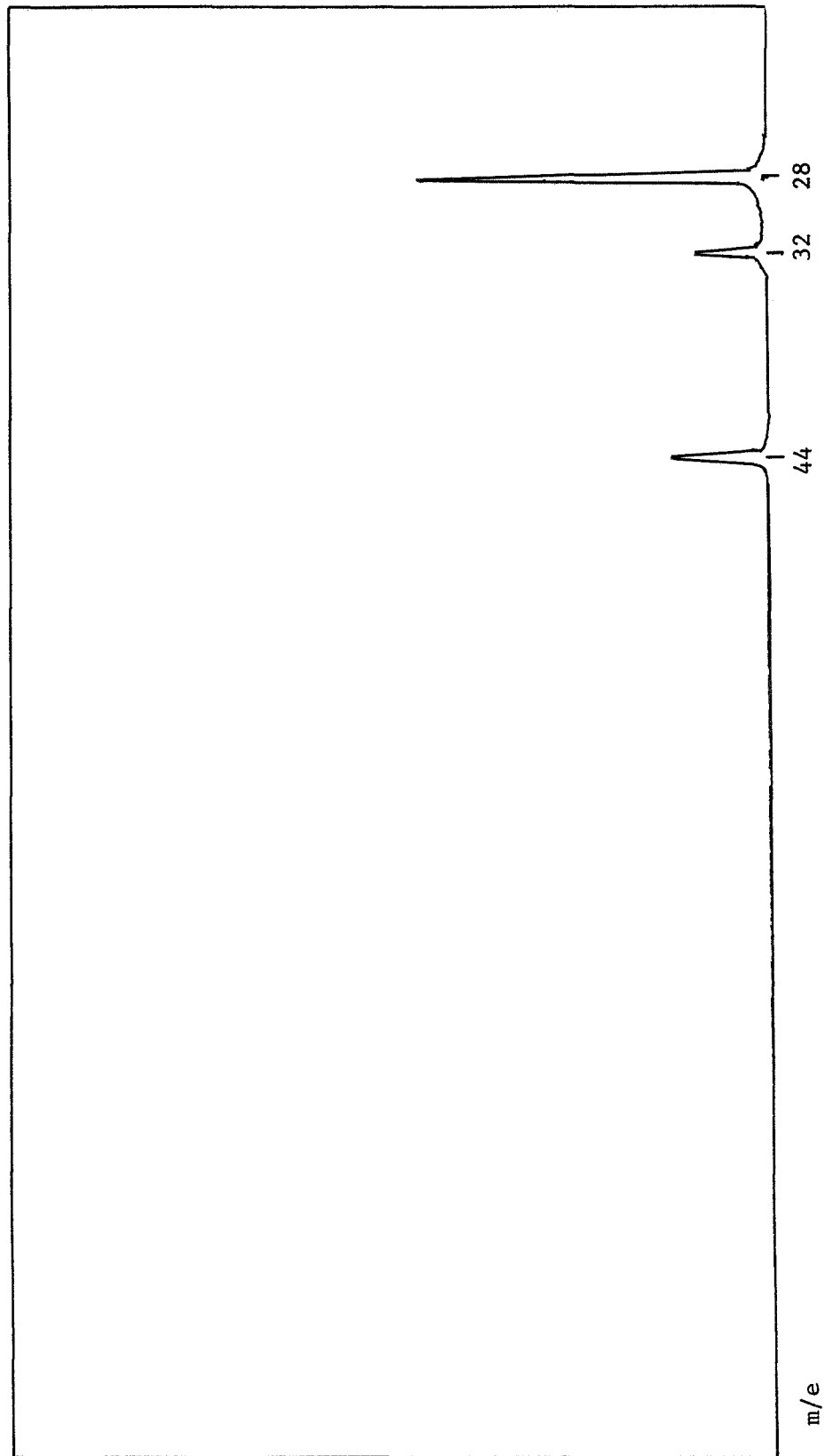


Figure 19. Mass Spectrum of  $\text{CO}_2$  at  $-140^\circ$  from the Pyrolysis of CIT  
Followed by Quenching at  $-196^\circ$ .



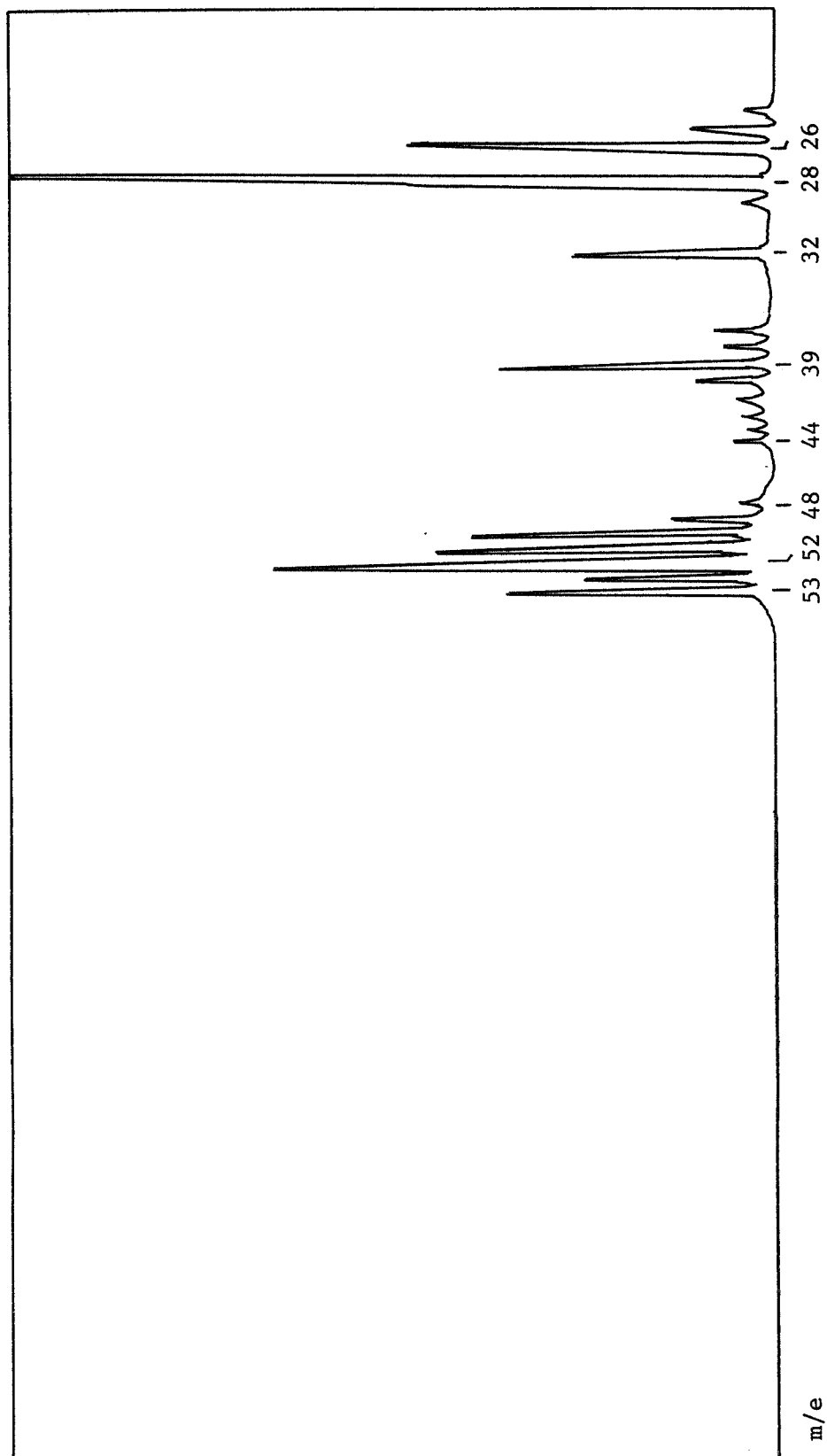


Figure 20. Mass Spectrum of  $C_4H_6$  and  $C_4H_4$  at  $-115^\circ$  from the Pyrolysis of

CIT Followed by Quenching at  $-196^\circ$ .

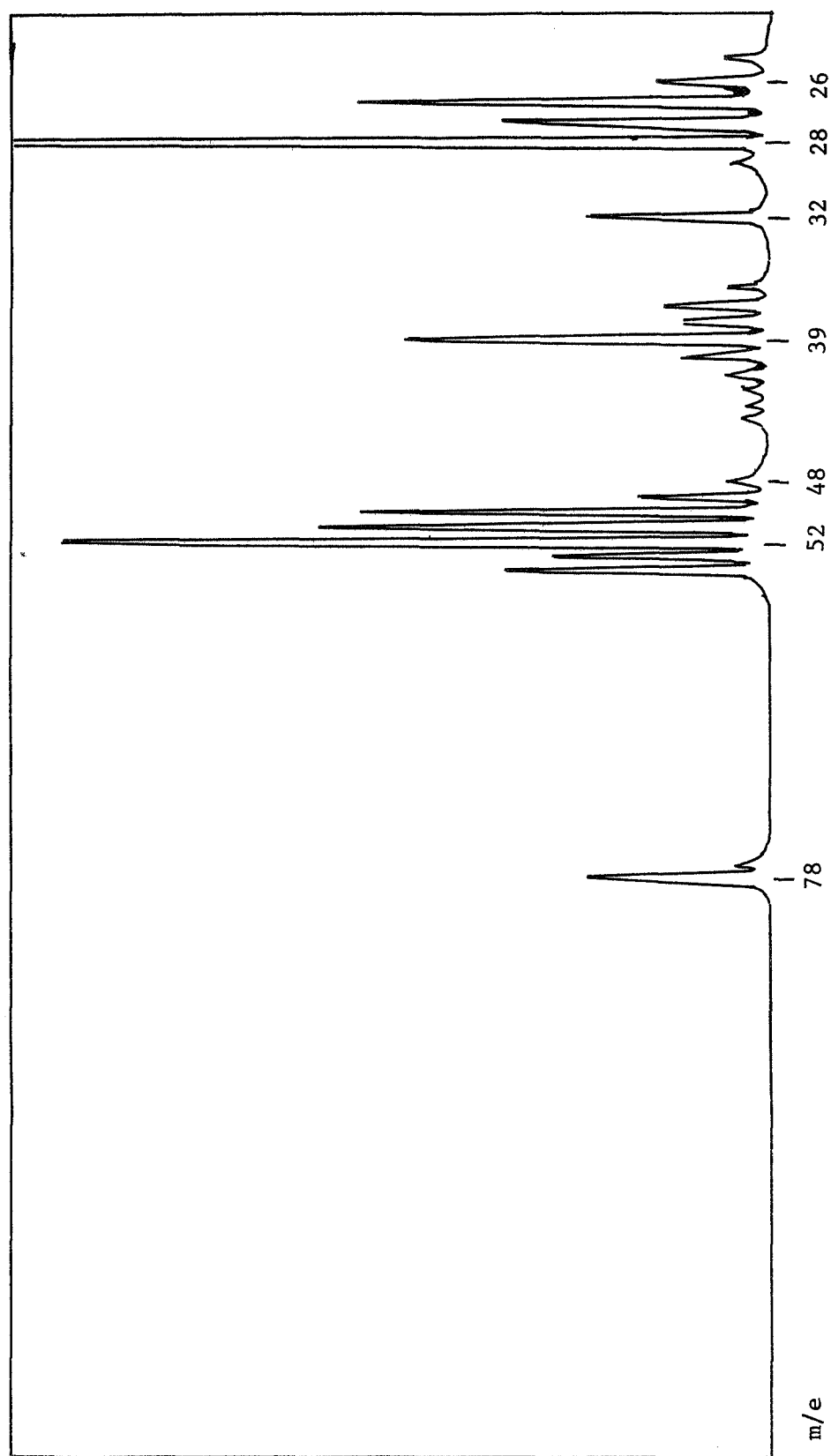


Figure 21. Mass Spectrum of  $C_6H_6$ ,  $C_4H_6$  and  $C_4H_4$  at  $-100^\circ$  from the Pyrolysis of CIT Followed by Quenching at  $-196^\circ$ .

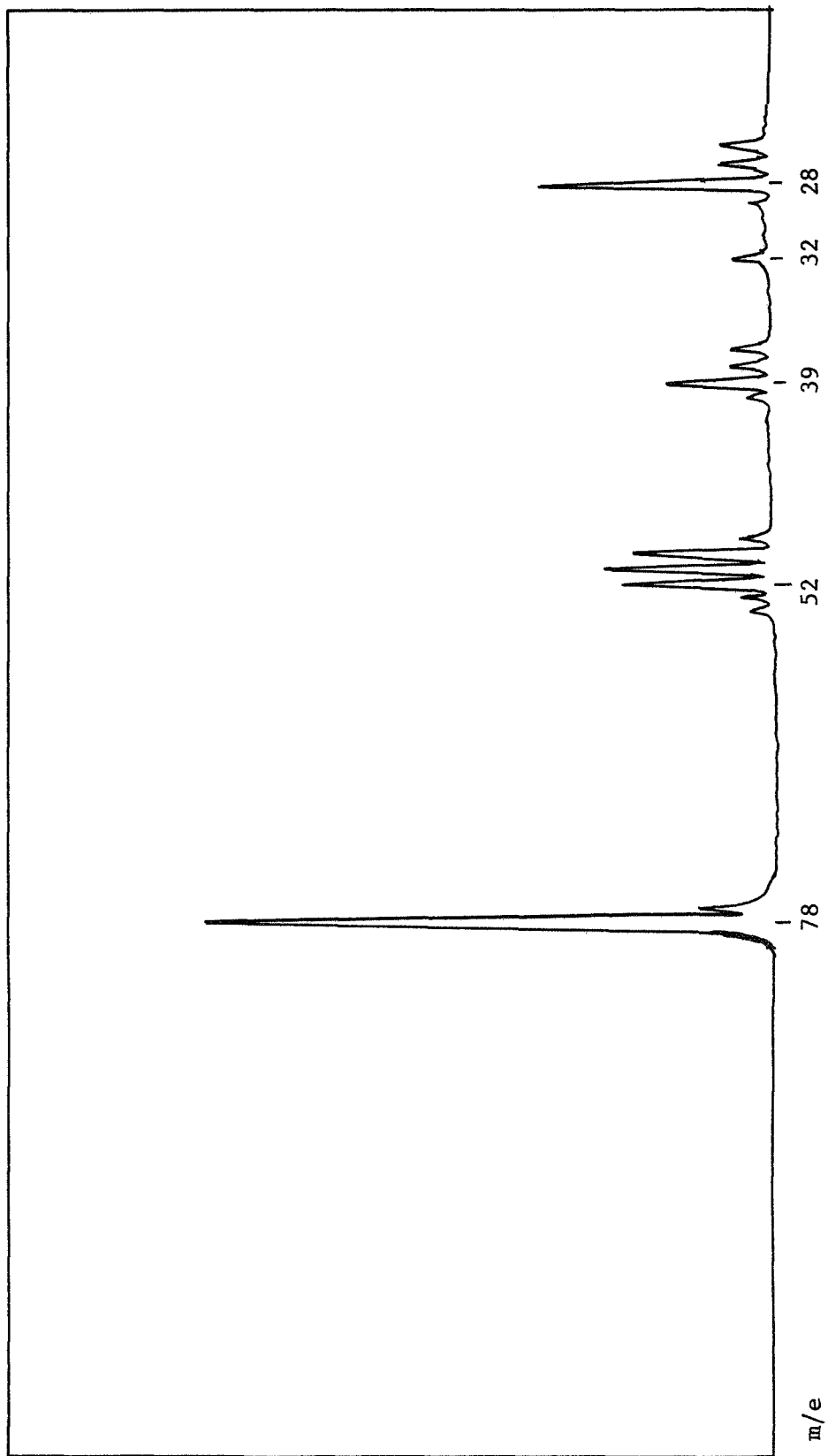


Figure 22. Mass Spectrum of  $C_6H_6$  at  $-90^\circ$  from the Pyrolysis of CIT Followed by Quenching at  $-196^\circ$ .

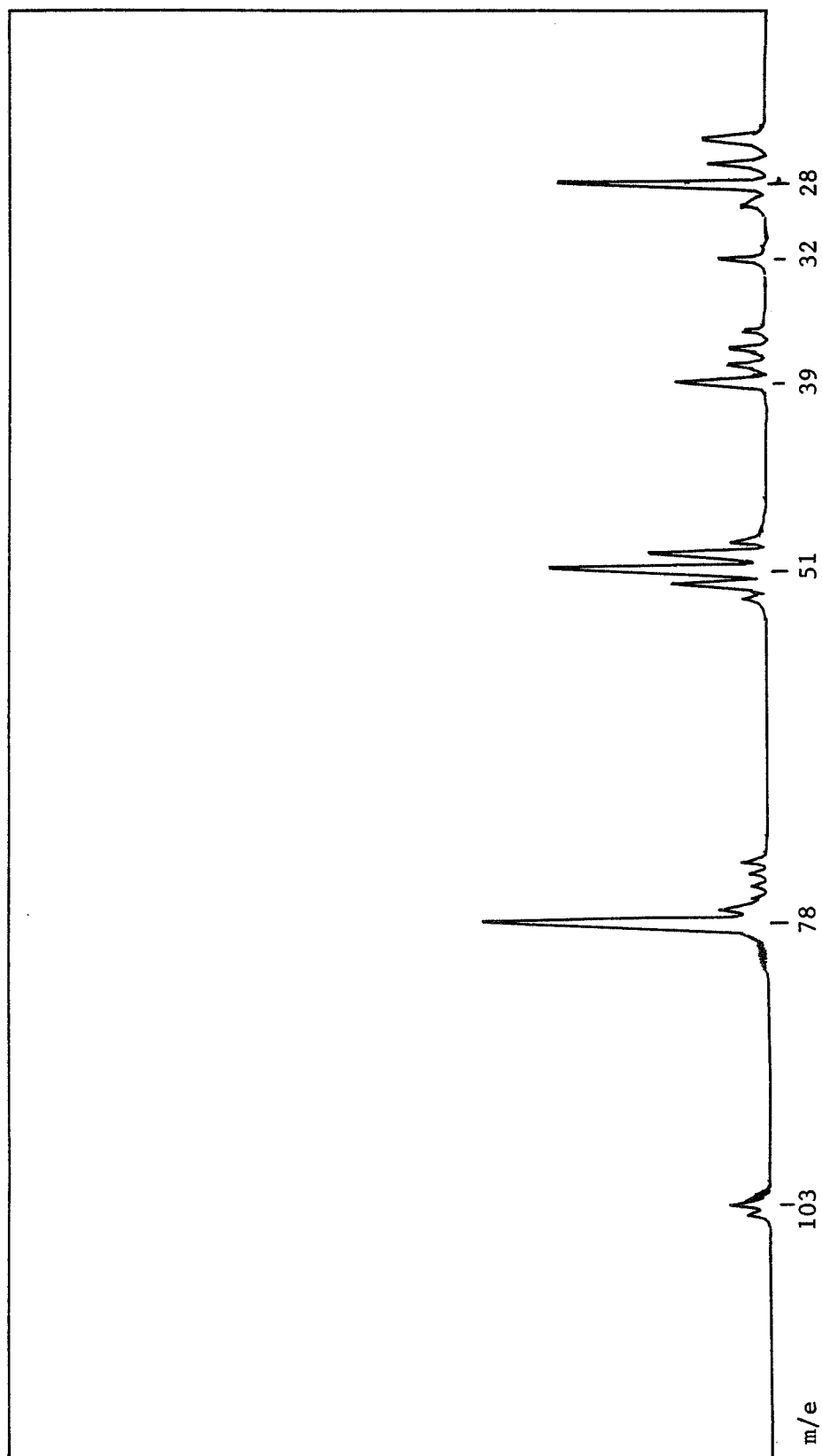


Figure 23. Mass Spectrum of  $C_8H_8$  and  $C_6H_6$  at  $-80^\circ$  from the Pyrolysis of CIT  
Followed by Quenching at  $-196^\circ$ .

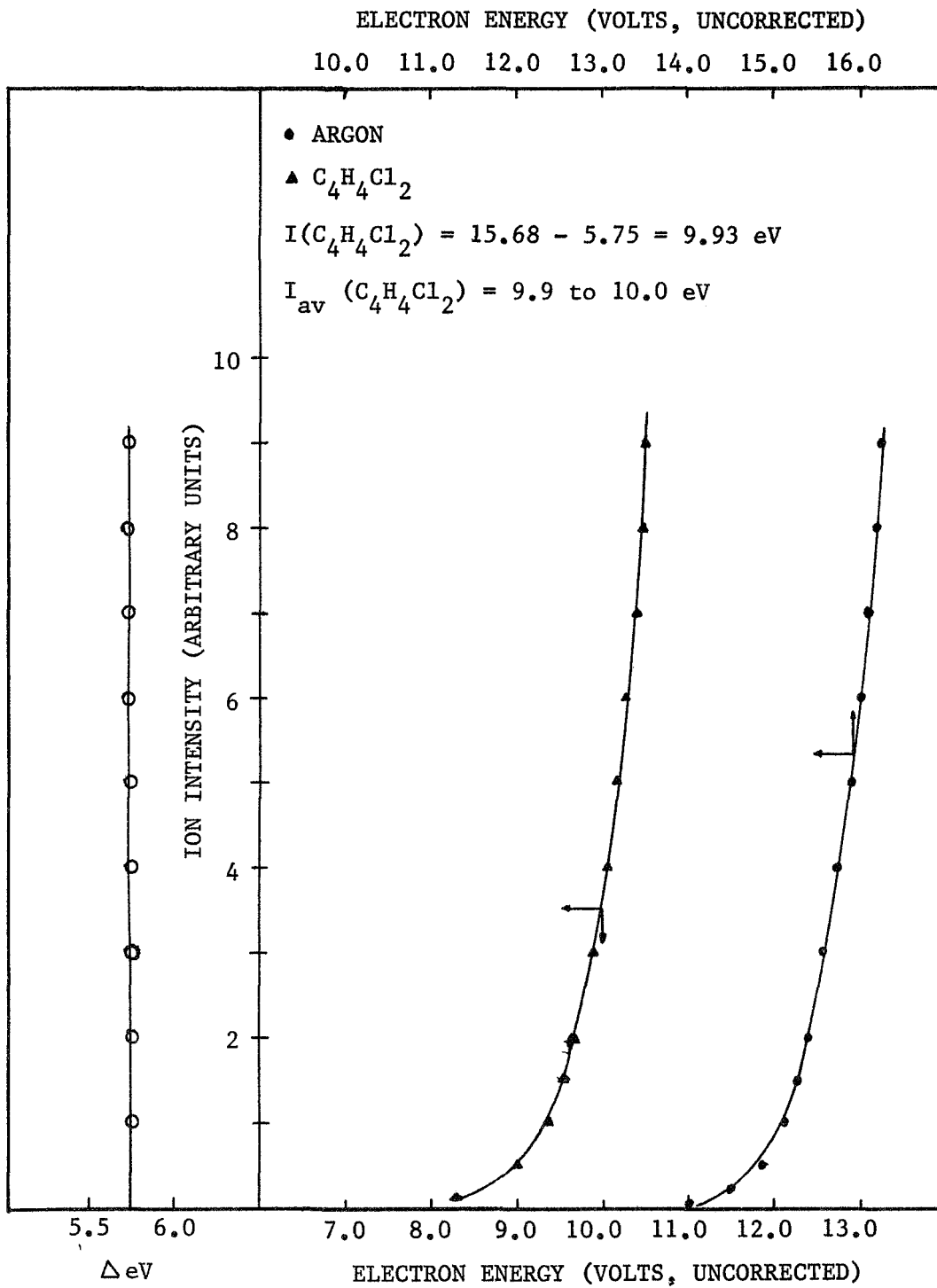


Figure 24. Ionization Efficiency Data for Cis-3,4-dichlorocyclobutene.

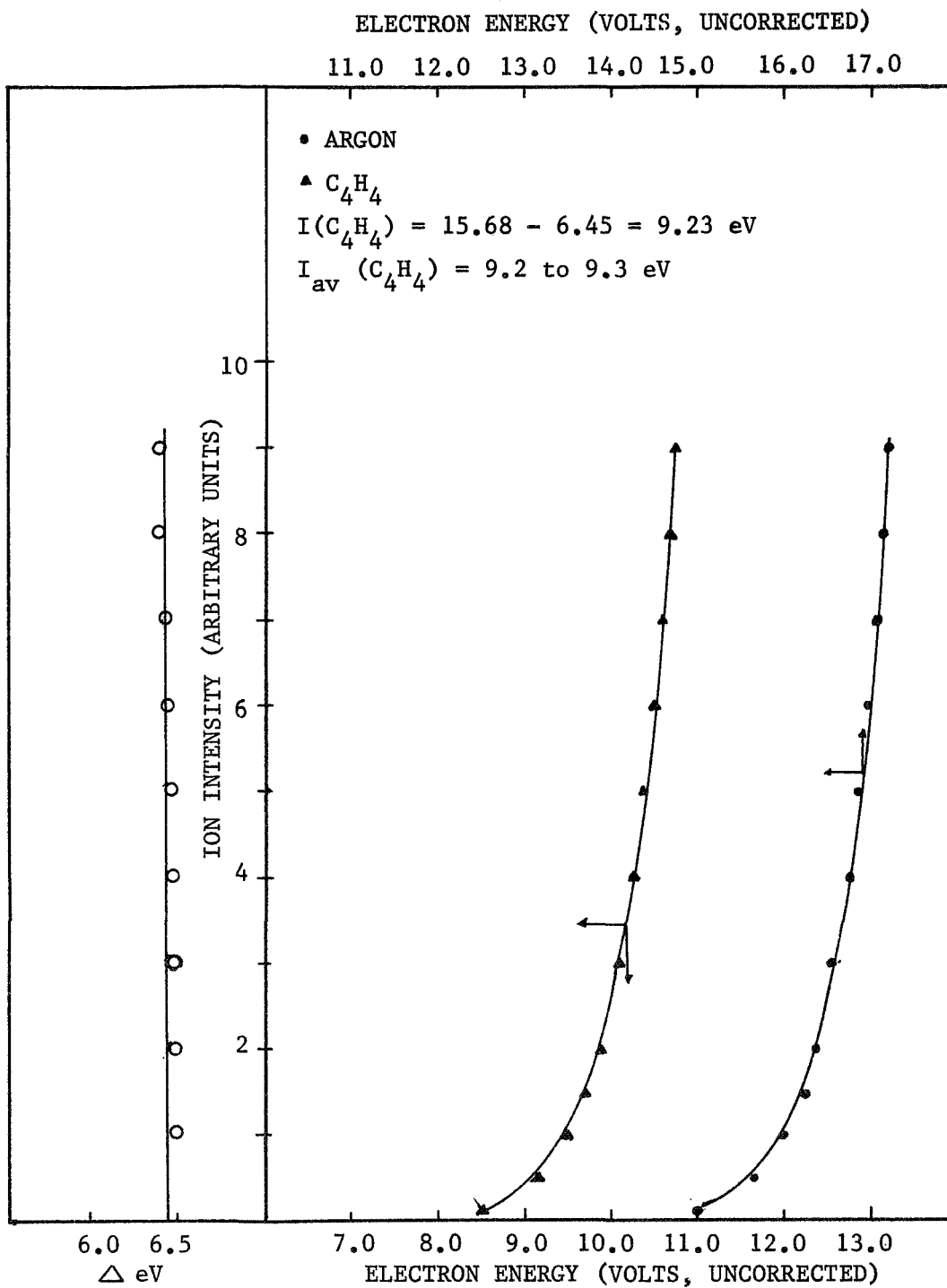


Figure 25. Ionization Efficiency Data for Butatriene.

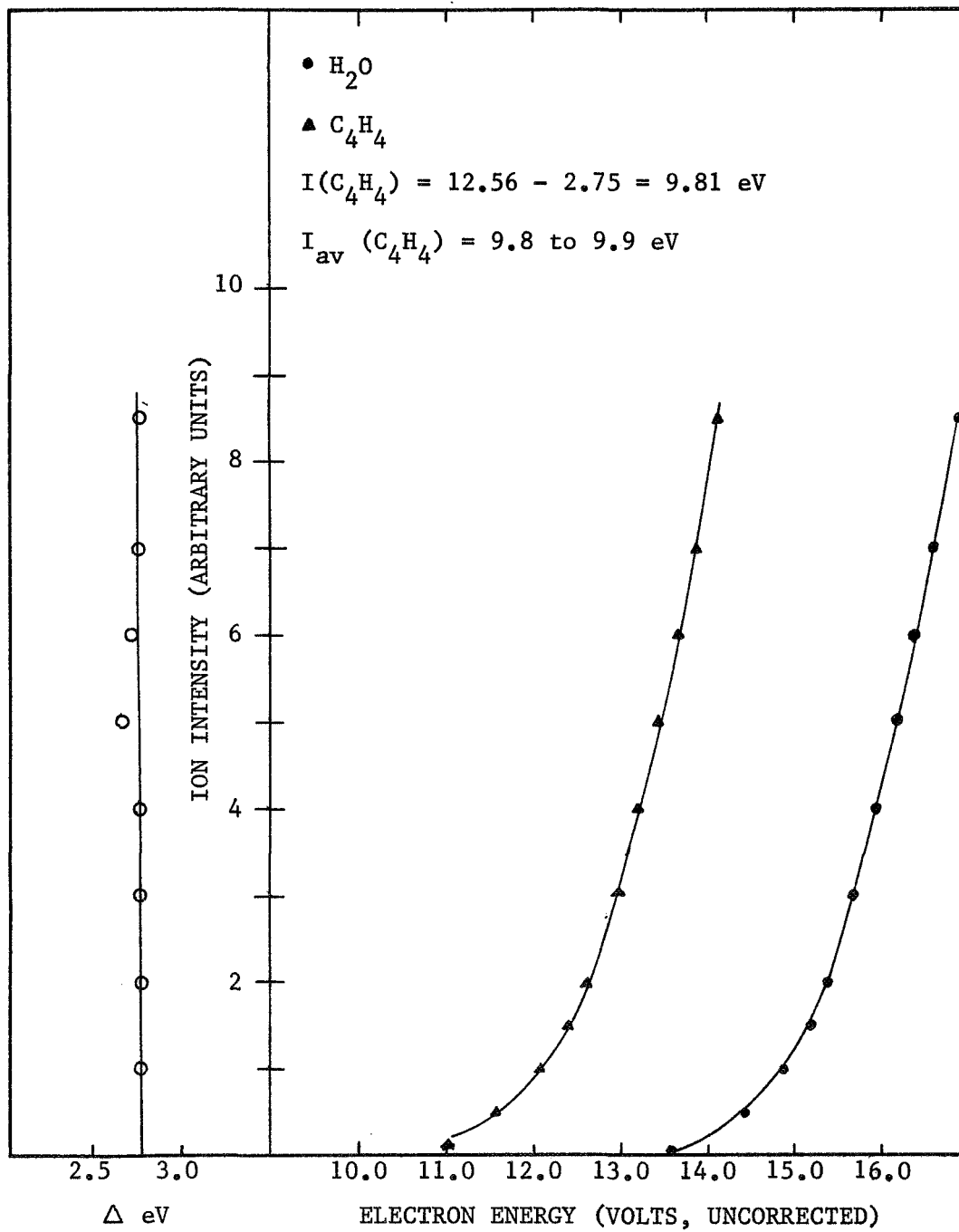


Figure 26. Ionization Efficiency Data for Vinylacetylene.

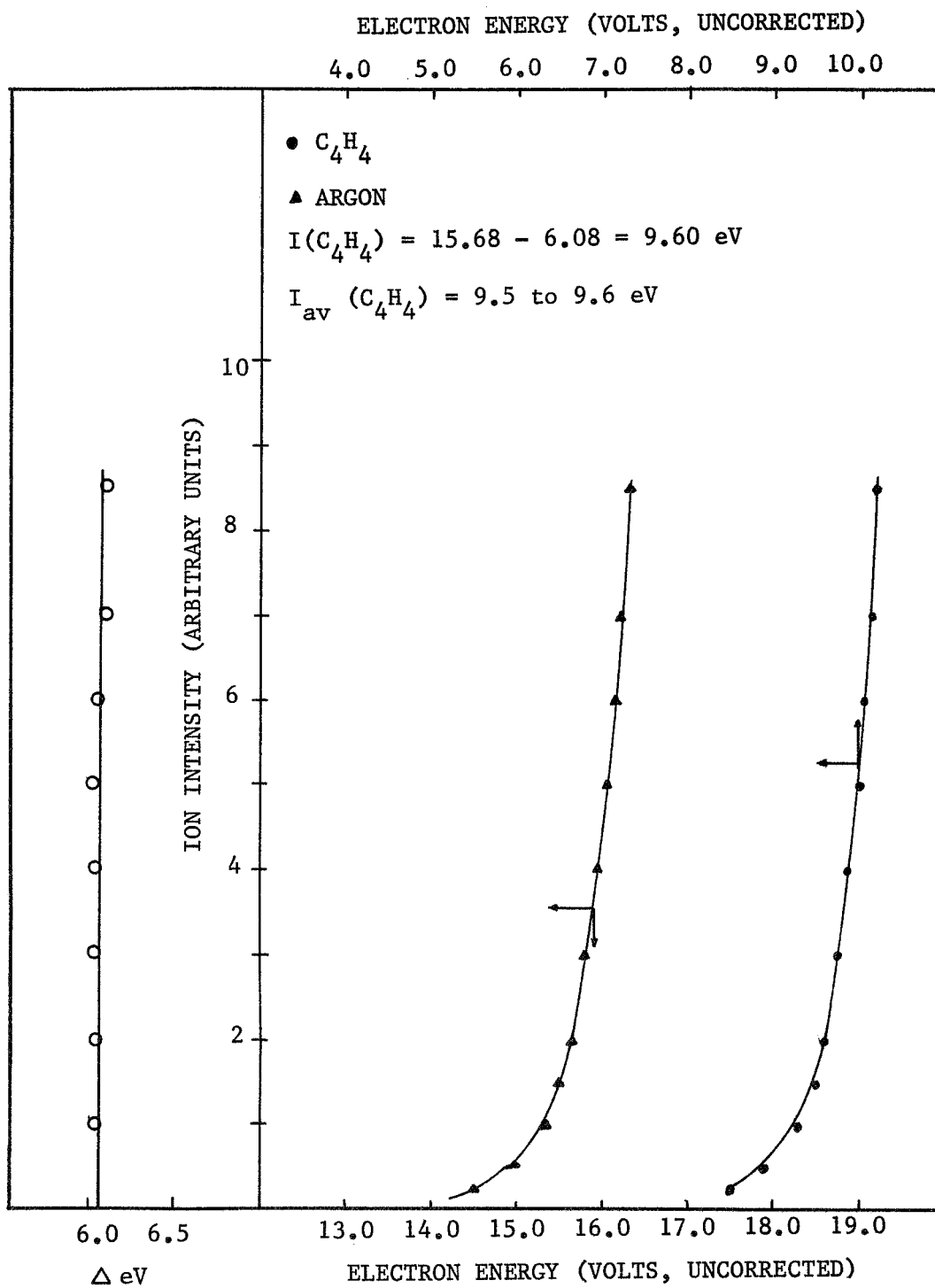


Figure 27. Ionization Efficiency Data for Condensed C<sub>4</sub>H<sub>4</sub>  
at -100° from Pyrolysis of CIT.



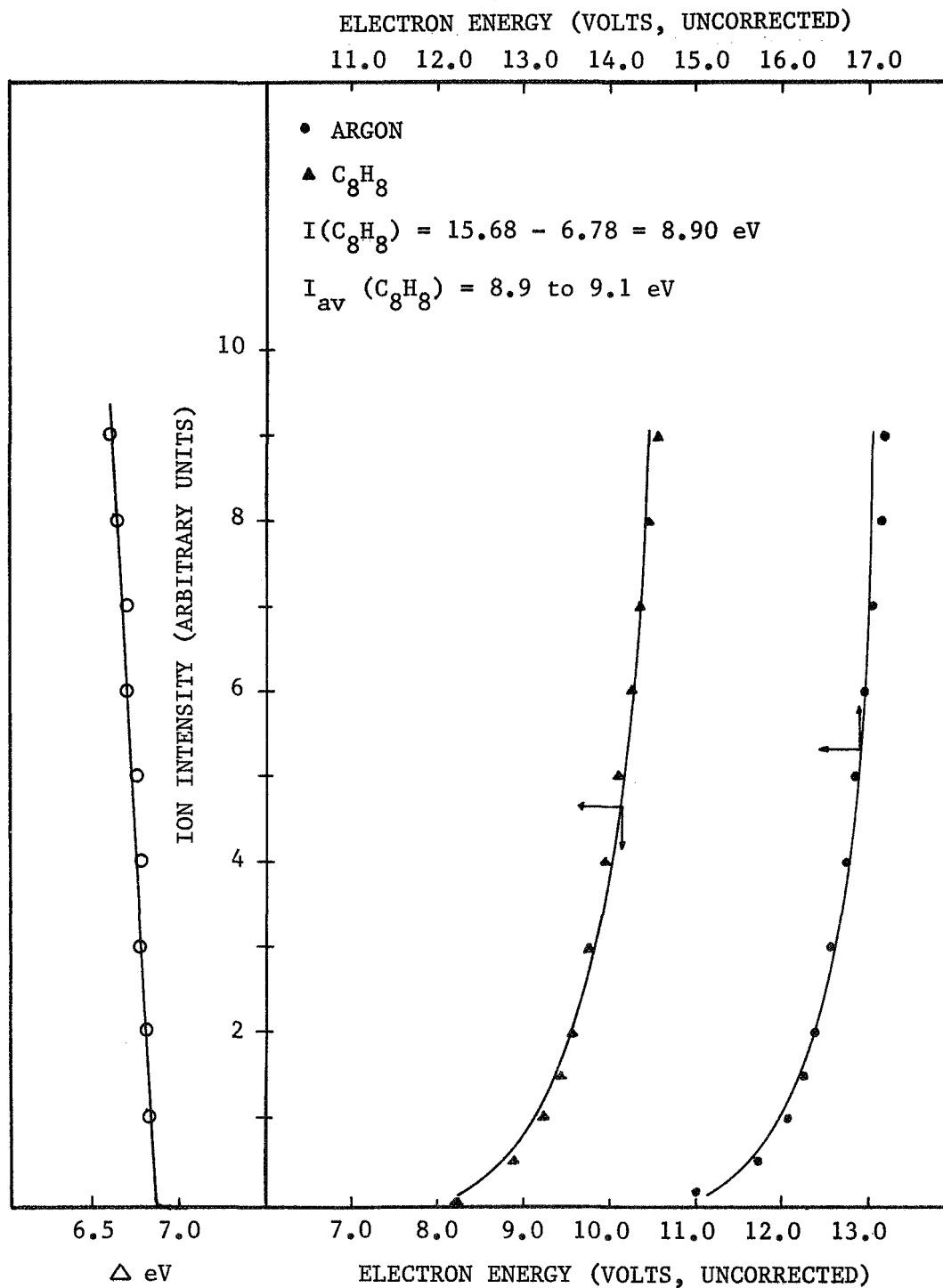


Figure 28. Ionization Efficiency Data for Condensed C<sub>8</sub>H<sub>8</sub>  
at -70<sup>o</sup> from Pyrolysis of CIT.

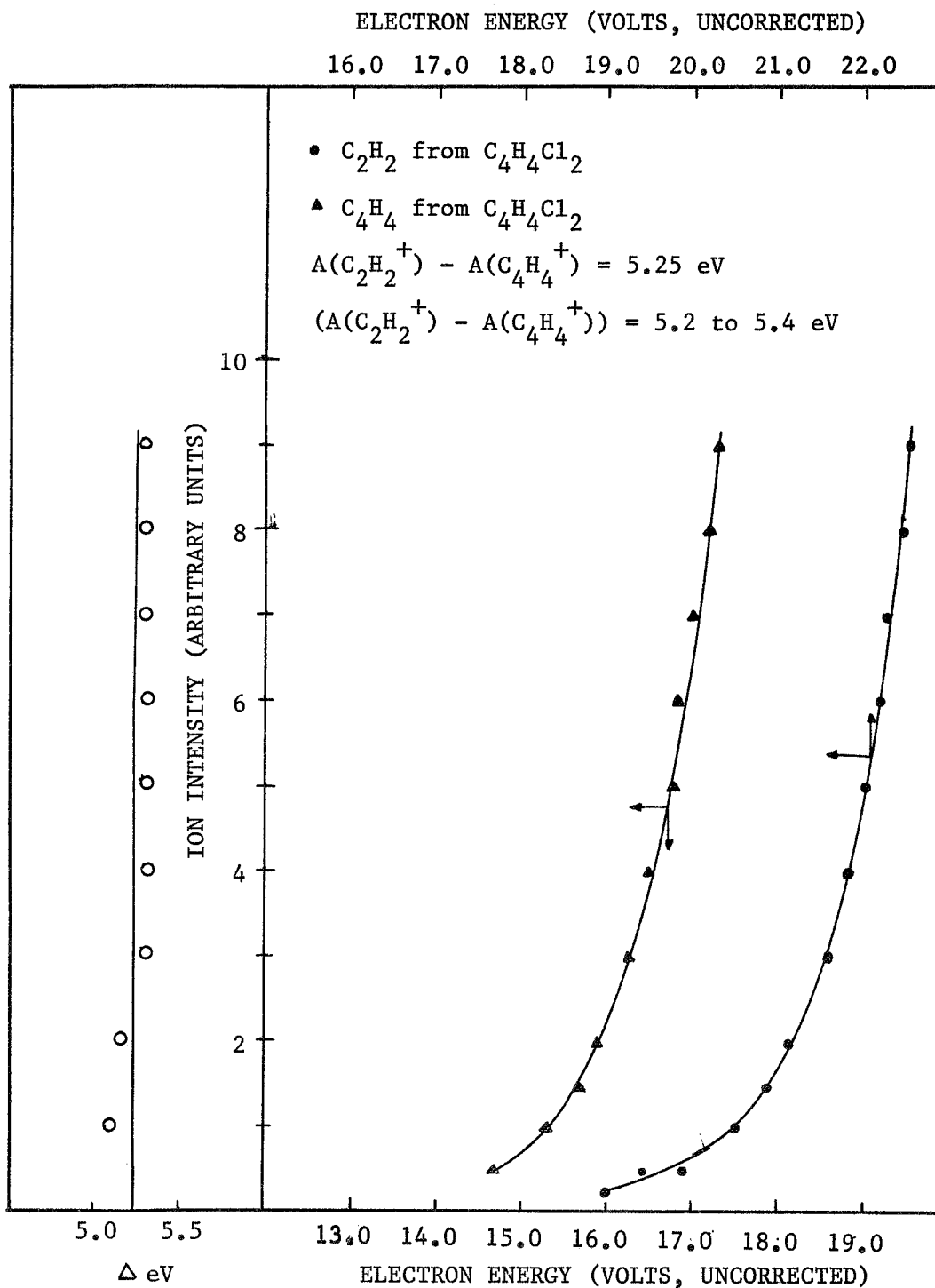


Figure 29. Ionization Efficiency Data for  $C_4H_4^+$  and  $C_2H_2^+$   
 from Cis-3,4-dichlorocyclobutene.

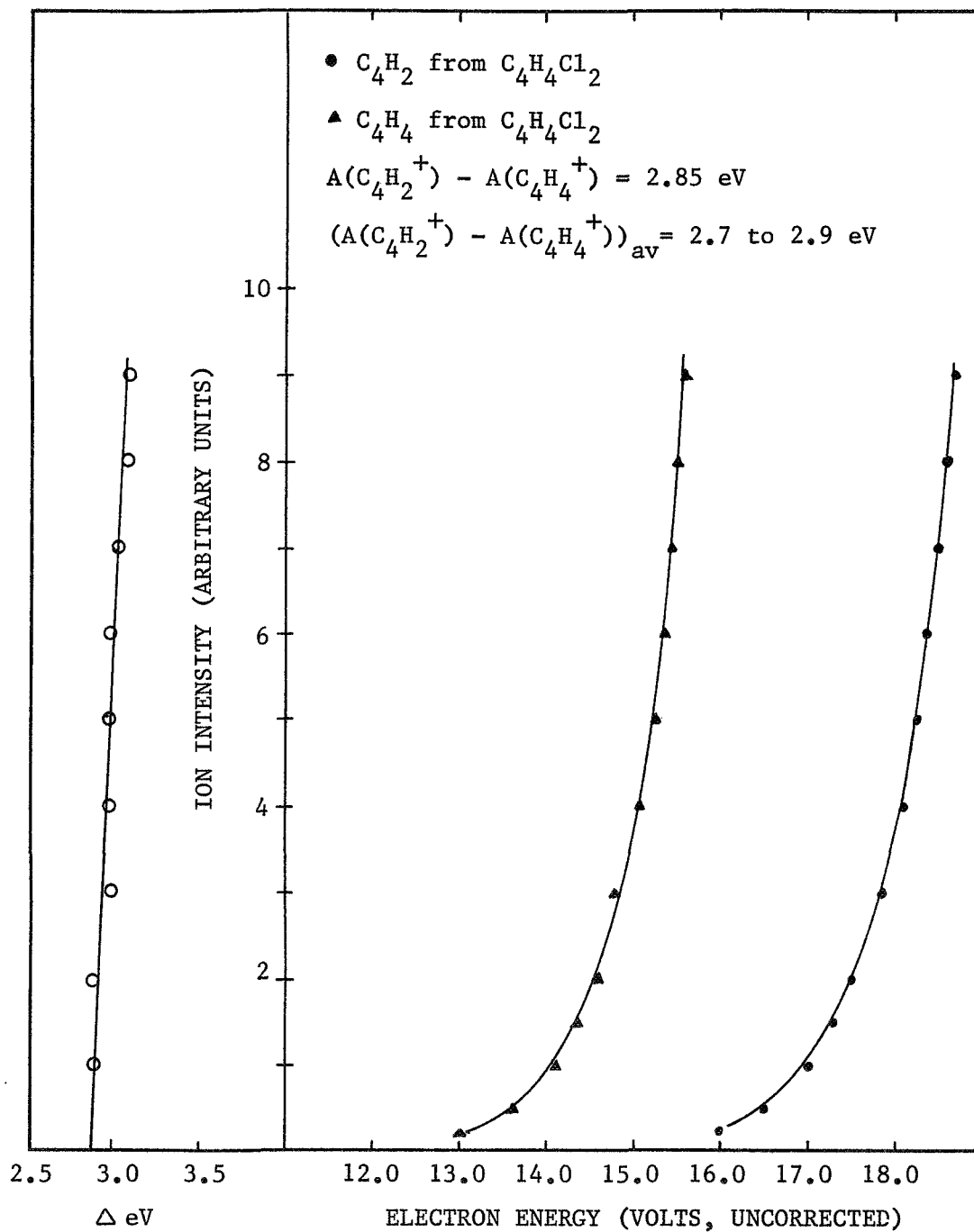


Figure 30. Ionization Efficiency Data for  $C_4H_4^+$  and  $C_4H_2^+$  from Cis-3,4-dichlorocyclobutene.

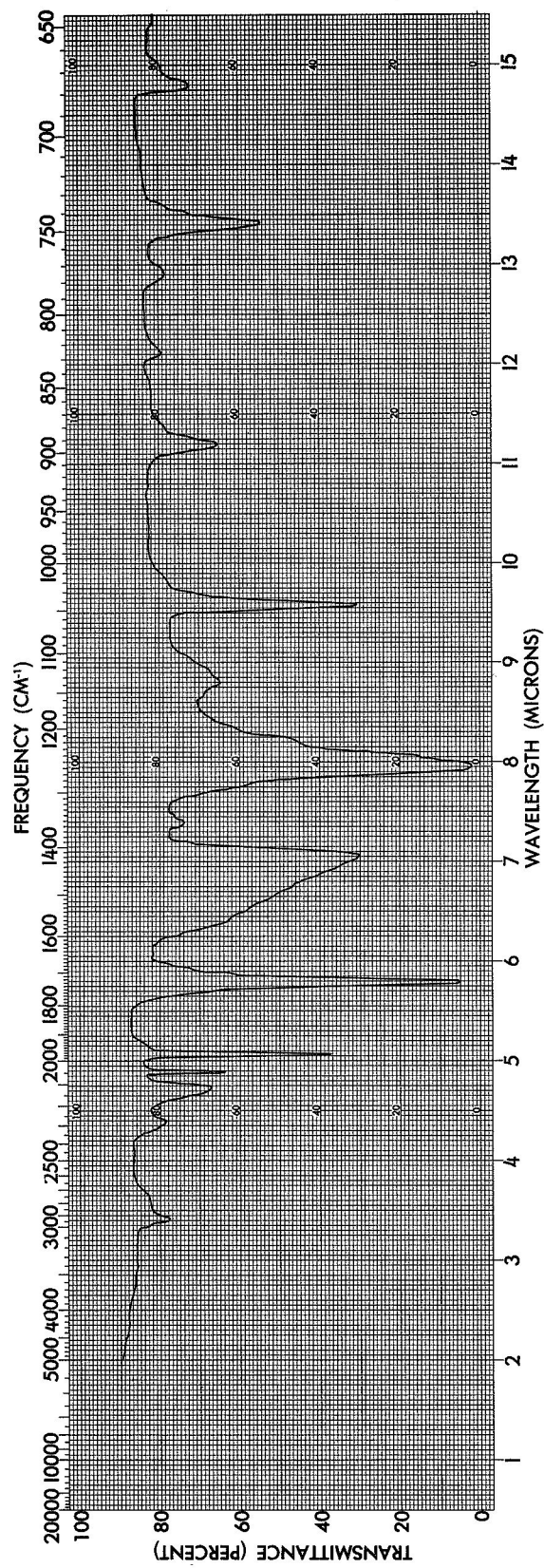


Figure 31. Infrared Spectrum of the Reaction Mixture of Dimethyl Acetylenedicarboxylate and Condensed C<sub>4</sub>H<sub>4</sub> from the Pyrolysis of CIT.

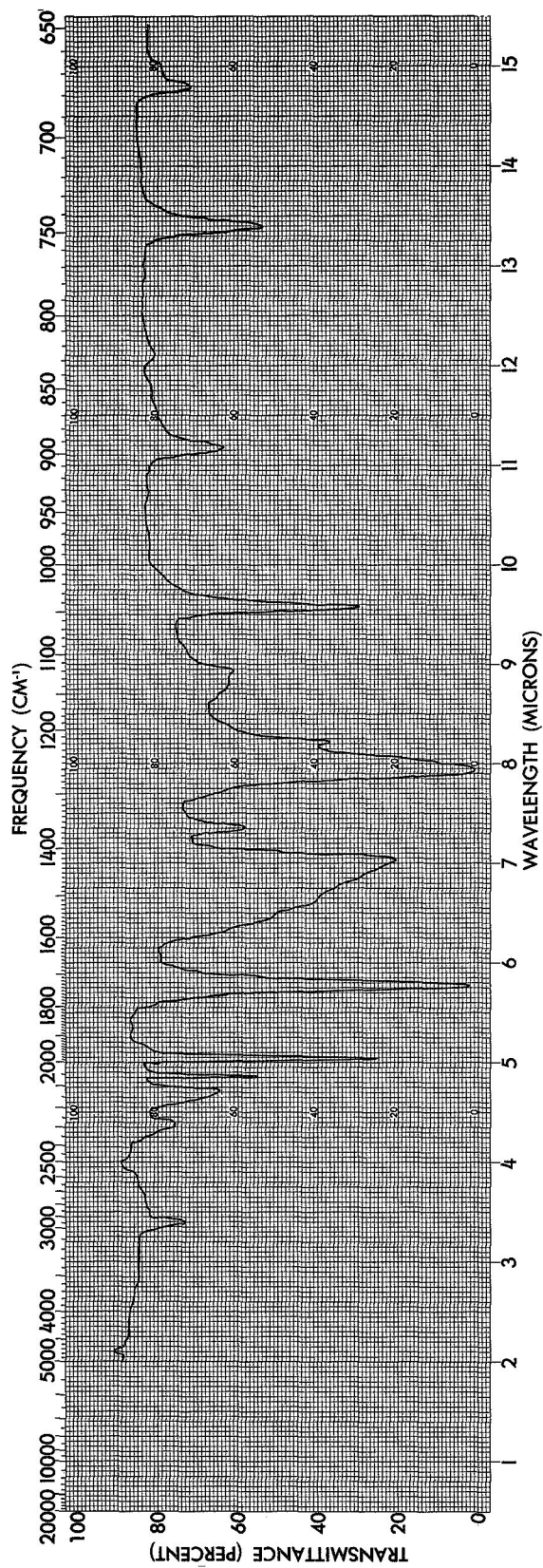


Figure 32. Infrared Spectrum of the Mixture of CIT and Dimethyl Acetylenedicarboxylate after 1/2 hr of Heating at 90°.

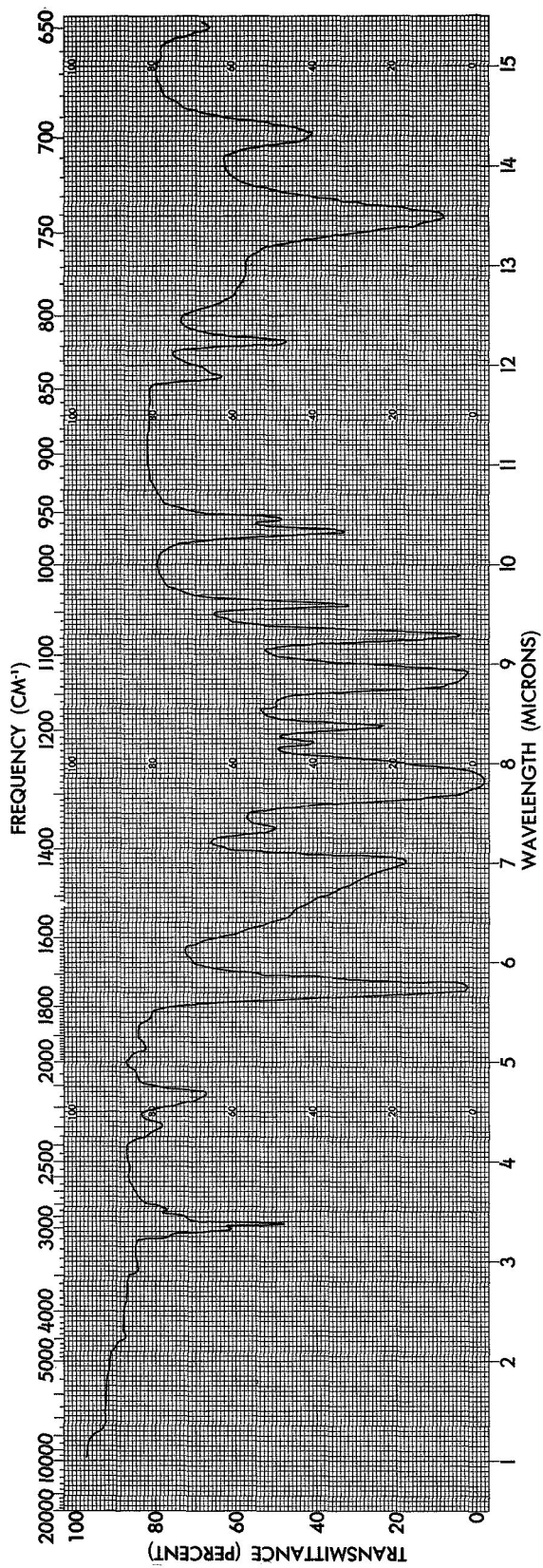


Figure 33. Infrared Spectrum of Authentic Dimethyl 1, 2-Benzenedicarboxylate.

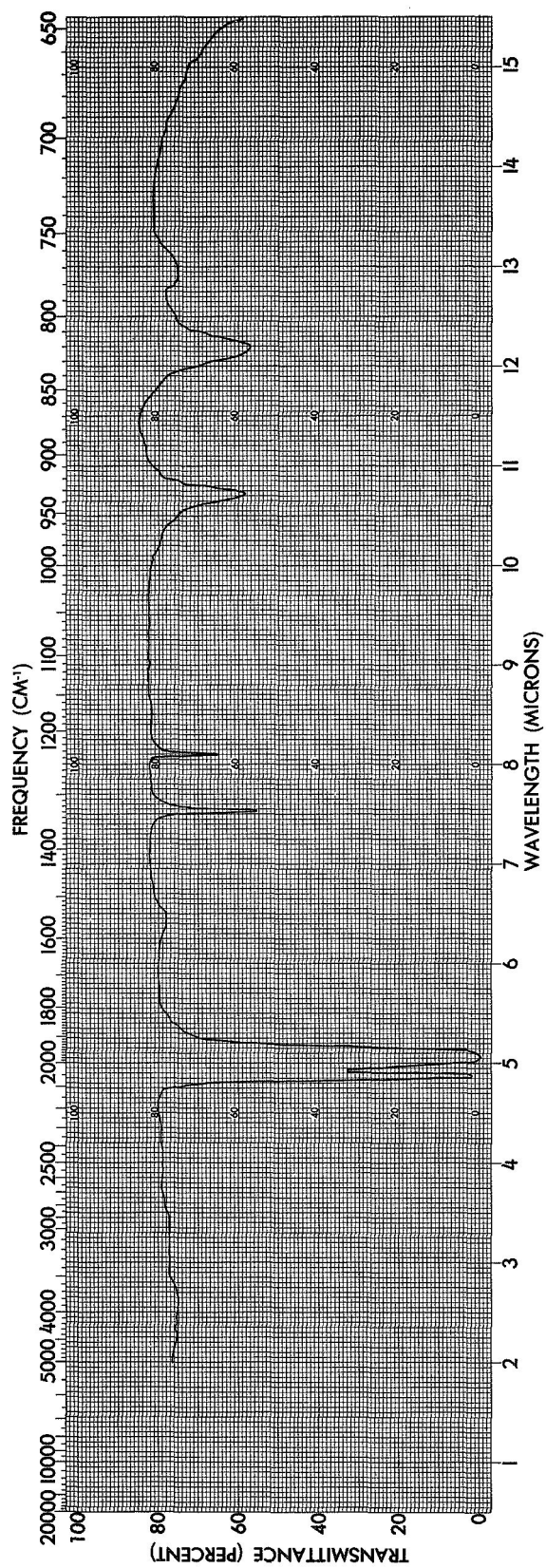


Figure 34. Infrared Spectrum of Cyclobutadieneirontricarbonyl

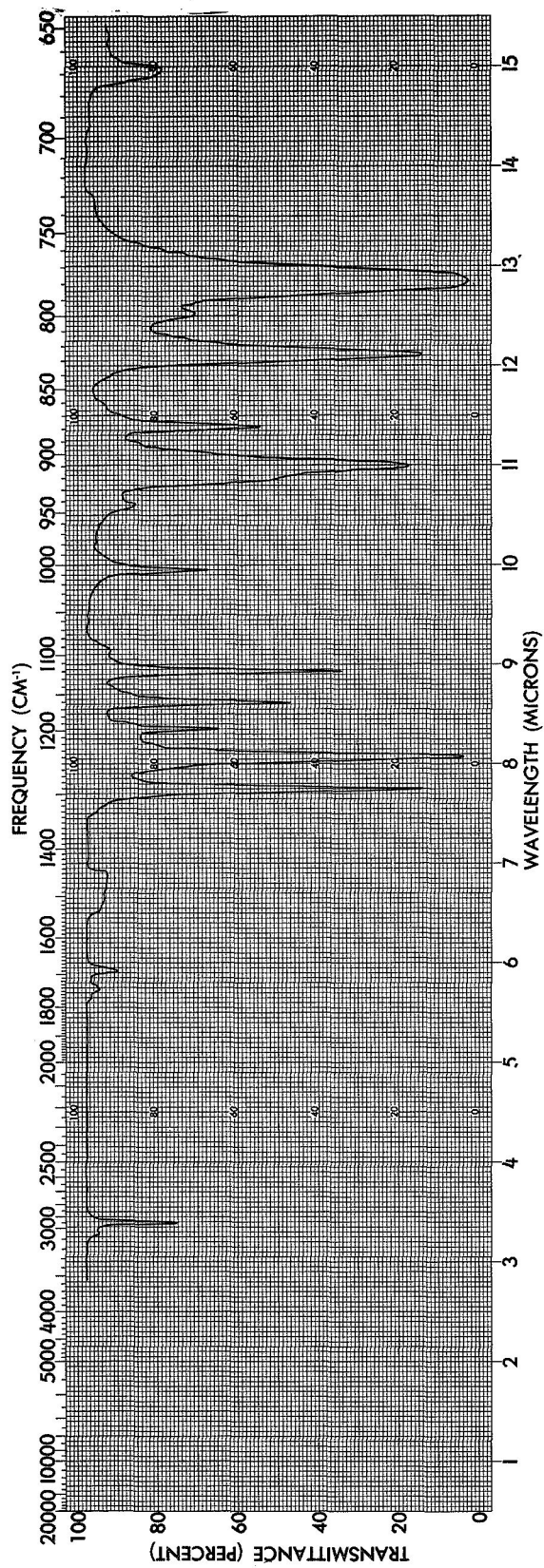


Figure 35. Infrared Spectrum of Cis-3,4-dichlorocyclobutene



## APPENDIX C

DERIVATION OF HEAT OF FORMATION OF  
CYCLOBUTADIENE FROM ENERGETIC STUDY

Electron impact studies have been used to obtain bond dissociation energies of molecules by measuring the appearance potential of their fragments. In the electron impact of the AB and B, the following processes can occur.



The energy required to produce  $AB^+$  in (1) or  $B^+$  in (3) is defined as the ionization potential of AB or B, and is expressed by the symbol  $I(AB)$  or  $I(B)$ . The energy required to produce  $B^+$  in (2) is defined as the appearance potential of  $B^+$  from molecule AB, and is represented by the symbol  $A(B^+)$ . In process (2),  $A(B^+)$  is the sum of several energies: (1) the ionization potential of B, (2) the bond dissociation energy of AB,  $D(A - B)$ , (3) the excess energy,  $\sum E_e$ , attained if the electronically excited states of  $B^+$  or A should be produced, and (4) the possible excess kinetic energies,  $\sum E_k$ , a term which includes rotational, translational and vibrational contributions. The appearance potential of  $B^+$  may then be written

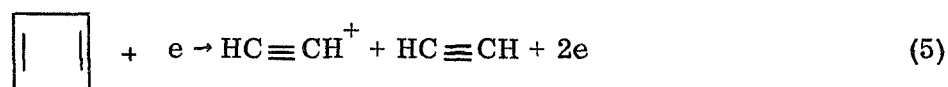
$$A(B^+) = I(B) + D(A - B) + \sum E_e + \sum E_k$$

where  $D(A - B)$  is defined as the difference in energy between the parent molecule and the two fragments after bond cleavage. When the excess energy terms are neglected,  $D(A - B)$  is calculated directly from  $A(B^+)$  and  $I(B)$ .

When electron impact is assumed to occur at  $25^\circ$ , the relation between energy change and enthalpy change is small since  $H = E + PV = E + RT$ , and  $RT$  is only about 0.6 kcal at  $25^\circ$ . Therefore,  $D(A - B)$  is assumed to be equal to the enthalpy change at  $25^\circ$ . The enthalpy balance may then be written

$$D(A - B) = \Delta H_f(A) + \Delta H_f(B) - \Delta H_f(AB) \quad (4)$$

The heat of formation of cyclobutadiene can be derived by measuring  $A(C_2H_2^+)$  from  $C_4H_4$  in process (5). From equation (6),  $D(C_2H_2 - C_2H_2)$  can be calculated, and subsequently from equation (7),  $H_f(C_4H_4)$  can be obtained.



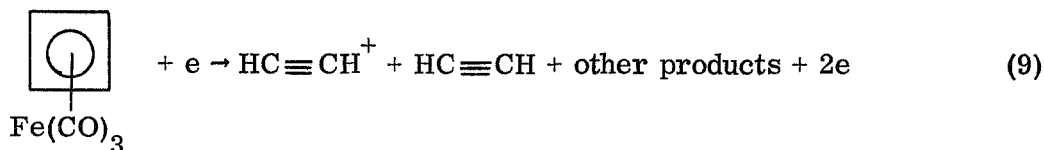
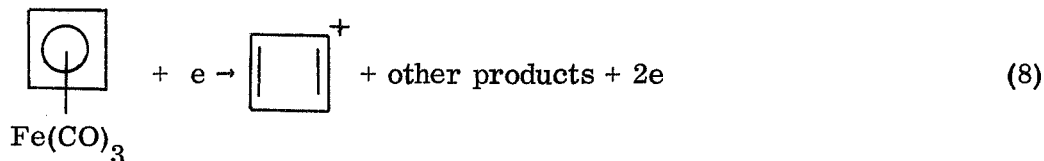
$$A(C_2H_2^+) = I(C_2H_2) + D(C_2H_2 - C_2H_2) \quad (6)$$

$$D(C_2H_2 - C_2H_2) = 2 \Delta H_f(C_2H_2) - \Delta H_f(C_4H_4) \quad (7)$$

Cyclobutadiene, along with vinylacetylene and acetylene, was produced in the pyrolysis of CIT. The appearance potential of  $C_2H_2^+$  measured in the pyrolysis of CIT at  $380^\circ$  would be less than the actual value of  $A(C_2H_2^+)$  from cyclobutadiene because of the unavoidable presence of acetylene. In the quenched products of the

pyrolysis,  $C_2H_2$  could be removed by vacuum pumping at temperatures below  $-100^\circ$ . However, a problem remained in that the quenched  $C_4H_4$  at  $-100^\circ$  was a mixture of both vinylacetylene and cyclobutadiene. Therefore,  $A(C_2H_2^+)$  could have been a somewhat incorrect value of  $A(C_2H_2^+)$  from cyclobutadiene.

From the electron impact of CIT in processes (8) and (9), equations (10) and (11) can be derived by assuming that the other products are identical in processes (8) and (9), and by neglecting the excess energies.



$$A(C_4H_4^+) = I(C_4H_4) + D_1 \quad (10)$$

$$A(C_2H_2^+) = I(C_2H_2) + D(C_2H_2 - C_2H_2) + D_1 \quad (11)$$

where  $D_1$  is the total bond dissociation energy of processes (8) and (9) with the exception of  $D(C_2H_2 - C_2H_2)$ . Then by combining equations (10) and (11), one obtains the relation.

$$A(C_2H_2^+) - A(C_4H_4^+) = I(C_2H_2) - I(C_4H_4) + D(C_2H_2 - C_2H_2) \quad (12)$$

When the measured value of  $A(C_2H_2^+) - A(C_4H_4^+)$  and  $I(C_4H_4)$  from this thesis research and the known  $I(C_2H_2)$  value ( $11.40 \text{ eV}^{60}$ ) were substituted into

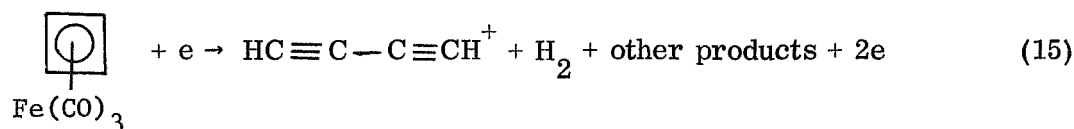
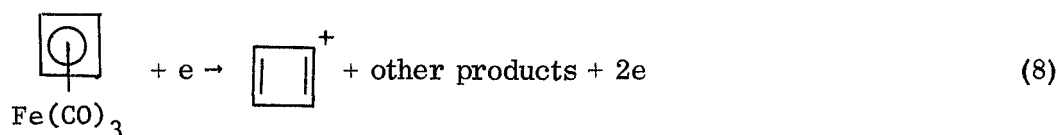
equation (12),  $D(C_2H_2 - C_2H_2)$  was calculated to be 3.45 eV. That is,

$$5.50 = 11.40 - 9.35 + D(C_2H_2 - C_2H_2) \quad (13)$$

When this calculated  $D(C_2H_2 - C_2H_2)$  value (3.45 eV) and the known  $\Delta H_f(C_2H_2)$  value (54.2 kcal/mole) were substituted into equation (7),  $\Delta H_f(C_4H_4)$  was calculated to be 28.9 kcal/mole:

$$3.45 \times 23.06 = 2 \times 54.2 - \Delta H_f(C_4H_4) \quad (14)$$

Equation (16) can be derived from the electron impact of CIT in processes (8) and (15) by applying the same methods and assumptions used to obtain equation (12). That is,



$$A(C_4H_2^+) - A(C_4H_4^+) = I(C_4H_2) - I(C_4H_4) + D(C_4H_2 - H_2) \quad (16)$$

When measured values of  $A(C_4H_2) - A(C_4H_4)$  and  $I(C_4H_4)$  from this thesis and the known  $I(C_4H_2)$  value ( $10.2 \text{ eV}^{56}$ ) were substituted into equation (16),  $D(C_4H_2 - H_2)$  was calculated to be 1.85 eV:

$$2.70 = 10.2 - 9.35 + D(C_4H_2 - H_2) \quad (17)$$

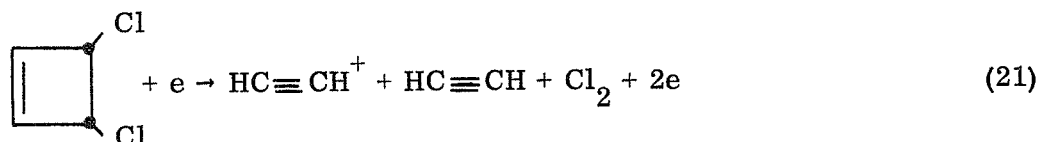
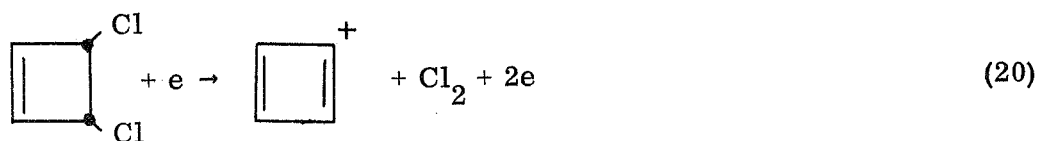
When this calculated  $D(C_4H_2 - H_2)$  value (1.85 eV), the known  $\Delta H_f(C_4H_2)$  value (114.6 kcal/mole),\* and the known  $\Delta H_f(H_2)$  value were substituted into equation (18),  $\Delta H_f(C_4H_4)$  was calculated to be 71.9 kcal/mole:

$$D(C_4H_2 - H_2) = \Delta H_f(C_4H_2) + \Delta H_f(H_2) - \Delta H_f(C_4H_4) \quad (18)$$

$$1.85 \times 23.06 = 114.6 + 0 - \Delta H_f(C_4H_4) \quad (19)$$

From electron impact of cis-3,4-dichlorocyclobutene in processes (20), (21) and (22), equations similar to (12) and (16) can be derived. When the measured  $A(C_2H_2^+) - A(C_4H_4^+)$  value (5.30 eV) and  $A(C_4H_2^+)$ ,  $-A(C_4H_4^+)$  value (2.80 eV) were substituted into equation (12) and (16) respectively,  $D(C_2H_2 - C_2H_2)$  was calculated to 3.25 eV and  $D(C_4H_2 - H_2)$  was calculated to be 1.95 eV.

When these calculated  $D(C_2H_2 - C_2H_2)$ ,  $D(C_4H_2 - H_2)$ , and the known  $\Delta H_f(C_4H_2)$  value were substituted into equation (7) and (18) respectively,  $\Delta H_f(C_4H_4)$  was calculated to be 33.5 kcal/mole and 69.6 kcal/mole.



-----

\*  $\Delta H_f(C_4H_2)$  was calculated to be 118.0 kcal/mole from heat of combustion (11.25 kcal/mole, E. I. du Pont de Nemours and Company, personal communication).  $\Delta H_f(C_4H_2)$  was derived to be 111.3 kcal/mole from heat of hydrogenation (M. Cowperthwaite and S. H. Bauer, J. Chem. Phys. **36**, 1743 (1962)). Therefore, an average value, 114.6 kcal/mole, was used in these calculations.

Table 14. Heat of Formation of Cyclobutadiene

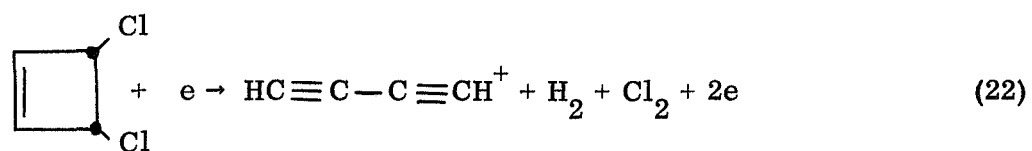
Derived from Energetic Study

Compound	$A(C_2H_2^+) - A(C_4H_4^+)$ , eV	$I(C_4H_4)$ , eV	$\Delta H_f(C_4H_4)$ , kcal/mole
CIT	5.50	9.35 <sup>a</sup>	28.9
CIT	5.50	8.83 <sup>b</sup>	40.9
$C_4H_4Cl_2$	5.30	9.35 <sup>a</sup>	33.5
$C_4H_4Cl_2$	5.30	8.83 <sup>b</sup>	43.5

Compound	$A(C_4H_2^+) - A(C_4H_4^+)$ , eV	$I(C_4H_4)$ , eV	$\Delta H_f(C_4H_4)$ , kcal/mole
CIT	2.70	9.35 <sup>a</sup>	71.9
CIT	2.70	8.83 <sup>b</sup>	83.9
$C_4H_4Cl_2$	2.80	9.35 <sup>a</sup>	69.6
$C_4H_4Cl_2$	2.80	8.83 <sup>b</sup>	81.6

<sup>a</sup>9.35 eV is measured value.<sup>b</sup>8.83 eV is theoretical value.



In all of these calculations, when the theoretical value of  $I(\text{C}_4\text{H}_4)$ , 8.83 eV, was used,  $\Delta H_f(\text{C}_4\text{H}_4)$  was obtained to be 40.9, 45.5, 83.9 and 81.6 kcal/mole.

## APPENDIX D

THEORETICAL IONIZATION POTENTIALS AND HEATS  
OF ATOMIZATION OF C<sub>4</sub>H<sub>4</sub> ISOMERS

This appendix is a literature survey of molecular orbital studies of ionization potentials and heats of atomization of C<sub>4</sub>H<sub>4</sub> isomers. Several methods have been used to calculate these values. Streitwieser<sup>61</sup> reported a molecular orbital study of ionization potentials of organic compounds utilizing the "ω-technique." In the Hückel molecular orbital theory, the electron repulsion terms were neglected. This ω-technique used a parameter to provide for electron repulsion effects in an empirical manner. The ionization potentials of butatriene and vinylacetylene calculated by this method are in Table 14. The other methods, developed by Dewar and his co-workers, were all based on the semiempirical SCF MO treatment. Dewar and Gleicher<sup>3</sup> reported the heats of atomization of cyclobutadiene by the PPP method (Pariser-Parr-Pople method) and by SPO method (split-p-orbital method). Recently Dewar and his co-workers reported two methods, Klopman<sup>54</sup> and MINDO<sup>55</sup>, to calculate heats of atomization and ionization potentials of organic compounds. However, they did not use their methods to calculate the heats of atomization and ionization potentials of C<sub>4</sub>H<sub>4</sub> isomers. Since L. P. Gordon in this laboratory was interested in the molecular orbital calculations, it was decided to calculate the heats of atomization and ionization potentials of C<sub>4</sub>H<sub>4</sub> isomers by Klopman and MINDO methods. In the Klopman method, the π MO's of conjugated



molecules were calculated by a Semiempirical SCF MO method. The  $\alpha$  electrons being treated as localized. The procedure similar to that suggested by Pople et al.,<sup>62</sup> and by Klopman<sup>63</sup> was used to include all the valence electrons in a molecule. The following geometries and bond lengths were used for the calculations. The bond lengths were the standard ones used by Klopman<sup>54</sup>. However, in his paper, the bond length for the carbon-carbon bond in  $=C=C\equiv$  was not listed. The bond length 1.446 Å used here was the actual bond length observed in the vinylacetylene.<sup>64</sup>

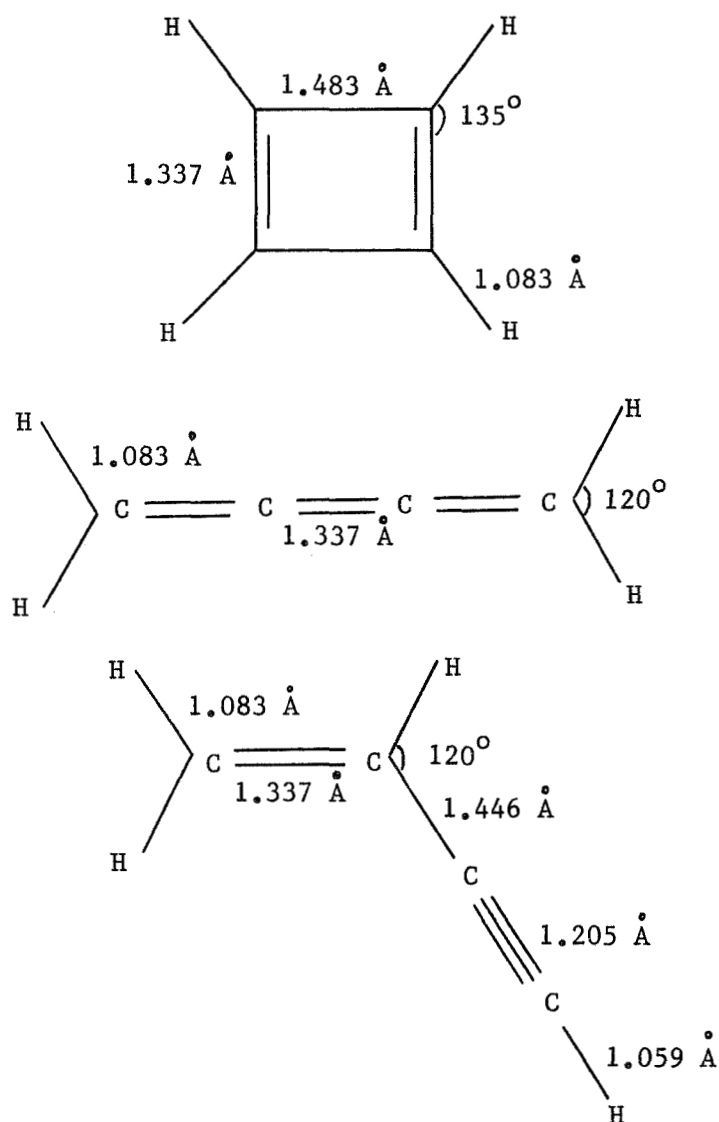


Table 15. Theoretical Ionization Potential and Heat  
of Atomization of C<sub>4</sub>H<sub>4</sub> Isomers

Compound	IONIZATION POTENTIAL, eV			
	$\pi$ (adiabatic)	Klopman	MINDO	$\omega$ -technique
Cyclobutadiene, Singlet	8.51 <sup>a</sup>	8.83 <sup>b</sup>	8.56 <sup>b</sup>	
Cyclobutadiene, Triplet		8.43		
Vinylacetylene		9.60		9.46 <sup>c</sup>
Butatriene		8.99	9.16	9.28

Compound	HEAT OF ATOMIZATION, kcal/mole			
	SPO	PPP	Klopman	MINDO
Cyclobutadiene, Singlet	830.1 <sup>d</sup>	830.1 <sup>d</sup>	836.25 <sup>b</sup>	812.33 <sup>b</sup>
Cyclobutadiene, Triplet	808.9	816.0		
Vinylacetylene			859.32	
Butatriene			802.09	808.46

<sup>a</sup>M. J. S. Dewar, S. D. Worley, J. Phys. Chem. **50**, 654 (1969)

<sup>b</sup>Calculated by L. P. Gordon, Georgia Institute of Technology

<sup>c</sup>A. Streitwieser, Jr., J. Am. Chem. Soc. **82**, 4123 (1960)

<sup>d</sup>M. J. S. Dewar, G. J. Gleicher, J. Am. Chem. Soc. **87**, 3255 (1965)

In the MINDO method, all the valence electrons, both  $\pi$  and  $\alpha$ , were included. The  $\pi$  and  $\alpha$  ionization potentials were estimated. In the original paper<sup>55</sup>, the bond lengths used for four-membered rings were different from the standard ones used in Klopman's paper.<sup>54</sup> The  $sp^2-sp^2$  C=C bond was not listed. The bond lengths in cyclobutadiene used for the MINDO calculation were the same ones used in the Klopman method. The heat of formation and ionization potential of vinylacetylene calculated from the MINDO method are not listed here because no converged results were obtained from the computation.

BIBLIOGRAPHY<sup>\*</sup>

1. R. Willstätter and W. Von. Schmädell, Ber. 38, 1992 (1905)
2. R. Willstätter and E. Waser, Ber. 44, 3423 (1911)
3. M. J. S. Dewar, G. J. Gleicher, J. Am. Chem. Soc. 87, 3255 (1965)
4. W. H. Perkin, Jr., Ber. 26, 2243 (1893)
5. R. C. Jones, Ph.D. Thesis, Harvard (1941)
6. R. Knoche, Ph.D. Thesis, Münster (1925)
7. E. R. Buchman, Abstr. ACS Meeting, Sept. 13, 1954
8. M. Avram, C. D. Nenitzescu and E. Marica, Ber. 90, 1857 (1957)
9. H. C. Longuet-Higgins and L. E. Orgel, J. Chem. Soc., 1969 (1956)
10. R. Criegee and G. Schroder, Ann. Chem. 62, 31 (1959)
11. W. Hubel, E. H. Braye, A. Clauss, E. Weiss, A. Kruerke, D. A. Brown, G. S. D. King and C. Hoogzand, Inorg. Nucl. Chem. Lett. 9, 204 (1959)
12. L. Malatesta, G. Santarella, L. Vallarino and F. Zingales, Angew. Chem. 72, 34 (1960)
13. T. I. Bieber, Chem. Ind. (London), 1126 (1957)
14. M. Avram, E. Marica and C. D. Nenitzescu, Ber. 92, 1088 (1959)
15. M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam and C. D. Nenitzescu, Ber. 97, 382 (1964)
16. G. F. Emerson, L. Watts and R. Pettit, J. Am. Chem. Soc. 87, 131 (1965)
17. M. Rosenblum and C. Gatsonis, J. Am. Chem. Soc. 89, 5074 (1967)

-----  
\* Abbreviations in this Bibliography followed the form used by Chemical Abstracts, as found in the Guide for Abbreviating Periodical Titles (1967).

18. R. G. Amiet, P. C. Reeves and R. Pettit, Chem. Comm. 1208 (1967)
19. L. Watts, J. D. Fitzpatrick and R. Pettit, J. Am. Chem. Soc. 87, 3253 (1965)
20. G. D. Burt and R. Pettit, Chem. Comm. 517 (1965)
21. W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strauz and H. E. Gunning, Chem. Comm. 497 (1967)
22. E. Hedaya, R. D. Miller, D. W. McNeil, P. D. D'Angelo and P. Schissel, J. Am. Chem. Soc. 91, 1875 (1969)
23. M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press Inc., New York, N.Y. (1967)
24. P. S. Skell and R. J. Petersen, J. Am. Chem. Soc. 86, 2530 (1964)
25. H. H. Freedman, J. Am. Chem. Soc. 83, 2195 (1961)
26. J. H. Beynon, R. C. Cookson, R. R. Hill, D. W. Jones, R. A. Sanders and A. E. Williams, J. Chem. Soc. 7052 (1965)
27. A. T. Blomquist and P. M. Maitlis, J. Am. Chem. Soc. 84, 2329 (1962)
28. V. R. Sandel and H. H. Freedman, J. Am. Chem. Soc. 90, 2059 (1968)
29. P. S. Skell and R. C. Woodworth, J. Am. Chem. Soc. 78, 4496 (1956)
30. P. P. Gaspar and G. S. Hammond, "Carbene Chemistry," W. Kirsme, ed., Academic Press Inc., New York, N.Y. (1964) pp. 258-261
31. L. Watts, J. D. Fitzpatrick and R. Pettit, J. Am. Chem. Soc. 88, 623 (1966)
32. W. J. Martin, Ph.D. Thesis, Georgia Institute of Technology (1965)
33. T. J. Malone, Ph.D. Thesis, Georgia Institute of Technology (1966)
34. J. H. Wilson, Ph.D. Thesis, Georgia Institute of Technology (1966)
35. C. E. Berkoff, R. C. Hudec and R. O. Williams, Proc. Chem. Soc. 312 (1961)
36. M. Avram, I. Dinulescu, M. Elian, M. Farcasiu, E. Marica, G. Mateescu and C. D. Nenitzescu, Chem. Ber. 97, 372 (1964)

37. H. G. Viehe and E. Franchimont, Chem. Ber. 97, 602 (1964)
38. J. Dewar and H. O. Jones, Proc. Roy. Soc., Ser. B. 76 564 (1905)
39. H. G. Cutforth and P. W. Selwood, J. Am. Chem. Soc. 65, 2414 (1943)
40. G. F. Hennion, C. C. Price and T. F. McKeon, Jr., J. Am. Chem. Soc. 76, 5160 (1954)
41. W. M. Schubert, T. H. Libbicoet and W. A. Lanka, J. Am. Chem. Soc. 76, 1929 (1954)
42. H. B. Dykstra, J. Am. Chem. Soc. 56, 1625 (1934)
43. F. A. Miller and I. Matsubara, Spectrochim. Acta. 22, 173 (1966)
44. "Selected Mass Spectral Data," API Research Project 44, College Station, Texas, Serial No. 175 (1962)
45. F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N.Y. (1957) pp. 268
46. C. F. Cullis and N. H. Franklin, Proc. Roy. Soc. Ser. A. 139 (1964)
47. R. E. Winters and R. W. Kiser, J. Phys. Chem. 69, 3198 (1965)
48. M. A. Haas and J. M. Wilson, J. Chem. Soc. Ser. B. 104 (1968)
49. R. G. Denning and R. A. D. Wentworth, J. Am. Chem. Soc. 88, 4619 (1966)
50. M. J. D. Dewar and S. D. Worley, J. Chem. Phys. 50, 654 (1969)
51. D. B. Bivene, Ph.D. Thesis, Georgia Institute of Technology (1966)
52. L. Watts, Ph.D. Thesis, University of Texas (1966)
53. A. G. Harrison and T. W. Shannon, Can. J. Chem. 40, 1730 (1962)
54. M. J. S. Dewar and G. Klopman, J. Am. Chem. Soc. 89, 3089 (1967)
55. N. C. Baird and M. J. S. Dewar, J. Chem. Phys. 50, 1262 (1969)
56. C. Baker and D. W. Turner, Chem. Comm. 797 (1967)
57. G. Subrahmanyam, J. Scient. Ind. Res. 26, 158 (1967)

58. R. Griegea, Angew. Chem. 74, 703 (1962)
59. J. W. Warren, Nature 165, 811 (1950)
60. J. E. Collin and J. Delwiche, Can. J. Chem. 45, 1883 (1967)
61. A. Streitwieser, J. Am. Chem. Soc. 82, 4123 (1960)
62. J. A. Pople and G. A. Segal, J. Chem. Phys. 44, 3289 (1966)
63. G. Klopman, J. Am. Chem. Soc. 87, 3300 (1965)
64. L. Pauling, "The Nature of Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N.Y. (1960) pp. 299
65. "Selected Mass Spectral Data," API Research Project 44, College Station, Texas, Serial No. 71, 125, 37 and 38, (1962)
66. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953
67. M. J. S. Dewar and E. Haselbach, personal communication

## VITA

Ping Hung Li was born in [REDACTED] on [REDACTED]. He was graduated from the Tainan First High School in 1955. He entered the first class of Tunghai University in the Fall of 1955 and received the degree of Bachelor of Science in Chemical Engineering in 1959. He served as a Second Lieutenant in the Army of the Republic of China from 1959 to 1961 and was stationed in Taiwan and on the island of Quemoy.

He was employed as a teaching assistant at Tunghai University from 1961 to 1963. In September 1963, he came to the United States to enroll in the Graduate Division of the Georgia Institute of Technology and received the degree of Master of Science in Chemical Engineering in June, 1965. He was employed as a research assistant in the Engineering Experiment Station from 1964 to 1966, working in the field of fertilizer technology. Since 1966, he has held a graduate research assistantship in the School of Chemical Engineering.

In 1965, he was married to the former Grace Shu Yueh Yu and they have one daughter, Jenny Yi-chieh.