4993

NATIONAL LIBRARY
OTTAWA

CANADA

BIBLIOTHÈQUE NATIONALE
OTTAWA

NAME OF AUTHOR......BRENDAN WOODS

TITLE OF THESIS....THE PHOTOCHEMISTRY OF
SOME FLUORINATED
COMPOUNDS

UNIVERSITY....OF ALBERTA

DEGREE FOR WHICH THESIS WAS PRESENTED.....Ph. D.

YEAR THIS DEGREE GRANTED......1969

Permission is hereby granted to THE NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

(Signed)..Brendan Woods

PERMANENT ADDRESS:

3551 - Allen Ave.
Regina
Sask

DATED 21/ Aug....1969.

NL-91 (10-68)

THE UNIVERSITY OF ALBERTA

THE PHOTOCHEMISTRY OF SOME FLUORINATED COMPOUNDS

BY

BRENDAN WOODS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE

DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1969

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled,

THE PHOTOCHEMISTRY OF SOME FLUORINATED COMPOUNDS

submitted by Brendan Thomas Woods in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

H. E. Gunning, Supervisor

Otto P. Strausz
O. P. Strausz

W. A. Ayer
W. A. Ayer

P. Kebarle
P. Kebarle

K. B. Newbound

W A Sheppard
W. A. Sheppard,
External Examiner

August 20, 1969

ABSTRACT

The photolysis of perfluorovinylchloride led to its decomposition by two different modes. The first of these was formation of $\cdot C_2F_3$ and $\cdot Cl$. The second mode of decomposition was by fission of the double bond, which produced :CFCl and $:CF_2$. :CFCl reacted with the substrate forming 1,2-dichloroperfluorovinylcyclopropane and 3,3-dichloroperfluoropropene. $:CF_2$ reacted with the substrate yielding 1,4-perfluoropentadiene. When photolysis was carried out in the presence of isobutane a product of molecular formula $C_5F_2H_{10}$ was found. It is proposed that this arises by insertion of $:CF_2$ into a C-H bond of isobutane.

In the photolysis of 1,2-dichlorofluoroethylene, decomposition was principally by C-Cl bond fission. Some evidence was obtained for the formation of CFCl=C:.

1,2-Difluorochloroethylene, on photolysis, decomposed by three processes. These were:

(1) C-Cl bond fission
(2) Rupture of the double bond, yielding :CFH and :CFCl
(3) Elimination of HF and the formation of CFCl=C:.

In the photolysis of 1,1-difluorochloroethylene three modes of decomposition were observed. These were analogous to those found for the decomposition of

1,2-difluorochloroethylene.

On addition of isobutane to the system a product of molecular formula $C_5F_2H_{10}$, similar to that found in the photolysis of perfluorovinylchloride, was produced. Thus, the $:CF_2$ formed by rupture of the double bond in 1,1-difluorochloroethylene appears to insert into C-H bonds. The $CF_2=C:$, produced by elimination of HCl from 1,1-difluorochloroethylene, showed the same reactivity as that generated in other systems.

The photolysis of 1,3-perfluorobutadiene led to formation of $:CF_2$ and C_3F_4. Isomerisation of the substrate to perfluorocyclobutene, 2-perfluorobutyne and 1,2-perfluorobutadiene was also observed. In the photolysis of perfluorocyclobutene and 2-perfluorobutyne, analogous reactions to those of 1,3-perfluorobutadiene were found.

Perfluorocyclopentene was photolysed and three reaction processes were observed. These were:

(1) Formation of C_2F_4 and C_3F_4
(2) Formation of $:CF_2$ and perfluorocyclobutene
(3) Formation of perfluorovinylcyclopropane.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation for the assistance and direction given to him by Dr. H. E. Gunning and Dr. O. P. Strausz throughout the course of his work.

A special thanks goes to the author's colleagues for their helpful advice and criticism. Particular indebtedness is due to Dr. J. L. W. Jones who performed some of the experiments described in Chapter V.

The invaluable help of the technical staff is acknowledged. The assistance of Mr. W. A. Lehman is appreciated.

The financial assistance of the University of Alberta and the National Research Council is acknowledged.

The author would like to express his gratitude to his wife for her help and forbearance throughout the course of his studies.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Photochemistry is the study of the interaction of light and matter. Chemical change may be brought about by this interaction and this change is of primary interest in photochemical studies. Since most chemical changes require in excess of 40 kcal/mole the light absorbed must have such an energy content, i.e., its wavelength must be <7,000Å. If the species which one wishes to investigate does not absorb in this region of the spectrum, it is possible to use photosensitization as an alternative method of providing the required energy. In this case, an atom or molecule which absorbs in a suitable region is added to the system and the absorbing species can transfer its energy by collision to the molecule under investigation. In the gas phase the mercury atom is the most widely employed as a photosensitizer. In photosensitization it is possible to know exactly how much energy is in the excited species, whereas in direct photolysis, unless one employs a monochromatic source, variable amounts of energy are absorbed by the molecule. It should be noted however, that in photosensitization, when a reaction is taking place with more than one species present, the photosensitizing agent will transfer energy to all species present.

The photochemistry of olefins has received much study.

Excitation within the first singlet-singlet absorption band may be followed by a variety of fragmentation steps such as molecular or atomic hydrogen elimination or radical formation. Ethylene can only undergo the first two of these decomposition processes and is less complex than the others. The photochemistry of ethylene is dealt with in greater detail in the next section.

Photolysis and Photosensitization of Ethylene

The photolysis of ethylene has been studied by a number of workers (1,2,3). The overall mechanism of decomposition has been found to be the same at all wavelengths at which it has been examined and can be represented by the following scheme:

[1] $C_2H_4 \xrightarrow{h\nu} C_2H_4^*$

[2] $C_2H_4^* \longrightarrow CH_2C: + H_2$

[3] $\longrightarrow CH_2C: + H + H$

[4] $\longrightarrow HC{\equiv}CH + H_2$

[5] $\longrightarrow HC{\equiv}CH + H + H$

[6] $CH_2C: \longrightarrow HC{\equiv}CH$

A very small amount of decomposition to vinyl radicals and hydrogen atoms takes place. Approximately 60% of hydrogen is formed by molecular elimination of H_2 from one carbon atom, with formation of vinylidene which quickly isomerises to acetylene. At 1470Å, molecular elimination and formation of two hydrogen atoms are equally probable. However, at 1236Å, atomic hydrogen formation is favored. It was also shown by photolysis of trans-1,2-dideuteoetheylene, that in the excited state, free rotation around the C-C double bond of the molecule was probable.

$Hg(^3P_1)$ photosensitization of ethylene and deuterated ethylenes has been studied by a number of authors. Cvetanovic and Callear (4) have shown that the results can be explained by a mechanism as follows:

[7] $C_2H_4 + Hg(^3P_1) \longrightarrow C_2H_4{}^* + Hg(^1S_0)$

[8] $C_2H_4{}^* \longrightarrow C_2H_4{}^{**}$

[9] $C_2H_4{}^* + M \longrightarrow C_2H_4 + M$

[10] $C_2H_4{}^{**} \longrightarrow C_2H_2 + H_2$

[11] $C_2H_4{}^{**} + M \longrightarrow C_2H_4 + M$

They postulated that $C_2H_4{}^*$ was the first excited triplet state of ethylene and $C_2H_4{}^{**}$ was a triplet state of ethylidene. Support for the intervention of an ethylidene type of structure was found in the results obtained from the photosensitization of cis-1,2-dideuteroethylene (5). All possible acetylene and hydrogen molecules were found to be present and trans-1,2-dideuteroethylene and 1,1-dideuteroethylene were also formed. The yield of

1,1-dideuteroethylene increased initially with substrate pressure and then decreased. This shows that the state from which it is formed is being collisionally stabilized and, as the pressure is increased, the precursor of this state is being collisionally deactivated, confirming the mechanism as set out above.

It has been suggested, by analogy with the decomposition of the hot ethylene formed in the photolysis of ethane (6), that decomposition is in fact occurring from a vibrationally excited ground state ethylene. Thus, the ethylidene would be an intermediate in the crossover from the triplet to the ground state.

In the photosensitization of dideuteroethylenes by benzene (7), and Cd($^3P_1$) (8), isomerisation and molecular scrambling of hydrogens occurs, but decomposition is unimportant. Since, in both these cases, the sensitizer contains insufficient energy to form triplet ethylene with unchanged geometry, the energy transfer must be non-vertical, i.e. it must form triplet ethylene, in which the CH_2 groups are at right angles; for this configuration the energy difference between it and the ground state is $\sim$1.9 e.v. which is less than the energy in triplet benzene or Cd($^3P_1$).

Hunziker (7) has proposed the following reaction scheme to account for all triplet state sensitizations of dideuteroethylenes.

[12] $E + S^* \longrightarrow E^* + S$
[13] $E^* + M \longrightarrow E_c + E_t + M$
[14] $E^* \longrightarrow E^{**}$
[15] $E^{**} \longrightarrow E^*$
[16] $E^* + M \longrightarrow E_c + E_t + E_g + M$
[17] $E^{**} \longrightarrow E^{\ddagger}$
[18] $E^{\ddagger} + M \longrightarrow E_c + E_t + E_g + M$
[19] $E^{\ddagger} \longrightarrow C_2H_2 + H_2$

Where S is the sensitizer, E is any dideuteroethylene, E_c is cis-, E_t is trans- and E_g is gem-dideuteroethylene, E^* is triplet ethylene, E^{**} is triplet ethylidene and $E^{\ddagger}$ is vibrationally excited ground state ethylene.

Hunziker proposes that in $Cd(^3P_1)$ and benzene photosensitization that cross-over from E^{**} to $E^{\ddagger}$ is very slow and that, because of this, little or no decomposition occurs. However, since the rate of decomposition of vibrationally excited ground state ethylene, will depend on the energy content of the ethylene, it would be more correct to say that k_{19}/k_{18} will be very small in the case of Cd and benzene photosensitization.

The photochemistry of fluorinated olefins has not received much attention. Such studies should provide data of considerable interest since the chemical properties of the fluorocarbons show marked differences from their hydrogen containing analogues. In the next section these differences are discussed.

Physical and Chemical Properties of Fluorocarbons

The strengths of carbon-fluorine bonds are similar to those of carbon-hydrogen. Thus in CH_3F the C-F bond strength is 107 kcal (9). However as fluorination is increased the bond strengths are increased and bond lengths are shortened. It has been suggested (10) that this is due to an increase in the number of resonance structures as fluorination is increased. A molecular orbital treatment of fluoromethanes (11) has suggested that, in fact, the change in bond lengths and in bond strengths is due to a change in hybridization. Thus, the fluorine attracts electrons from the carbon and will attract the p-electrons preferentially, these being less tightly bound. In CH_3F the hybridization may be $sp^{2.85}$. As the number of fluorine atoms is increased, the partial withdrawal of p-electrons is increased and the hybridization in CF_4 could be $sp^{2.4}$. This would give a shorter bond and consequently increased bond strength.

Several factors appear to indicate that the double bonds of fluoroethylenes, and other olefins containing the $CF_2{=}C$ group, are considerably weaker than those of their hydrogen containing analogues. Patrick (12) has calculated the C=C bond energy to be 105 kcal/mole for C_2F_4 and 142 kcal/mole for ethylene. However, he points out in a later article (9), that there may be objections to his method of calculation which ignores changes in bond energy caused by change in bond character. It has been widely accepted that, because of the similarity of the bond stretching force constants of C_2F_4 and C_2H_4, their bond strengths must be very close. Patrick feels that, due to widely differing stretching frequencies, differences in force fields and contributions of interactions of non bonded atoms, care should be taken in comparing these constants. Certainly, in comparison to ethylene, the anomalously low heats of formation of C_2F_4 and of 1,1-difluoroethylene, and the greater heats of addition of H_2, Cl_2, and others to olefins containing the $CF_2{=}C$ group would tend to indicate a lowering of the double bond strengths in the fluoroethylenes. Thermodynamic calculations have been made in which it is confirmed that the double bond in C_2F_4 is weakened relative to that of ethylene (13).

The chemical behaviour of the fluoroethylenes is also indicative of a decreased π-electron density. For example, the relative rate of addition of CH_2 to fluoroethylenes is found to decrease by a factor of 1.8 for each fluorine substituent (14). This indicates a lowering of the π electron density which would be expected to weaken the double bond. The weakening of the double bond of C_2F_4, relative to ethylene, is also shown by the higher rate of addition of methyl radicals to C_2F_4 (15).

Spectroscopically, fluorination of ethylene appears to cause a shift in the absorption in the ultraviolet (u.v.) towards longer wavelengths. This is similar to the shifts found when hydrogen is replaced by any substituent which has lone pairs of non-bonded electrons which can be coupled by resonance with the π-electrons of the double bond (16). The inductive effect of the substituent has little influence on the "red shift", but, since it will be very large in the case of fluorine, it may cause an overall destabilization of the double bond relative to ethylene, even though the resonance effect tends to stabilize the double bond.

Despite their similarities in physical characteristics, such as bond strengths, boiling points, etc., the chemical behaviour of hydrocarbons and fluorocarbons show marked differences. Processes such as fluorine atom and molecular fluorine elimination, whose analogues occur readily in hydrocarbons, are not known to occur in fluorinated compounds. Migration of the fluorine atom, which was thought to occur only in exceptional radicals such as CF_3CH: (17), appears, from results found in the present study, to occur when sufficient energy is available, particularly in perfluorinated compounds. Other systems in which fluorine migration has been observed include the isomerisation of $(CH_3)_2C$: (18), Hg photosensitization of perfluorocyclopropene (19), and the isomerisation of products formed by addition of :CFH and CF_2=C: to the substrate in the photolysis of trifluoroethylene (20).

The elimination of HF from activated molecules has been studied by a number of workers (21 and references therein). In general, for activated fluoroalkanes, the following reactions can be written:

$$A^* \xrightarrow{k_e} \text{alkene} + HF$$

$$A^* + M \xrightarrow{k_d} A + M$$

Where A* is the energised fluoroalkane.

The ratio of k_e to k_d varies widely, depending on the alkane in question and the method of generation of the activated alkane. However, it is found that the activation energy for HF elimination decreases with α-fluoro-substitution. Thus, for HF elimination for CH_3CHF_2, E_a = 47 - 48 kcal/mole, whereas for CH_2FCH_2F, where the final product is the same, E_a has been found to be in the range 52 - 62 kcal/mole. This illustrates the strongly destabilizing effect of fluorine through its inductive effect, as this will be much more in evidence when both fluorine atoms are on the same carbon.

Another interesting example of the peculiarities of fluorine containing compounds is the elimination of $:CF_2$ from activated fluoro-cyclopropanes. The thermal decomposition of perfluorocyclopropane has been shown to proceed solely by elimination of $:CF_2$ (22). In contrast, the pyrolysis of cyclopropane leads only to isomerisation to propene. This is undoubtedly a reflection of both the relative instability of the perfluoroolefin and the stability of $:CF_2$ in comparison to $:CH_2$, as well as the relative difficulty of F atom shift. The pyrolysis of chlorofluorocyclopropanes has also been shown to proceed via elimination of $:CF_2$ (23). In the addition of $:CH_2$ to tetrafluoroethylene, the cyclopropane formed decomposed by elimination of $:CF_2$ unless collisionally stabilized (24). In contrast, $:CH_2$ addition to partially fluorinated ethylenes gives rise to vibrationally excited cyclopropanes, which are either stabilized or isomerise to propenes (14). This also illustrates the destabilization of the olefin with increasing fluorination.

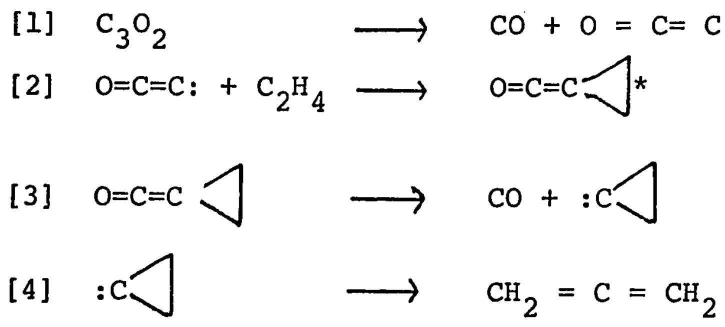
The photochemistry of the fluoroethylenes is considered in the next section.

The Mercury Photosensitization and Photolysis of Fluoroethylenes.

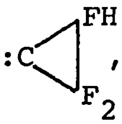
The $Hg(^3P_1)$ photosensitization of mono-, 1,1- and 1,2-di- and trifluoroethylene has been studied (25). In all these cases, it was found that decomposition occurred by HF elimination. However, there were some differences in each system. In vinyl fluoride, it was found that ϕ

(decomposition) was between 0.9 and 1.0. Little variation of ϕ (decomposition) with pressure was found, implying an excited state of lifetime 1.0×10^{-10} sec or shorter. Thus, it was not possible to decide, in this case, whether more than one excited state was involved in the decomposition mechanism. In the difluoroethylenes, it was found that ϕ° (decomposition) = 0.80. From the effects of pressure, it was deduced that there were two deactivable states in the decomposition sequence, the first state being the first excited triplet and the second a singlet, which could either be an ethylidene or a vibrationally excited ground state. Since ϕ° (decomposition) = 0.80, it was necessary to postulate decay of the triplet to some non product-forming state. The nature of this state could not be ascertained from the results obtained.

In trifluoroethylene, decomposition took place by geminal elimination of HF with formation of the carbene $CF_2=C:$. The latter reacted with the substrate to form 1,3-pentafluorobutadiene trifluoroallene and tetrafluoroethylene. The latter two products were formed by decomposition of the initially formed cyclopropane which eliminated $:CF_2$. The $:CF_2$ radicals combined to give tetrafluoroethylene. The butadiene was formed by rearrangement of the partially collisionally stabilized cyclopropane. The elimination of $:CF_2$ from the initially formed methylene cyclopropane has an analogy in a reaction found in the photolysis of C_3O_2 (26).

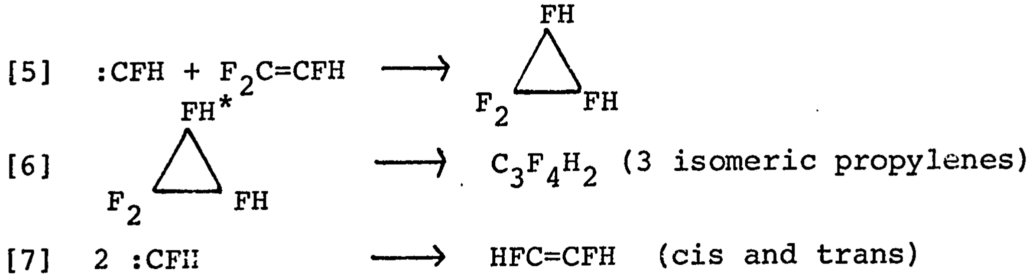


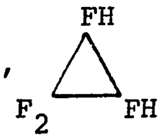
The CF_2=C: was also found to add to the double bond of olefins and to insert into carbon hydrogen bonds of alkanes and alkenes.

In the photolysis of trifluoroethylene (20), it was found that two different decomposition processes were occurring. The first, which was similar to that found for Hg($^3P_1$) photosensitization, generated CF_2=C: radicals. The reactions of CF_2=C: were found to be the same in this case as in photosensitization, with the exception that no pentafluorobutadiene was formed. Since the CF_2=C: will probably be formed containing more energy in photolysis, this is to be expected. The cyclopropylidene, formed by CF_2 elimination, gave allene and also rearranged to 1,3,3-trifluoropropyne. This is probably due to excess energy in the , resulting from a greater amount of energy in the precursor. In its reactivity with C-H bonds, the CF_2=C: displayed the same selectivity found in the photosensitization, showing that it is in the same electronic state.

The second mode of decomposition of trifluoroethylene was by fission of C=C bond with the consequent formation of :CFH and $:CF_2$.

The reactions of :CFH were as follows:



The cyclopropane, 

, was found at high pressures of added CF_4 and its yield was greater than that of the isomeric propenes in the absence of CF_4.

The ratio of the 1,2-difluoroethylenes to the $C_3F_4H_2$ products was about 2:1. From the above reaction scheme, this would imply that k_7 is very much greater than k_6. In their work on the reactions of monofluorocarbene with olefins in the gas phase, Yang and Rowland (27) did not appear to find any recombination products of :CHF, even in the absence of olefins. They found no rearrangement of the cyclopropanes formed by addition of :CHF to olefins. Thus, it would appear that the :CHF formed in the photolysis of C_2F_3H is more energetic than that formed in their system. Despite the probable lower affinity of C_2F_3H for

:CHF, it does not appear likely that k_7 should be so much larger than k_6. A more probable explanation for the formation of the 1,2-difluoroethylenes is that, as was found for the "hot" cyclopropane formed by addition of $:CH_2$ to tetrafluoroethylene (24), the cyclopropane formed by addition of :CFH to C_2F_3H can decompose by elimination of $:CF_2$. This would also explain the large amount of the cyclopropane found at the higher pressures of CF_4. No products attributable to the reaction of :CHF with alkanes were found. This is in agreement with the results of Yang and Rowland, who found no insertion of :CHF into C-H bonds.

The $:CF_2$ formed by fission of the C=C bond is also found to be reactive. Although no pentafluorocyclopropane, the product expected from reaction between $:CF_2$ and C_2F_3H, was found, tetrafluoroallene was a product in this system. The latter could arise by elimination of HF from the hot cyclopropane. Due to there being at least two or possibly three sources of $:CF_2$ in the system, it is difficult to know how much of the C_2F_4 results from recombination of $:CF_2$ formed in the primary process. However, if one accepts the mechanism postulated above, for formation of the 1,2-difluoroethylenes by elimination of $:CF_2$ from the hot adduct of :CHF to C_2F_3H, then the results obtained would indicate little or no recombination of $:CF_2$ which was formed by C=C bond fission. Most of this $:CF_2$ must be lost as polymer, as the yield of tetrafluoroallene is quite low. As will be discussed in a later chapter, $:CF_2$ is relatively inert. However, in this instance, it is probable that the $:CF_2$ is vibrationally excited and this would explain its reactivity.

$:CHF$ and $:CF_2$ display marked differences from $:CH_2$ in their reactivities. In the next section the reactions of the halogenated carbenes are discussed.

Reactions of halogen containing carbenes

A comprehensive review of the reactions of halogen containing carbenes has been given by Kirmse (28), however it is of interest to review briefly some of the results obtained.

In general most of these carbenes have been generated in solution. The major source of the carbenes is hydrolysis of partially or fully halogenated compounds, such as haloforms, acetates or acetones. There has been some debate as to whether the reactive species in these systems is not in fact a trihalocarbanion and not a carbene. Studies of the effects of added Cl^- ion in the hydrolysis of chloroform indicate that the rate determining step is

$$CCl_3^- \longrightarrow :CCl_2 + Cl^-$$

and not

$$CCl_3^- + H_2O \longrightarrow H_2O^{+}\text{--}\bar{C}Cl_2 + Cl^-$$

It is expected that this will be true for reactions with other nucleophiles such as olefins. In its reactions with olefins, $:CCl_2$, which has received the most study of all the dihalocarbenes, adds readily to the double bond to form a cyclopropane. The reaction is stereospecific, indicating that the carbene is in a singlet state.

The relative reactivities of the halocarbenes toward olefins have been studied (27 and refs. therein), (29). The reactivity of the carbene increases as the nucleophilicity of the olefin increases, indicating the electrophilic nature of the carbene. The selectivity of the carbene increases in the order $:CHBr < :CHCl < :CHF < :CBr_2 < :CCl_2 < :CFCl$, and :CFCl is by far the most selective. The rate of reaction of :CFCl with 2,3-dimethylbutene is 31 times that of its rate of reaction with isobutene. For $:CCl_2$ this ratio is 6.5:1. Thus, substitution of fluorine greatly increases the electrophilicity of the carbene. It has been reported (30) that $:CF_2$ reacts 12.8 times more radpily with isobutene than with cis-2-butene. For :CFCl the comparative figure is seven. Thus, $:CF_2$ would appear to be the least electrophilic of the halocarbenes. The reactions of $:CF_2$ and :CFCl will be discussed in more detail in a later chapter.

Aims of the present study.

The photochemistry of mixed haloethylenes has not received any study. It is to be expected that these will behave differently from both ethylene and the fluorinated ethylenes.

By analogy with the photolysis of C_2F_3H it was hoped that photolysis of chlorofluoroethylenes would lead to decomposition of the substrate by either C=C bond fission or HX elimination, where X is Cl or F.

The first of these processes would lead to formation of various halocarbenes, the study of whose reactions in the gas phase would be of great interest as comparatively little work has been done in this field.

The second process would lead to formation of $CF_2=C:$ or CFCl=C: depending on the starting material. The latter α-unsaturated carbene is not known and so a study of its reactions would be of interest. Although $CF_2=C:$ has been generated previously by HF elimination from C_2F_3H in the present instance its precursor would generate $CF_2=C:$ by HCl elimination. It would be possible to compare the reactivities of this carbene generated by two different means. The photolysis of perfluorinated olefins has not been previously studied although some work has been done on the $Hg(^3P_1)$ photosensitization of compounds such as C_2F_4 (31), C_3F_6 (32), 1,3-perfluorobutadiene and perfluorocyclobutene (33). It would be of value to compare the processes which occur from the first excited singlet state of these compounds with those found to occur from the triplet state formed in Hg($^3P_1$) photosensitization.

CHAPTER II

EXPERIMENTAL

APPARATUS

High Vacuum System

A conventional high vacuum apparatus constructed from pyrex was employed in the course of this investigation. The system was evacuated by means of a mercury diffusion pump connected to a Welch Duoseal Model 1405 mechanical pump. The storage system, distillation train and cell assembly are illustrated in Fig. I. This section was kept grease free, to avoid absorption of substrates or products by the grease, by using Delmar float valves, Hoke and Republic valves. Substrate pressures were measured on a mercury manometer. LKB tubes connected to a Consolidated Vacuum Corp. Autovac gauge were used to monitor pressures <1 torr. Following distillation, samples could be measured in the gas burette or transferred to the gas chromatography (g.c.) sampling system.

Cell and Lamp Assembly

In the experiments described in Chapters III & IV a quartz cylindrical cell, 5 cm in diameter by 10 cm in length, was used in conjunction with a circulating pump as illustrated in Fig. 2. This system allows for faster mixing of gas mixtures and also helps to minimize deposition of polymer on the cell face.

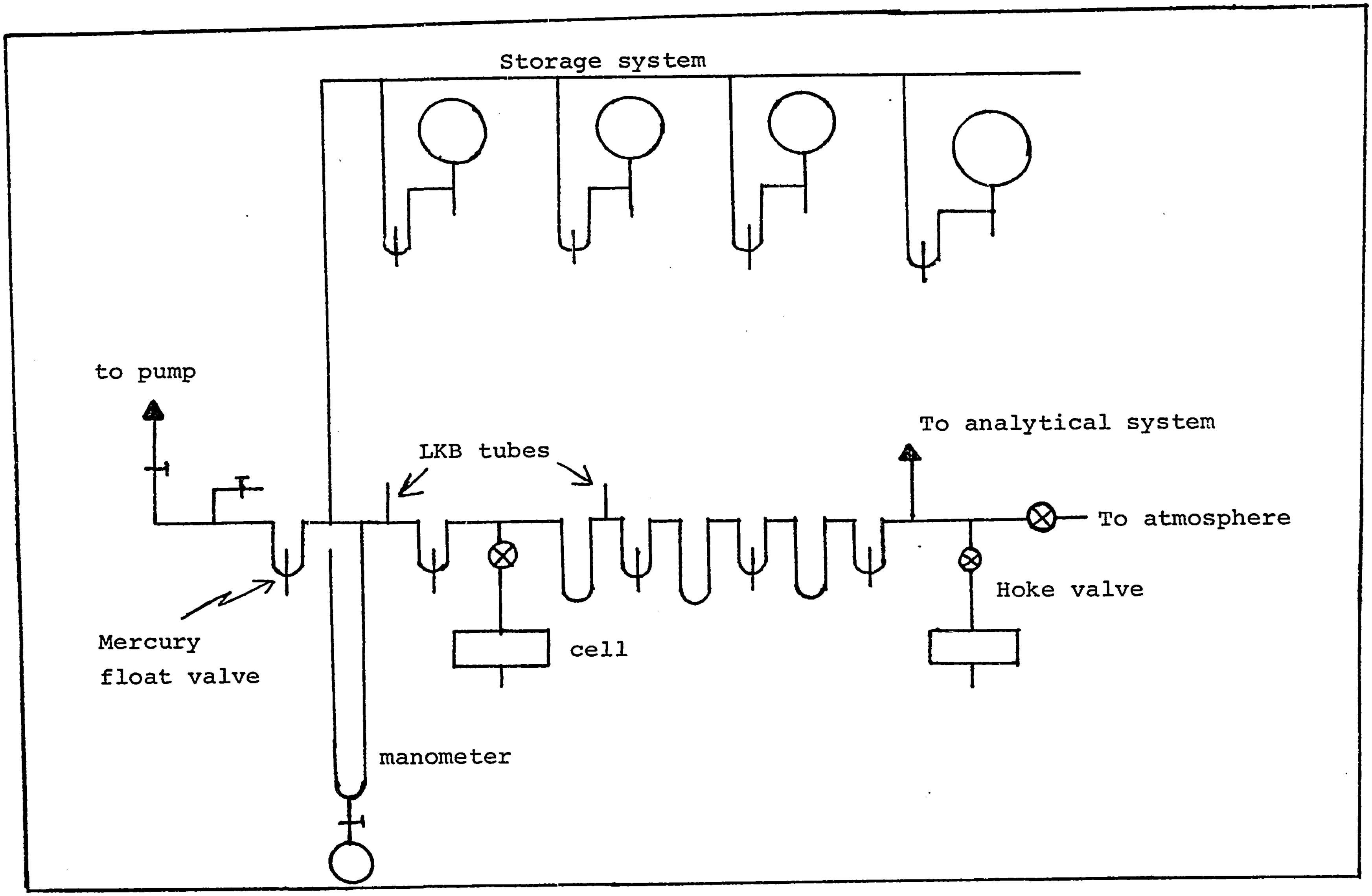


Fig. 1. Cell and distillation train.

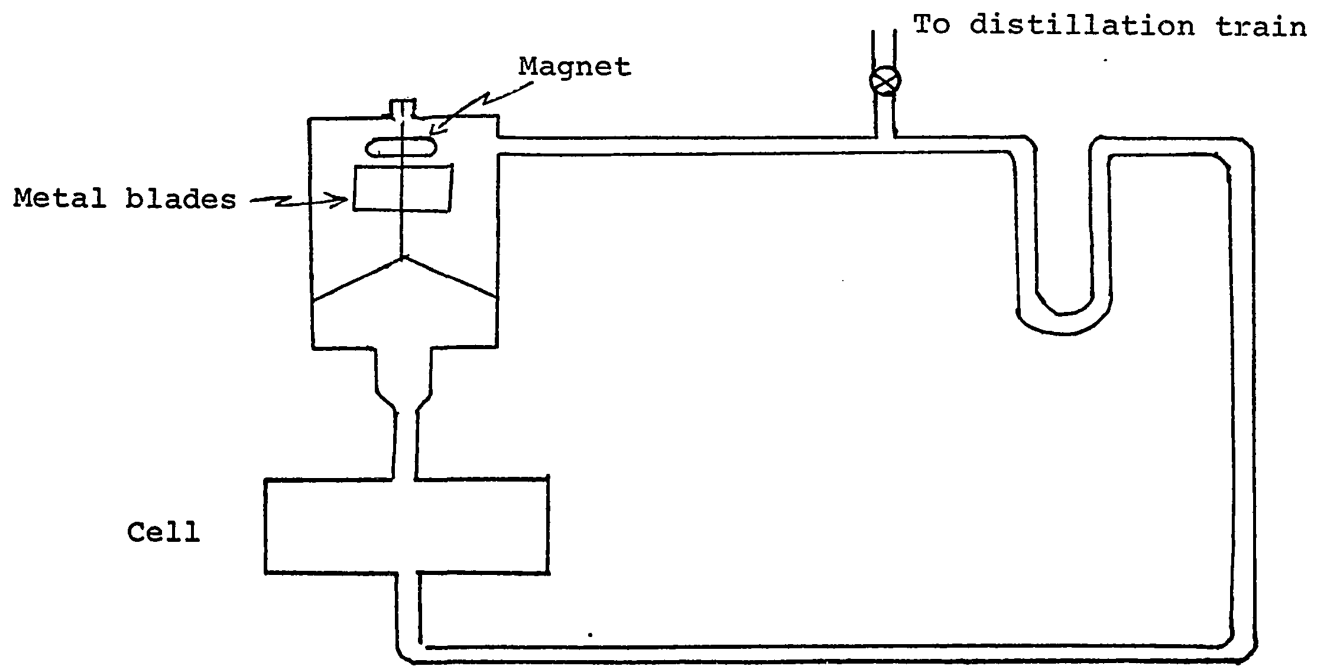


Fig. 2. Circulation pump and cell.

In the remainder of the experiments a static photolytic system was employed. The cells were either 5 cm x 5 cm or 5 cm x 2 cm. The use of cells of small volume was necessary since the products of photolysis could not be separated from the starting material by distillation and the total mixture of substrate and products had to be analysed by g.c. Thus it was necessary to use as small a quantity of substance as was feasible.

The light sources used were a Hanovia 687A45 low pressure mercury resonance arc and a Hanovia, type SH, medium pressure mercury arc. The low pressure resonance arc was used in conjunction with a 7910 vycor filter in investigating Hg $^3P_1$ photosensitization. The light from the medium pressure arc, used in direct photolysis, was not filtered as most of the compounds being investigated did not absorb light above 2300Å. In the experiments described in chapter VI a cowling, through which air could be blown, was attached to the lamp to enable it to be brought close to the cell, increasing the light intensity, without causing the cell to heat up.

ANALYTICAL ASSEMBLY

The analytical assembly is illustrated in Fig. 3. The gas burette was used to measure those products which could be isolated from the reaction mixture. It was also employed to measure out exact amounts of sample to calibrate

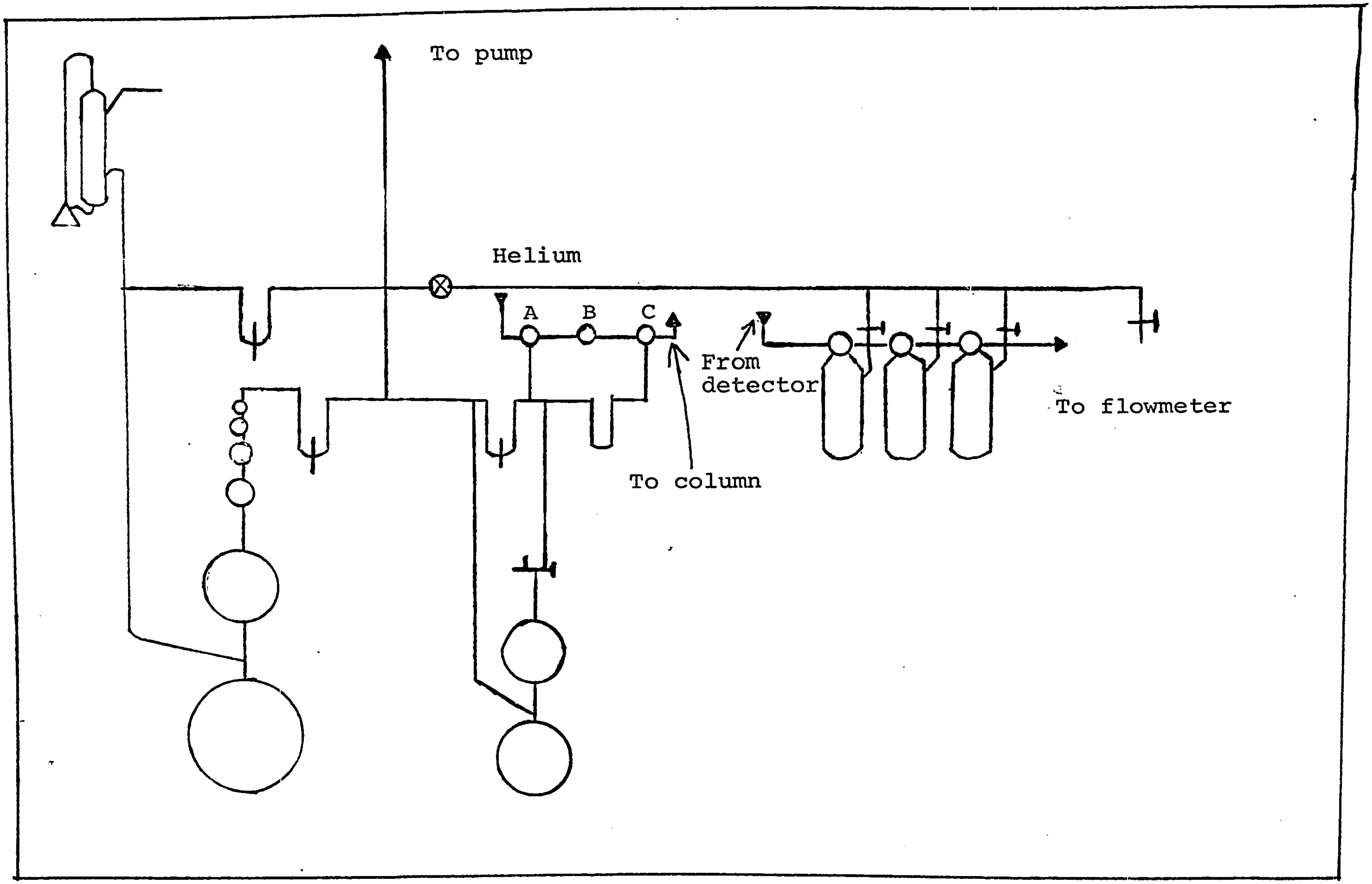


Fig. 3. Analytical system.

the thermal conductivity unit of the gas chromatograph. Where authentic samples of products were available, these were used for calibration. If these were not readily available, a number of runs were carried out to generate a sufficient amount of product to enable a calibration to be carried out. This was then isolated by g.c.

Gas chromatography was employed for qualitative and quantitative analysis and for the purification of some starting materials. The g.c. unit was made up of a Gow Mac Model TR II B hot wire detector to which power was supplied by a Gow Mac Model 9999-C power supply. A Sargent Model S-72180 recording potentiometer was connected to the detector to record the signals. The recorder was fitted with an attenuator with ranges XI, X3, X10 etc. The filament current in the power supply was maintained at 250 ma. The detector wire was thermostated at 250° F. Helium (Matheson) was used as a carrier gas. This was purified by passing it through a molecular sieve column. The flow rate was measured on an oil manometer in parallel with a short capillary tube. This was calibrated with a soap-bubble flowmeter.

PROCEDURE

MATERIALS AND PURIFICATION

Table 1 gives a list of the materials used in the course of this work. All materials were degassed at -196°. Where

TABLE 1

Materials Used

Material	Source	Grade & Purity	Purification
Nitric Oxide	Matheson	99%	Distilled at -183°
Isobutane	Phillips	Research 99.9%	None
Trifluorochloroethylene	Columbia	Research	Distilled at -104°
1,2-Dichlorofluoroethylene	Columbia	Research	Distilled at -78°
1,2-Difluorochloroethylene	Columbia	Research	Degassed at -130° Distilled at -105°
1,1-Difluorochloroethylene	Columbia	Research	Degassed at -130° Distilled at -105°
Tetrafluoroethylene	Peninsular	Inhibited	Preparative Gas Chromatography
1,3-perfluorobutadiene	Peninsular		Preparative Gas Chromatography
Perfluorocyclobutene	Peninsular		Preparative Gas Chromatography
2-perfluorobutyne	Columbia		Preparative Gas Chromatography
Perfluorocyclopentene	Pierce Chemical		Preparative Gas Chromatography

purification by g.c. was necessary, the material was first distilled at a convenient temperature (that is when distillation could be completed in a relatively short time) to remove as much impurity as was possible. Aliquots of the distillate were admitted to the g.c. sampler and the substrate fraction was trapped out following separation.

EXPERIMENTAL PROCEDURE

The reactant pressures were measured on a mercury manometer. Where only a single reactant was involved, the Hoke valve on the cell was closed following the pressure reading and the reactant photolysed in situ. In the case where mixtures were involved, it was necessary to transfer the first reactant from the cell to a trap at -196° to allow measurement of the second reactant. When the second reactant had been measured out it was frozen down into a cold finger at -196°. The premeasured amount of first reactant was then distilled into the cold finger. The mixture was allowed to warm up and equilibrate for one hour. Lamps were also allowed to warm up for one hour.

Following photolysis the mixture from the cell was transferred to the distillation train. Products, which could be separated from the reactants by low temperature distillation, were transferred to the g.c. sampling system for analysis. The reactants were then removed by distillation, if possible, and the remaining fraction was analysed by g.c.

For g.c. analysis the fraction to be analysed was distilled into the u-trap of the g.c. sample inlet. The mercury in the toepler pump and float valve was raised and helium was admitted by opening the hoke valve A. (Fig 3). The liquid nitrogen was then removed from the u-trap and, when this had warmed to room temperature, Hoke valve B was closed and valves A & C were opened simultaneously allowing helium to flow through. When it was necessary to isolate a sample from the mixture for analysis or any other purpose, this was done by allowing the helium to flow through a trap (downstream from the column and detector) which was kept at -196°. This trap was connected to the system by means of a four-way stopcock and could thus be open or closed to helium flow. By opening and closing the stopcock at the appropriate time, the sample could be isolated without contamination. A list of columns used and the retention times of the principal products is shown in Table 2.

TABLE 2

G. C. Operating Conditions and Retention Times

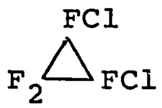
Column	Flow Rate (ml/min)	Temperature °C	Retention Time (min)	
High Activity Silica gel (6 ft)	60 ml/min	48°	C_2F_4	7.9
			C_2F_3H	21.6
20% Mineral Oil on Fire-brick (20 ft)	60 ml/min	25°	1,4-perfluoropentadiene	5.2
				16.2
			$CFCl_2-CF=CF_2$	19.7
			$CF_2=CF-CF-Cl_2$	39.7
			$CF_2=CF-CF$ CFClH	13.5
			CFH=CF-CF=CFH isomers	10.6 12.8

TABLE 2 (continued)

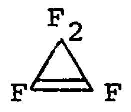
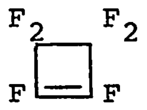
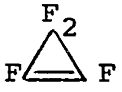
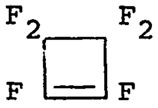
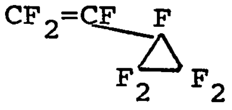
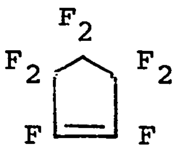
Column	Flow Rate ml/min	Temperature °C	Retention Time (mins)	
20% Mineral Oil on Firebrick (20 ft)	75	25°	CF_2=CH-CF_2-CH=CF_2	20.3
			CF_2=CH-CF_2-$CHCL_2$	48.0
			$C_5F_2H_{10}$	15.5
			$C_6F_2H_{10}$ (isomers)	28.1 31.4
30% Kel-F3 on Firebrick (12 ft)	40	0°	C_2F_4	3.8
			CF_3-C≡CF	4.8
			CF_3C≡CCF_3	5.2
				7.4
			CF_2=C=CF-CF_3	8.8
				11.4
			CF_2=CF-CF=CF_2	16.0

TABLE (continued)

Column	Flow Rate ml/min	Temperature	Retention Time (min)	
30% Kel-F3 on Firebrick	60	0°	C_2F_4	3.6
			$CF_3C\equiv CF$	4.7
			$CF_2=C=CF_2$	6.0
				7.7
				12.7
				17.1
				34.5

CHAPTER III

THE MERCURY PHOTOSENSITIZATION & PHOTOLYSIS OF PERFLUOROVINYLCHLORIDE

RESULTS

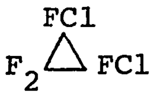
In the Hg $^3P_1$ photosensitization of perfluorovinylchloride the only product found was C_4F_6, which was identified by mass spectrometry. A large amount of white substance was seen to be formed in the photolytic system. This presumably was Hg_2Cl_2.

In photolysis the following products were found. Tetrafluoroethylene (C_2F_4), 1,4-perfluoropentadiene (C_5F_8), 1,2-dichloroperfluorocyclopropane, 1,1-dichloroperfluoropropene 4,4-dichloroperfluorobut-1-ene. C_2F_4 was identified by mass spectrometry and by comparison of its retention time with that of authentic C_2F_4. C_5F_8 was identified by its mass and I.R. spectra. The I.R. Spectrum showed a strong absorption at 1775 cm^{-1}. This can be attributed to the stretching vibration of a perfluorovinyl group (34). If this were a conjugated diene one would expect more complex absorption for C=C stretching. In comparison 1,3-perfluorobutadiene, shows C=C stretching absorption at 1766 cm^{-1} and 1796 cm^{-1} (35).

The dichlorocyclopropane was identified by mass spectral, I.R. and N.M.R. analysis. The I.R. spectrum showed no absorption attributable to C=C stretching. A strong absorption was observed at 1045cm^{-1}. In a series of substituted cyclopropanes, it was shown that the strong absorption due to ring deformation occurred between $1000cm^{-1}$ and $1055cm^{-1}$ (36). In the compound 1,1-difluoroperchlorocyclopropane a very strong absorption was observed at $1009cm^{-1}$ (37). Thus the absorption at $1045cm^{-1}$ in the present case can be attributed to ring deformation in the cyclopropane. The F^{19} N.M.R. spectrum showed five sets of multiplets. Three of these can be assigned to the cis-dichloro and two to the trans-dichlorocyclopropane. A previously published F^{19} N.M.R. of a mixture of these compounds showed the same pattern (38).

Dichloropropene was identified by its mass spectrum The mass spectrum was very similar to that of the dichlorocyclopropane but the I.R. spectrum showed strong absorption at $1790cm^{-1}$. Since this is characteristic of the CF_2=CF stretching. frequency this compound was assigned the structure $CF_2=CFCFCl_2$.

I.R. spectroscopy and mass spectrometry were used to identify dichlorobutene as one of the products. The mass spectrum showed the molecular formula to be $C_4F_6Cl_2$. The largest peak in the mass spectrum was 131 from the fragment C_3F_5. This would indicate that both Cl atoms are on the same terminal carbon. The I.R. spectrum showed strong C=C stretching absorptions at $1790cm^{-1}$, again, characteristic of the perfluorovinyl system. Thus $CF_2=CF-CF_2-CFCl_2$ would seem to be the most likely structure. A product tentatively identified as C_6F_9Cl by mass spectrometry was also found. A large amount of polymer which could only be removed with HF was formed in the cell during each run.

Table 3 shows product yields at various pressures. The ratio $CF_2{=}CF{-}CFCl_2$ /  $F_2\overset{FCl}{\triangle}FCl$ is plotted in Fig. 4.

Photolysis of Perfluorovinylchloride in the presence of Isobutane

Two new products were found in these runs. These were identified from their mass spectra as $C_5F_2H_{10}$ and C_4F_6HCl. The products non-condensable at -169° were found to be a mixture of C_2F_4 and C_2F_3H with the latter predominating especially at higher pressures. The yield of perfluoro-1,4-pentadiene was very much decreased also. In Table 4 the variation in the yields of the products with isobutane pressure is shown and is plotted in Fig. 5. When 100μ torr of NO was added to the system at high pressure, it was found that only dichloroperfluorocyclopropane and $C_5F_2H_{10}$ were present. Although their overall yield had decreased, their ratio remained constant. These results are shown below.

P C_2F_3Cl 23 torr P Isobutane 106 torr

NO (torr x 10^{-3})	 $F_2\overset{FCl}{\triangle}FCl$ $+CFCl_2{-}CF{=}CF_2$ μmoles	$C_5F_2H_{10}$ μmoles
0	2.5	2.4
100	1.7	1.6

TABLE 3

Product Yields as a Function of Substrate Pressure in the Photolysis of C_2F_3Cl

P C_2F_3Cl(torr)	C_5F_8		CF_2=CF-$CFCl_2$	C_2F_4
10	1.08	5.2	1.1	.98
30	2.5	11.2	1.5	Not measured
58	3.0	14.2	1.6	" "
60	Not measured	15.45	1.7	" "
100	4.6	19.8	1.8	3.45
150	4.6	20.2	1.8	Not measured

All runs were of 60 minutes duration. Product yields in μmoles.

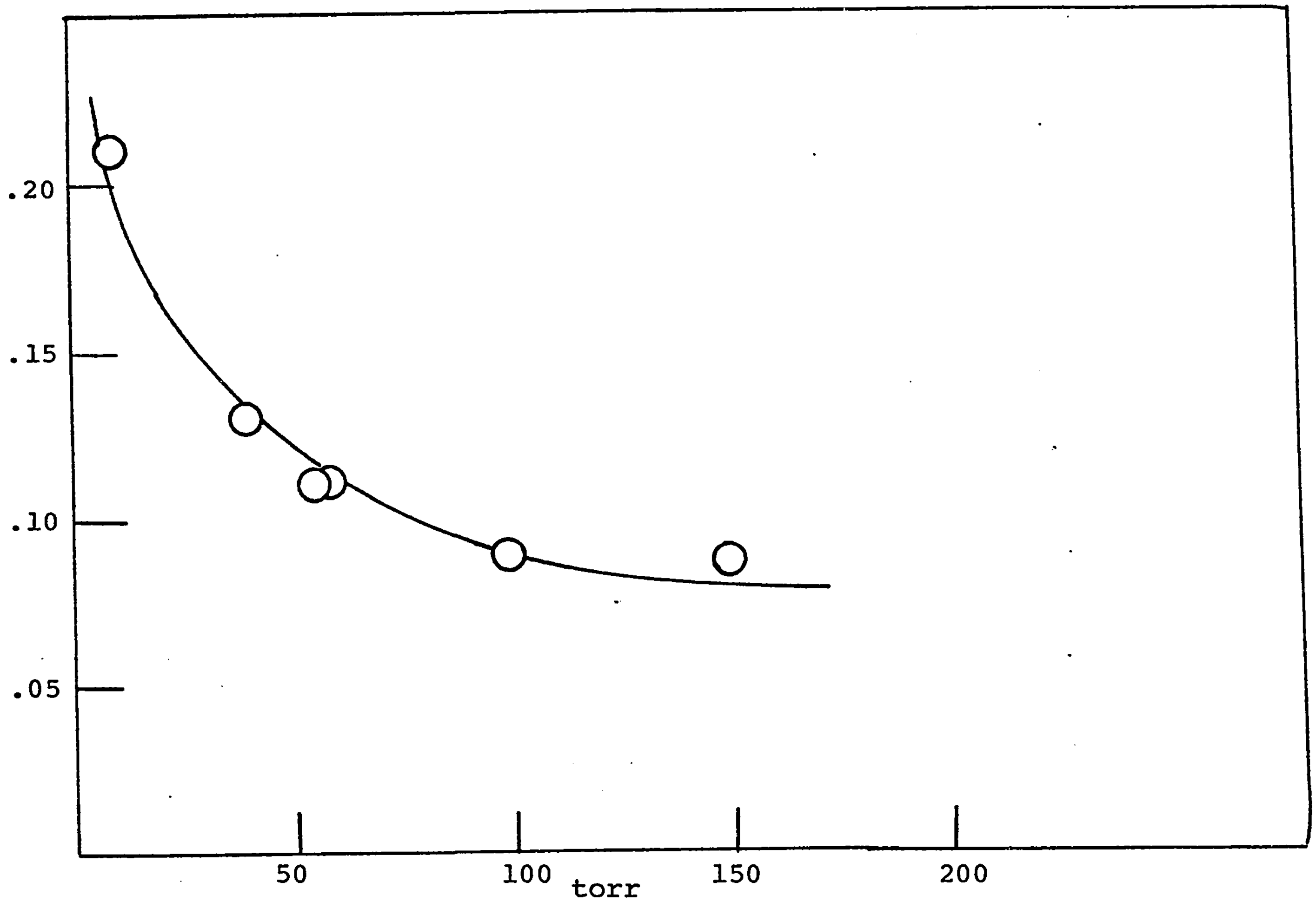


Fig. 4. Ratio of $CF_2=CF-CFCl_2$/ as a function of substrate pressure in the photolysis of C_2F_3Cl

TABLE 4

Product Yields as a function of Isobutane Pressure in the Photolysis of C_2F_3Cl

P C_4H_{10} (torr)	 + CF_2=CF-$CFCl_2$ (μmoles)	$C_5F_2H_{10}$ (μ moles)	C_4F_6ClH (μ moles)
0	27.5	0	0
102	12.6	5.05	7.95
202	11	8.2	7.0
290	9.9	9.5	6.8

Substrate pressure = 104 torr.

All runs of 60 minutes duration.

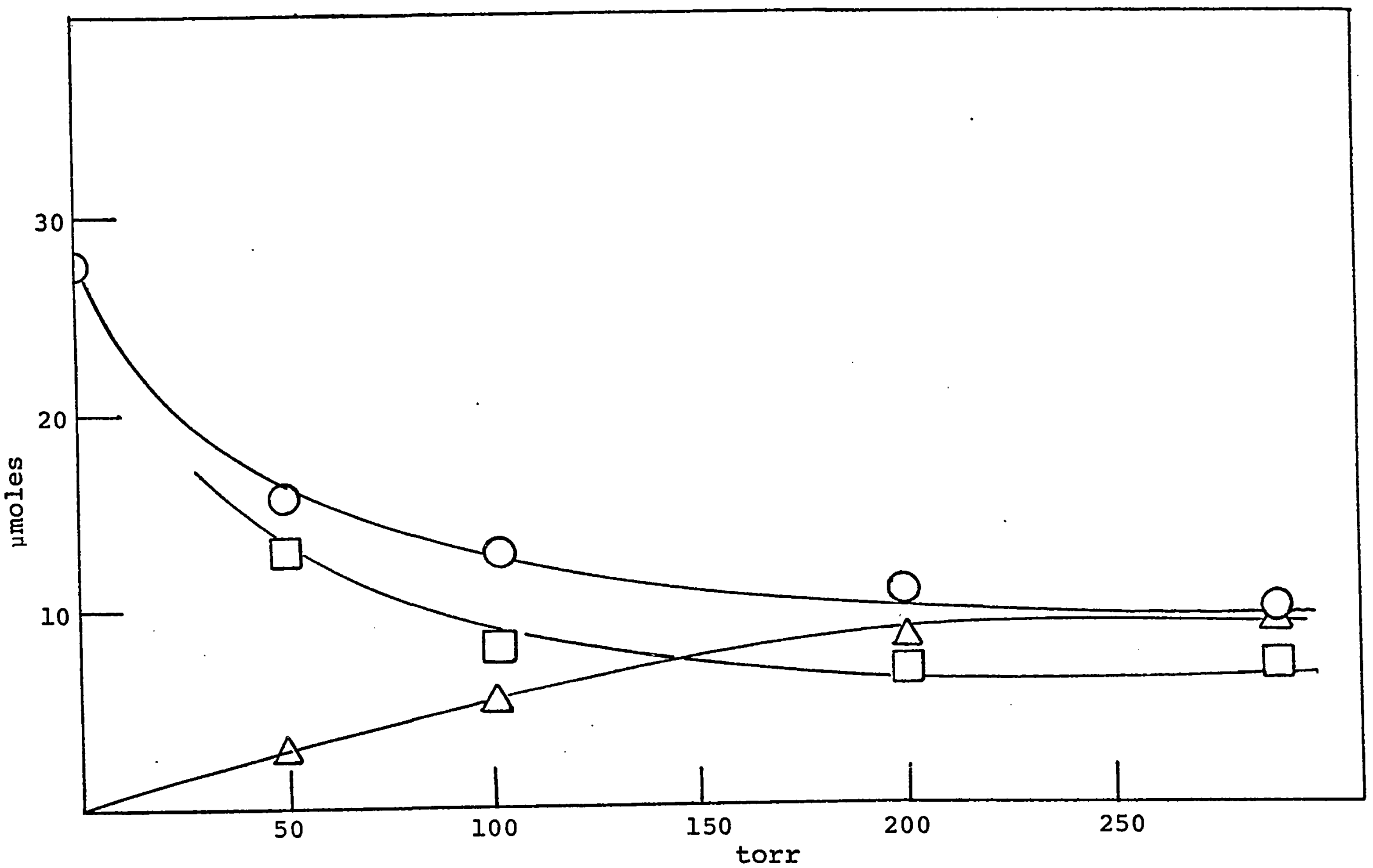


Fig. 5. Product yields as a function of added isobutene pressure in the photolysis of C_2F_3Cl.

○ $\Sigma C_3F_4Cl_2$ ☐ C_4F_6ClH △ $C_5F_2H_{10}$

DISCUSSION

MERCURY PHOTOSENSITIZATION OF C_2F_3Cl

The following mechanism explains the products found in this reaction:

$$[1] \quad Hg + h\nu \longrightarrow Hg^*$$

$$[2] \quad C_2F_3Cl + Hg^* \longrightarrow C_2F_3Cl^* + Hg$$

$$\longrightarrow \cdot C_2F_3 + \cdot Cl + Hg \text{ or } \cdot C_2F_3 + HgCl$$

$$[3] \quad C_2F_3Cl^* \longrightarrow \cdot C_2F_3 + \cdot Cl$$

$$[4] \quad 2C_2F_3 \longrightarrow C_4F_6$$

$$[5] \quad Hg + Cl \longrightarrow HgCl$$

$$[6] \quad 2HgCl \longrightarrow Hg_2Cl_2$$

It was shown (39) in the Hg photosensitization of vinyl chloride that a similar mechanism was operative. In that case the excited C_2H_3Cl could decompose by elimination of HCl and formation of acetylene. No such decomposition is possible in the case of perfluorovinylchloride. It was found with vinyl chloride that 55% of quenching occurred at the C-Cl bond. As perfluorination greatly reduces the quenching cross section of the $C{=}C$ π-bond (for example for $C_2H_4\ \sigma_Q^{\ 2}=26$ and for $C_2F_4\ \sigma_Q^{\ 2}= 7.9$),it is expected that in the present case quenching will occur primarily at the C-Cl site. Thus the major process will be C-Cl fission leading to formation of $C_2F_3\cdot$ + $Cl\cdot$ and the mechanism above will be operative.

PHOTOLYSIS OF C_2F_3Cl

The following reactions are proposed to account for the products observed.

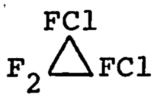
[7] $C_2F_3Cl + h\nu \longrightarrow C_2F_3Cl^*$

[8a] $C_2F_3Cl^* \longrightarrow :CF_2 + :CFCl$

[8b] $\longrightarrow \cdot C_2F_3 + \cdot Cl$

[9] $:CFCl + C_2F_3Cl \longrightarrow C_3F_4Cl_2^*$

[10] $C_3F_4Cl_2^* \longrightarrow CF_2{=}CF{-}CFCl_2$

[11] $+ M \longrightarrow$ 

[12] $:CF_2 + C_2F_3Cl \longrightarrow C_3F_5Cl^*$

[13] $C_3F_5Cl^* \longrightarrow \cdot C_3F_5 + \cdot Cl$

[14] $\longrightarrow$ polymer

[15] $\cdot C_3F_5 + C_2F_3Cl \longrightarrow \cdot C_5F_8Cl$

[16] $\cdot C_5F_8Cl \longrightarrow C_5F_8 + \cdot Cl$

[17] $\cdot C_2F_3 + C_2F_3Cl \longrightarrow \cdot C_4F_6Cl$

[18] $\cdot C_4F_6Cl + \cdot Cl \longrightarrow C_4F_6Cl_2$

[19] $\cdot C_4F_6Cl + \cdot C_2F_3 \longrightarrow C_6F_9Cl$

[20] $\cdot Cl + C_2F_3Cl \longrightarrow \cdot C_2F_3Cl_2$

[21] $\cdot C_2F_3Cl_2 + \cdot C_2F_3 \longrightarrow C_4F_6Cl_2$

[22] $2CF_2 \longrightarrow C_2F_4$

The following reactions are proposed to explain the products found when C_2F_3Cl was photolysed in the presence of isobutane.

[23] $:CF_2 + C_4H_{10} \longrightarrow C_5F_2H_{10}$

[24] $\cdot C_2F_3 + C_4H_{10} \longrightarrow C_2F_3H + \cdot C_4H_9$

[25] $\cdot C_2F_3 + C_2F_3Cl \longrightarrow \cdot C_4F_6Cl$

[26] $\cdot C_4F_6Cl + C_4H_{10} \longrightarrow C_4F_6ClH + \cdot C_4H_9$

[27] $C_2F_3Cl^* + C_4H_{10} \longrightarrow C_2F_3Cl + C_4H_{10}$

The last reaction is proposed to account for the decrease in product yield with increasing pressure of isobutane.

Since there are four radical species produced,the reactions of each are dealt with separately in the following sections.

REACTIONS OF :CFCl

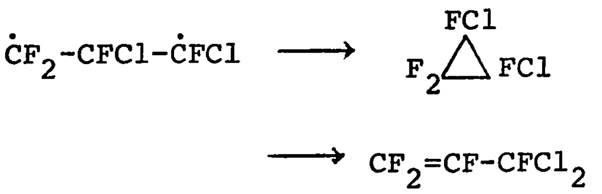
Two products attributable to the reaction of :CFCl with the substrate are found, 1,2-dichloroperfluorocyclopropane and 3,3-dichloroperfluoropropene. As can be seen from Fig.4 the ratio of propene to cyclopropane decreases with pressure but seems to level off at ∿ .09 at high pressure. Two explanations of this phenomenon are possible. If :CFCl is in a singlet electronic state, it can either add to the double bond forming the cyclopropane, or insert into C-Cl bond giving the propane. The cyclopropane will be vibrationally excited and at low pressures can isomerise to the propene. The shift of a Cl atom will probably be favored as it is a lower energy process than F atom shift. At high pressures the "hot" cyclopropane will be completely collisionally deactivated and the final ratio of propene to cyclopropane will represent the ratio of the rate of insertion to the rate of addition to the double bond.

Two things militate against the former mode of reaction. Firstly,if insertion into the C-Cl bond is occurring it would be expected that in the presence of isobutane some products attributable to insertion of :CFCl into the C-H bonds of the paraffin would be found. As insertion into C-H should be faster than insertion into C-Cl, due to steric hindrance in the latter case, one would expect the products from the reaction with isobutane to be favored. None of these did appear on addition of isobutane. Secondly, it was shown that the reaction of methylene with C-Cl bonds in solution, which appears to be an insertion process, is in fact the abstraction of a Cl atom followed by recombination of the two radicals (40). In the gas phase the two radicals would not recombine so readily as there is no solvent cage. The same type of mechanism would be expected for reaction of :CFCl with a C-Cl bond,particularly in view of the steric factor.

A more viable alternative is that the initial addition of :CFCl to the substrate yields a substituted trimethylene biradical. This biradical can then either ring close with the formation of the cyclopropane or undergo a chlorine shift to give the propylene.

Thus:

$$:CFCl + CF_2{=}CFCl \longrightarrow \dot{C}F_2\text{-}CFCl\text{-}\dot{C}FCl$$



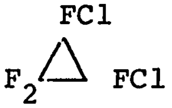
The initially formed adduct in the reaction of methylene with ethylene has been the source of a good deal of speculation. Skell and Woodworth (41) proposed that, since the addition of $:CH_2{}^1$ to an olefin was stereospecific, addition took place by the concerted formation of two bonds yielding a cyclopropane without formation of an intermediate. It was assumed, since $:CH_2{}^3$ addition was non-stereospecific, that the initially formed adduct was a trimethylene species in which rotation could take place. Cvetanovic et al (42) have shown that a trimethylene species is in fact formed on addition of $:CH_2{}^3$ to ethylene. This species can decompose, isomerise or form the cyclopropane by ring closure. Hoffmann (43) has shown, by calculation, that addition of $:CH_2{}^1$ forms a singlet trimethylene in which there is strong interaction between the terminal carbons. Thus, there is a large barrier to rotation in this species and this trimethylene goes rapidly to cyclopropane. The $:CH_2{}^3$, on addition forms a trimethylene species in which there is no barrier to rotation and thus, its addition reactions will be non-stereospecific.

In the present case, there is no indication of whether

:CFCl is in a singlet or triplet state. If it is in a singlet state, it is possible that the trimethylene would not be of the same type as that formed in the addition of $:CH_2{}^1$ to ethylene. Repulsion between the chlorine and fluorine atoms would tend to cause a fairly large CCC bond angle, reducing the interaction between the terminal carbons. This trimethylene would be more akin to the one formed in the addition of $:CH_2{}^3$ to ethylene, enabling it to isomerise or ring close. Since the yield of cyclopropane and propylene increases with pressure it would seem that some decomposition of the intermediate is taking place at lower pressure. Decomposition would probably be by loss of a chlorine atom and the resultant radical could then react with the substrate, leading to polymer formation. If :CFCl is in a triplet state, then presumably a triplet trimethylene is initially formed. This can either ring close or isomerize to the propene. If :CFCl is in a triplet state this would necessitate decomposition of C_2F_3Cl taking place from an excited triplet as the $:CF_2$ appears to be in a singlet state.

:CFCl has been studied in solution by a number of workers. (44 and references therein). It has been found to add readily to the double bonds of olefins giving 1,1-fluorochlorocyclopropanes. Moss and Gerstl (29,44) studied the reactivity of :CFCl with a number of methyl substututed ethylenes and found that the reactivity is related to the nucleophilicity of the double bond. Thus, :CFCl reacts with tetramethylethylene thirty-one times as fast as with isobutene. They have also shown that the formation of the cyclopropane with the Cl atom syn to the greatest number of CH_3 groups is favored. This is explained on the following basis. In the transition state the methyl groups of the olefin acquire a slight positive charge and will interact with the substituent on the carbene which eventually is syn to them in the resultant cyclopropane. In this case, the more polarisable of the substituents on the carbene will interact more readily with the methyl groups. In the case of :CFCl, this effect counteracts the steric factors which would favor the Cl being syn to the least possible number of methyl groups, since Cl is more polarisable than F.

In the present case, the ratio of cis-dichlorocyclopropane to trans-dichlorocyclopropane was ∿ 2:1. If the same type of transition state is formed in the gas phase as in the liquid phase we can rationalise the favorability of formation of the cis isomer as follows. The substituents on the olefin will tend to acquire a positive charge. Since Cl is less electronegative than F, the Cl atom will tend to acquire the greatest amount of positive charge. Thus, as in the above case it will interact with the more polarisable of substituents on the carbene which is adding to the double bond. The Cl atom is more polarisable so formation of the cis-dichlorocyclopropane will be favored despite the steric factors favoring formation of a trans isomer.

No isomerisation to a propene was found in the addition of :CFCl to olefins in solution. If the transition state in the gas phase is similar, this would seem to indicate that what we are observing in the present case is isomerisation of a hot cyclopropane, a process which would not occur in solution. This would imply that isomerisation does not occur from the intermediate and that the ratio of CF_2=CF-$CFCl_2$ to  should go to zero at high pressures and not level off as indicated in Fig. 4.

REACTIONS OF $\cdot C_2F_3$ + $\cdot$Cl

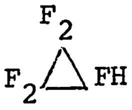
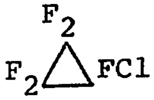
$\cdot C_2F_3$, as would be expected, adds to the starting material. However the adduct does not appear to lose a chlorine atom as no C_4F_6 was detected. The fate of the $\cdot C_4F_6Cl$ appears to be either recombination with a Cl atom forming the dichlorobutene or with another $\cdot C_2F_3$ forming the hexadiene tentatively identified. This latter could also be formed by attack on the substrate of $\cdot C_4F_6Cl$ followed by loss of a Cl atom. The dichlorobutene could also be formed by reaction of a Cl atom with the substrate, yielding a $\cdot C_2F_3Cl_2$ radical which subsequently attacks a substrate molecule, the adduct then losing a Cl atom to form $C_4F_6Cl_2$. Both $\cdot C_2F_3$ and $\cdot$Cl probably contribute greatly to polymer formation.

The difference between the reactions of $\cdot C_2F_3$ in

Hg photosensitization and in photolysis may be due to the intervention of different electronic states. In Hg photosensitization,the initially formed state is a triplet state whereas in photolysis it is a singlet. This will undoubtedly lead to differing energy contents in the $\cdot C_2F_3$ formed and may explain the variance in their reactions.

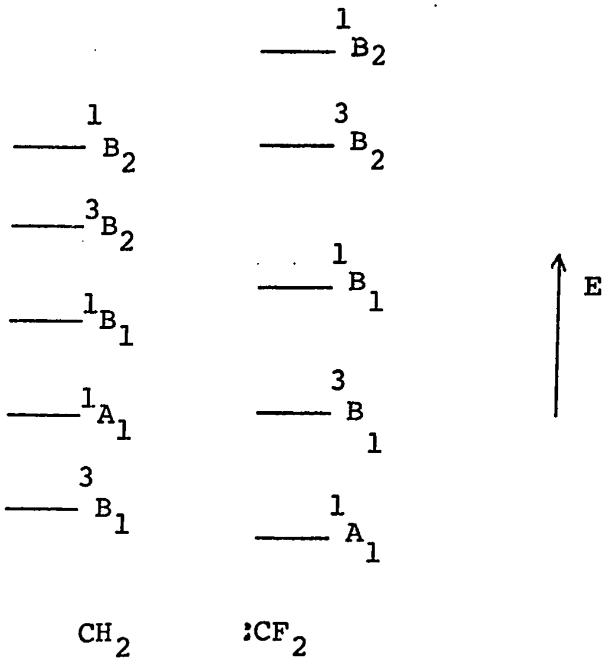
PRODUCTS OF $:CF_2$.

In the photolysis of C_2F_3Cl alone,two products attributed to the reaction of $:CF_2$ are found. These are C_5F_8 and C_2F_4. When photolysis is carried out in the presence of isobutane,a new product $C_5F_2H_{10}$ appears and the yield of C_5F_8 and C_2F_4 decreases. At a sufficiently high pressure of added isobutane,the $:CF_2$ appears to be completely scavenged by the isobutane as its yield is equal to the sum of the $:CFCl$ containing products. When C_2F_3Cl is photolysed alone,it can be seen that,if C_5F_8 and C_2F_4 account for all the $:CF_2$,then,the ratio of $C_5F_8 + 2\ C_2F_4$ to $\Sigma:CFCl$ containing products should equal 1. However,at 10 torr this ratio is = .52 and at 100 torr = .54. Thus,only 50% of the $:CF_2$ is appearing in the above products. Since it does not appear as any other product isolated, presumably it is going to polymer.
This can be explained if all the C_3F_5Cl formed in reaction 14

does not go to $\cdot C_3F_5$ + $\cdot$Cl but instead goes to polymer as postulated in reaction 14. Since no chloroperfluorocyclopropane was found, the C_3F_5Cl formed in reaction 13 must not be long-lived enough to be stabilised by collision. In the photolysis of C_2F_3H, where :CF_2 is also formed, only trace amounts of the cyclopropane formed by addition of :CF_2 to the substrate were observed (20). The :CF_2 in the latter case, was less energetic than :CF_2 formed in the present case since it did not appear to insert into C-H bonds, so the cyclopropane formed should not be as "hot" as the cyclopropane formed by addition of :CF_2 to C_2F_3Cl. Since the  is only partially stabilised even at high pressures one would not expect the  to be deactivable, the latter being more energetic.

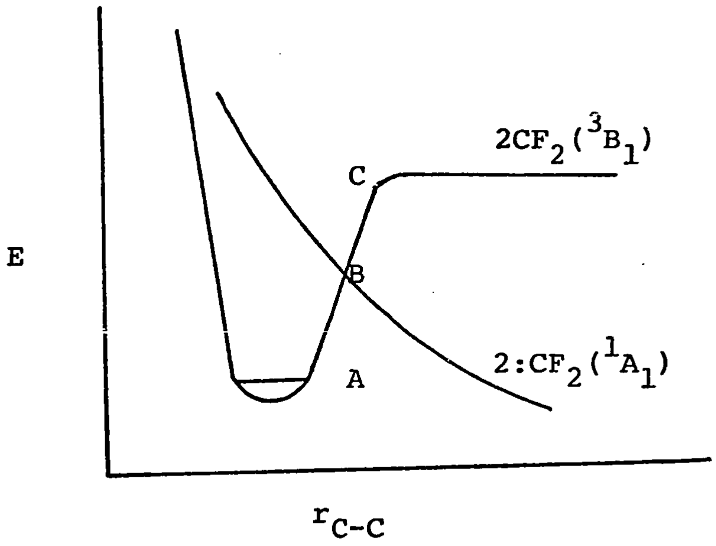
The reaction of :CF_2 with isobutane must be a direct insertion process, similar to the insertion of CH_2^1 into C-H bonds. This is shown by the fact that, although the yield of $C_5F_2H_{10}$ decreases on addition of NO to the system, the ratio of $C_5F_2H_{10}$ to the sum of :CFCl containing products remains the same. The decrease in product yield is caused by competitive absorption of the light by NO, which is a very strong absorber in the region where C_2F_3Cl absorbs.

:CF_2 was first observed spectroscopically in discharge through CF_4 vapor (45). It was suggested here that the ground state was a singlet in contrast to methylene where the ground state is a triplet. The various states of the two are shown below.



Not to scale

It was postulated that the emission bands were due to $^1B_2$ — $^1A_1$ transition. Mann and Thrush (46) have shown in the absorption spectrum of :CF_2 that the 0-0 band is at 2651Å. Thus the $^1B_2$ state would lie approximately 107 kcals/mole above the ground state. However, Matthews (47) has shown by detailed analysis of the spectrum that the transition is either $^{1}A_{1}$——$^{1}A_{1}$ or $^{1}A_{2}$——$^{1}A_{1}$. Thus the higher ^{1}A states are approximately 107 kcals/mole above the ground state. This means that the B_2 and B_1 states are certainly <107 kcals/mole above the ground state. A calculation by Simons (48) shows that $:CF_2$ $^{3}B_1$ lies, ∿45 kcal above the ground state. He based this on the following evidence. Since the bond energy of C_2F_4 is low, ∿77 kcal, the approach of two ground state $:CF_2$ radicals must be repulsive and the first excited singlet state must be predissociative.



In ethylene these curves do not cross since $^{3}:CH_2$ is the ground state of methylene and $^{1}:CH_2$ the excited state. It is assumed that in C_2F_4, AC, representing the energy required to dissociate C_2F_4,to two triplet $:CF_2$ radicals, will be the same as that in ethylene. Thus BC representing $D(CH_2{=}CH_2) - D(CF_2{=}CF_2), = 2\Delta E(:CF_2(^{3}B_1) - :CF_2(^{1}A_1))$. Using the value $D(CH_2{=}CH_2)$ = 167 kcal/mole and $D(CF_2{=}CF_2)$ = 77.5 kcal/mole.

$$\Delta E\left(:CF_2\left({}^3B_1\right) - :CF_2\left({}^1A_1\right)\right) = 45 \text{ kcal/mole.}$$

If the bond dissociation energy of ethylene is lower than this, this could appreciably lower the difference in energy in the two states. The assumption that the energy required for

$$C_2F_4 \rightarrow 2:CF_2\left({}^3B_1\right)$$

is the same as that for

$$C_2H_4 \rightarrow 2:CH_2\left({}^3B_1\right)$$

may not be justified.

Simons (49) has also treated $:CF_2$ by simple M.O. methods. He has calculated that the first excited state of CF_2 lies ∿4.2 ev above the ground state. He also attributes the absorption spectrum centered at 2650Å to the ${}^1B_1 \leftarrow {}^1A_1$ transition. This has been shown to be a ${}^1A_1 \leftarrow {}^1A_1$ or ${}^1A_2 \leftarrow {}^1A_1$ transition and thus, the calculations must be in error, in particular as the B_2 states, which are higher in energy than the ${}^1B_1$, must be lower than 108 kcal, the energy of the excited ${}^1A$ state. If, as hypothesised previously, the ${}^3B_1$ state is 45 kcal or less above the ground state, then it is hardly to be expected that the ${}^1B_1$ would be 60 kcals above that, as $\Delta E({}^3B_1 - {}^1A_1)$ should be larger than $\Delta E({}^1B_1 - {}^3B_1)$.

The reactions of $:CF_2$ have been studied by a number of workers. Atkinson (50) investigated the mercury photosensitization of C_2F_4 and found that $:CF_2$ was produced and reacted with the starting material to form hexafluorocyclopropane or polymer. A high proportion of the $:CF_2$ produced recombines to form C_2F_4. Cohen and Heicklen (51) re-examined this reaction and found that $k(\text{addition})/k\ (\text{recombination})^{\frac{1}{2}} = 4.3 \times 10^3$ at 25 °C. Using a value obtained by Dalby (52) for the rate constant for recombination they obtained the following values for the rate constants.

$$k \text{ recombination} = 3.4 \times 10^8 \exp - 1700/RT$$
$$k \text{ addition} = 6.4 \times 10^6 \exp - 7500/RT$$

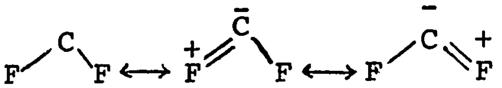
The low Arrhenius parameter and high energy of activation for addition to a double bond are not characteristic of the attack of an electrophilic biradical on a π-system. Typical values for such reactions are listed below.

Addition to ethylene.

Biradical	$O(^3P)$	$S^3(P)$	$Se(^3P)$
Activation (kcal/ mole) energy	2.6	>3.4	2.8
A factor	1.1×10^{10}	1.1×10^{10} assumed	1.1×10^{10}
Ref.	(53)	(54)	(55)

We can rationalise the above inconsistency in the following way.

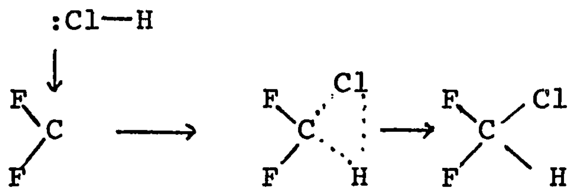
If we visualise the $:CF_2$ as described by Hoffman et al (56), the ground state will have an unoccupied p orbital on the carbon, perpendicular to the plane of the molecule. There can be interaction between this orbital and the filled p orbitals on the F atoms, resulting in back donation of electrons to the unfilled C orbital. We might write this as the resonance structures.



Or alternatively

Thus $:CF_2$ bears more resemblance to CO than to biradical species such as O. This will explain the low value of the rate constant for attack on the π system as the carbene will be a great deal less electrophilic than O or S and will not add nearly as readily as these. This is borne out by Simons' calculations, which show considerable overlap between the occupied p orbitals on the F atoms and the unoccupied p orbital of the C. In view of the error in the energy of the excited states calculated by his method, it is not possible to know how accurate the amount of overlap indicated is. However, assuming overlap is present this can explain the low A factor in the addition of $:CF_2$ to the double bond as there will be repulsion between the two negative centres, this making the A factor much smaller than for the electrophilic atomic biradical species.

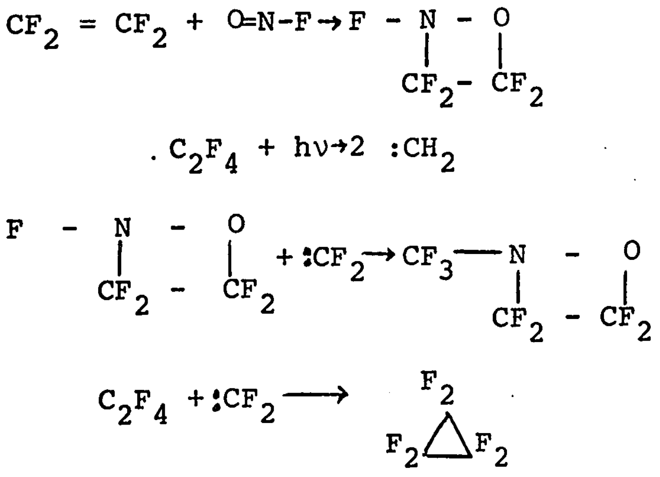
$:CF_2$ has been produced from several other sources. Pyrolysis of CF_2HCl produces $:CF_2$ (57). This was found to react with HCl and HBr to produce CF_2HCl and CF_2HBr. This reaction presumably proceeds by donation of unbonded electrons of the halogen to the empty p orbitals of the $:CF_2$. If the orbital is partially occupied, this would explain the activation energy found for this process, as some destabilisation of $:CF_2$ is necessary for reaction. The reaction would proceed presumably as follows.



Pyrolysis of various trifluoromethyl derivatives of group 5 elements gives $:CF_2$. The $:CF_2$ was found to be reactive and added to hexafluorobutyne in two successive steps (58,59,60).

Mitsch has produced $:CF_2$ by the pyrolysis and photolysis of  (30). This species added readily to the double bonds of several olefins yielding difluorocyclopropanes. No insertion into C-H bonds was found with olefins. However the compound was not photolysed in the presence of an alkane.

It would appear that the $:CF_2$ insertion into a C-H bond as was found in the present instance is unique. A previous case of insertion of $:CF_2$ into an N-F bond has been reported (61). $:CF_2$ was generated by photolysis of C_2F_4 in the presence of NOF. The mechanism postulated was:

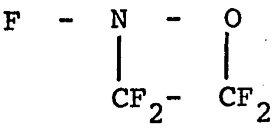


$$CF_2 = CF_2 + O{=}N{-}F \rightarrow \begin{array}{ccc} F - & N & - \; O \\ & | & | \\ & CF_2 - & CF_2 \end{array}$$

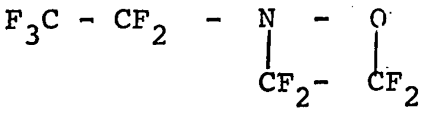
$$C_2F_4 + h\nu \rightarrow 2\ :CH_2$$

$$\begin{array}{ccc} F - & N & - \; O \\ & | & | \\ & CF_2 - & CF_2 \end{array} + :CF_2 \rightarrow \begin{array}{ccc} CF_3 - & N & - \; O \\ & | & | \\ & CF_2 - & CF_2 \end{array}$$

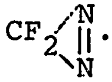
$$C_2F_4 + :CF_2 \longrightarrow$$

the intermediate  $\begin{array}{ccc} F - & N & - \; O \\ & | & | \\ & CF_2 - & CF_2 \end{array}$ was not isolated.

In the absence of light the only product was



formed by reaction of C_2F_4 with the intermediate.

There are two possible explanations for C-H insertion in the present study. If, as seems probable, there is resonance stabilization of $:CF_2$ in its $^1A_1$ ground state then an activation energy will be necessary for both addition to a π-system and insertion into a C-H bond as destabilization must occur before addition. The activation energy for the latter will undoubtedly be larger than the former. In the present instance, the $:CF_2$ formed will contain a large amount of excess energy and thus could overcome the problem of activation energy, as was found in the thermally "hot" $:CF_2$ produced from . Undoubtedly, $:CF_2$ in the present case will carry a larger amount of excess energy so making insertion easier than for that from the diazirine. Also, addition to the π-system of C_2F_3Cl in the present instance will not be highly favored, due to the steric hindrance of the Cl atom and the low electron density in the π-system, and insertion may be more favorable.

Another possibility is that the $:CF_2$ generated in the current study is electronically excited and behaves much more like $:CH_2$. The energy difference between the ground and first excited state is not known, so it is possible that in the present case we are forming $:CF_2$ in its first excited singlet state.

Although the bond dissociation energy of $CF_2=CFCl$ is not known, it will probably be similar to that of C_2F_4, though somewhat higher as Cl will not destabilise the bond as much, being less electronegative than F. We can calculate an approximate value in the following way.

$$CF_2 = CFCl \rightarrow :CF_2 + :CFCl$$

$$D(CF_2=CFCl) = \Delta H_f^o(:CF_2) + \Delta H_f^o(:CFCl) - \Delta H_f^o(CF_2=CFCl)$$

ΔH_f^o for :CFCl is not known but we can calculate an approximate value by taking the average of $H_f^o(:CF_2)$ and $H_f^o(:CCl_2)$

$\Delta H_f^o(:CF_2) =$ -36.8 kcal/mole (62)

$\Delta H_f^o(CCl_2) =$ 57 kcal/mole (63)

$\Delta H_f^o(CFCl) =$ 9 kcal/mole

$\Delta H_f^o(CF_2=CFCl) =$ 120 kcal/mole (64)

$D(CF_2=CFCl) = -36.8 + 9 + 120$

$= 93$ kcal/mole

This compares with $D(CF_2=CF_2) = 77.5$ kcal/mole.

Since photolysis in the present case is taking place at 2150Å, there is in excess of 40 kcal/mole to spare over the amount of energy required to break the bond. This may be sufficient to promote the $:CF_2$ to the $^1B_1$ state. If not however, the CF_2 produced will still be very "hot' and will thus be very reactive.

It seems probable that the two different dissociation processes are occurring from two excited states. There are two ways in which this may occur.

Firstly, we consider that absorption is leading to formation of two different electronically excited states. The first of these would be the excited singlet formed by promotion of a π-electron to the π-antibonding orbital. The second excited state would be formed by a $\pi-\sigma^*$ transition or a $\sigma - \pi^*$-transition i.e. a Berry or anti-Berry transition.

In the u.v. spectrum of ethylene a weak absorption is found centered at 6 e.v. which is at longer wavelength than the $\pi-\pi$ transition. Berry (65) suggested that this band was due to excitation of one of the C-H electrons to the π anti-bonding orbital. This was suggested by analogy with formaldehyde, where the lowest energy singlet transition is promotion of a non-bonding electron from a p orbital of O to the π^*-orbital. Later calculations (66) showed that in fact the excitation of a π-bonding electron to the CH anti-bonding orbital was the lowest lying singlet transition. In the case of C_2F_3Cl it is possible that $\pi-\sigma^*$(CCl) or $\pi-\sigma^*$ (CF) transitions occur. The u.v. spectrum of C_2F_3Cl shown in Fig. 6 does not show any fine structure,

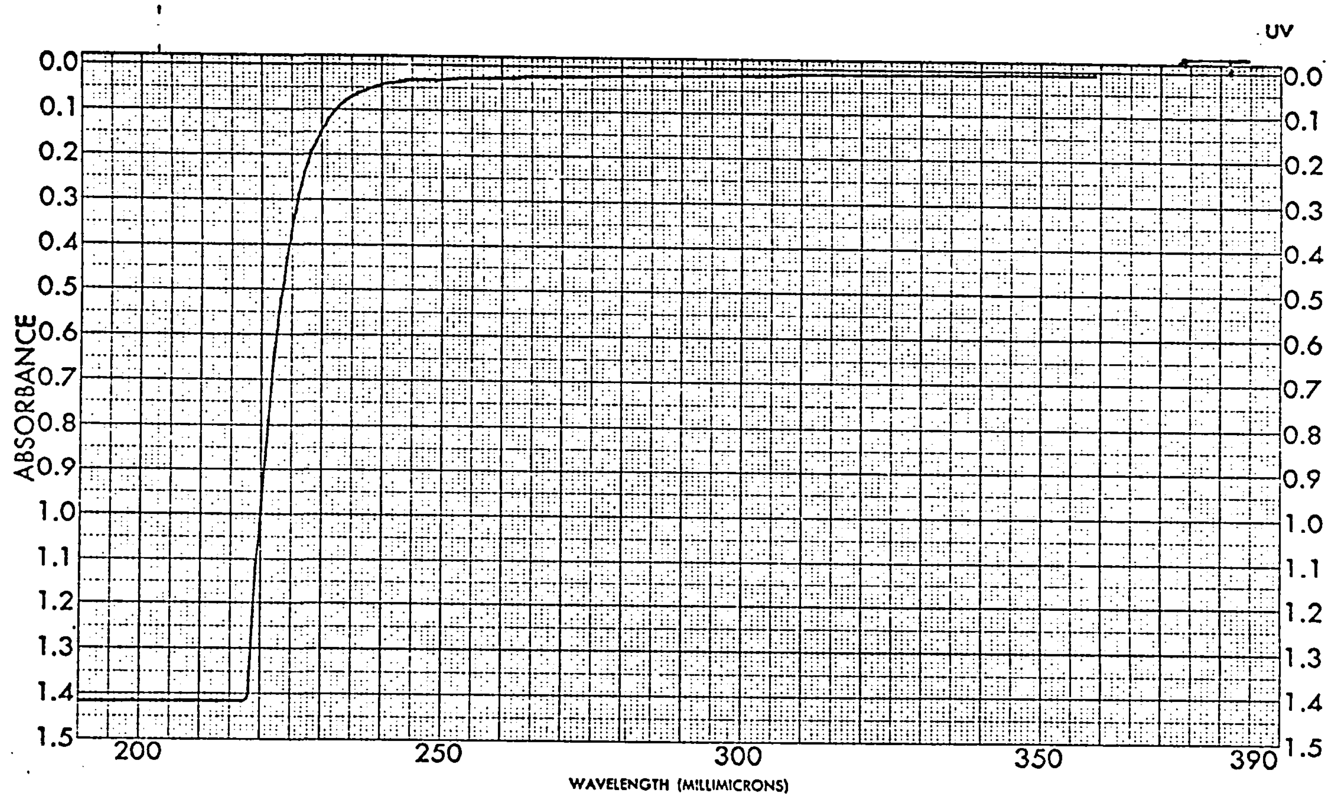


Fig. 6. U.V. Spectrum of perfluorovinylchloride.

so it is not possible to say whether or not this is occurring. It has been shown (67) that photolysis of cis-1, 2-dichloroethylene leads to decomposition by two different paths.

$$
\begin{aligned}
C_2H_2Cl_2 + h\nu &\longrightarrow C_2H_2 + 2Cl \\
&\longrightarrow C_2HCl + HCl
\end{aligned}
$$

Both of these are molecular processes as neither C_2H_2 nor C_2HCl yields were affected by radical scavengers. It was found however that the ratio C_2H_2/C_2HCl decreased from 9:1 to 3.3:1 when a filter, cutting off light of wavelength below 2200Å, was used. This indicated that two different electronically excited species were involved.

The u.v. spectrum of cis-1, 2-dichloroethylene, is similar to that of perfluorovinylchloride and does not indicate two different types of absorption. If the present system is analogous to the dichloroethylene it is to be expected that C=C bond scission is taking place from the higher electronically excited state, as this process will require more energy. Since the $\pi-\pi^*$ transition will probably be at <2000Å, this would imply that up to 60 or 70 kcal/mole excess energy over the bond strength is being absorbed, making the probability of formation of $:CF_2$ in an electronically excited state even greater. However, decomposition into $:CF_2$ and :CFCl may be occurring from an excited state which is formed initially. This state can cross over, by radiationless transition to a second excited state which can decompose forming $C_2F_3\cdot$ and $Cl\cdot$ In the presence of isobutane, both C_4F_6ClH, which is formed from the reaction of $C_2F_3\cdot$, and the products containing CFCl decrease with increasing pressure of isobutane. This would seem to indicate that quenching of the initially formed excited state of C_2F_3Cl is occurring, preventing both formation of :CFCl and crossover to the second excited state, from which C_2F_3 is formed.

If this second mechanism is operative, then this implies that the initially formed excited state, is not predissociative, as would be expected by analogy with C_2F_4.

If the first excited singlet is predissociative, then it would seem that two different types of absorption are involved. In this case, the shorter wavelength absorption presumably goes to the predissociative singlet, which forms $:CF_2$ in its ground state albeit very "hot" vibrationally.

CHAPTER IV

RESULTS

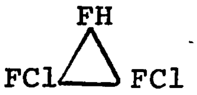
Photolysis of 1,2-dichlorofluoroethylene.

This substrate was a mixture of the *cis* and *trans* isomers. Before separating the isomers, a preliminary photolysis was carried out to ascertain the nature of the mechanism of decomposition. When this mixture was photolysed a large amount of brown polymer was formed. Analysis by gas chromatography of products condensable at -78° showed one major and a large number of minor products to be present. The major product was identified as dichlorodifluorobutadiene by mass spectrometry. When isobutane was added to the system two new products appeared. These proved to be octanes containing traces of some other material. The dichlorodifluorobutadiene from these runs contained some product of M.W. = 136 as determined by mass spectrometry. This gives a molecular formula C_6ClFH_{10}. As there appeared to be very little carbene formation, photolysis of the *cis* and *trans* isomers separately was not carried out.

Photolysis of 1,2-difluorochloroethylene.

Although not separable by g.c. this substrate was presumably a mixture of *cis* and *trans* isomers. During photolysis large amounts of polymer were also formed. When the fraction condensable at -105° was analysed by g.c.

several products were found. Two of these were identified by mass spectrometry as isomers of molecular formula $C_4F_4H_2$. The other products were of higher molecular weight and appeared to arise from further reaction of the initial radical addition products. When isobutane was added to the system two major components condensable at -105° were resolved. These were identified mass spectrometrically as (1) a mixture of $C_3Cl_2F_3H$ and C_6ClFH_{10} and (2) a mixture of $C_6F_2H_{10}$ and C_8H_{18}. An I.R. spectrum of mixture (1) showed strong absorptions at 1055 cm^{-1}, the region associated with a cyclopropane ring and at 1750 cm^{-1} attributable to CF_2=C stretching, so that the $C_3Cl_2F_3H$ is probably a mixture



and $CFCl_2$-CF=CFH. An N.M.R. spectrum of the product $C_6F_2H_{10}$ showed this to be a mixture of cis and trans-1,2-difluoro-4-methylpentene. When photolysis was carried out in the presence of NO the minor products, which were not identified but were probably due to monoradical reactions, disappeared and the yield of the two major components, (1) and (2) above, decreased.

Photolysis of 1,1-difluorochloroethylene.

When this compound was photolysed a large number of products condensable at -105° were formed. The two largest of these were identified mass spectrometrically as $C_5F_6H_2$ and $C_4Cl_2F_4H_2$. When isobutane was added several new products were found, three of which were fairly large. One was identified mass spectrometrically as $C_5F_2H_{10}$. Comparison of mass spectra showed the latter to be of the same structure as the product $C_5F_2H_{10}$ formed in the photolysis of a mixture of C_2F_3Cl and isobutane. The other two products were identified as (A) a mixture of $C_6F_2H_{10}$ and C_8H_{18} and (B) $C_6F_2H_{10}$. The latter was identified as 1,1-difluoro-4-methyl-1-pentene by comparison of its mass spectrum with that of an authentic sample reported by Norstrom (25). It was inferred that the $C_6F_2H_{10}$ in (A) was 1,1-difluoro-3,3-dimethyl-1-butene. The ratio of (A) to (B) was 3:1. However when NO was added to the system with the consequent removal of octane this ratio was reversed.

DISCUSSION

Photolysis of 1,2-dichlorofluoroethylene.

From the products found it seems as if most of the decomposition is initiated by fission of the C-Cl bond. Some elimination of HCl seems to be occurring as the product of C_6ClFH_{10} is probably formed by insertion of CFCl=C: into the C-H bonds of isobutane. Thus we can write the following steps to explain the products observed.

[1] $C_2Cl_2FH + h\nu \longrightarrow C_2Cl_2FH^*$

[2] $C_2Cl_2FH^* \longrightarrow C_2ClFH\cdot + Cl\cdot$

[3] $\longrightarrow CFCl{=}C: + HCl$

[4] $C_2ClFH\cdot + C_2Cl_2FH \longrightarrow C_4Cl_3F_2H_2\cdot$

[5] $C_4Cl_3F_2H_2\cdot \longrightarrow C_4Cl_2F_2H_2 + Cl\cdot$

[6] $C_4Cl_3F_2H_2\cdot + C_2Cl_2FH \longrightarrow$ polymer

[7] $CFCl{=}C{:}+C_2Cl_2FH \longrightarrow C_4Cl_3F_2H^*$

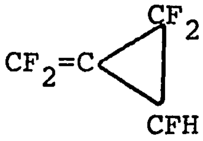
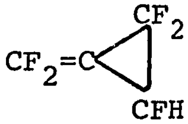
[8] $C_4Cl_3F_2H^* \longrightarrow C_4\,Cl_2F_2H\cdot + Cl\cdot$

[9] $C_4Cl_2F_2H\cdot \longrightarrow$ polymer

[10] $CFCl{=}C{:} + C_4H_{10} \longrightarrow C_6ClFH_{10}$

[11] $\cdot Cl + C_4H_{10} \longrightarrow \cdot C_4H_9 + HCl$

[12] $2\,\cdot C_4H_9 \longrightarrow C_8H_{18}$

The elimination of Cl by a vinylic radical is similar to the decomposition reactions of C_2F_3 and C_2H_3(39). The insertion of CFCl=C: into the C-H bonds of isobutane is similar to the reaction of $CF_2{=}C{:}$ (25). In the absence of isobutane, CFCl=C: would be expected to add to the double bond of the substrate, reaction [7], forming a hot methylene cyclopropane by analogy with the reaction of $CF_2{=}C{:}$. The hot cyclopropane probably decomposes by loss of a Cl· atom, the remaining fragment then forming polymer by reaction with the substrate. The methylene cyclopropane which was formed by the addition of $CF_2{=}C{:}$ to $CF_2{=}CFH$ decomposed by elimination of $:CF_2$. However in the present instance loss of a Cl· atom, from the resulting cyclopropane, is probably more energetically favorable than loss of :CFCl. The latter reaction, which would be analogous to loss of $:CF_2$ from , is less likely as the C-Cl bond is probably weaker than the C-C double bond. In the case of  both the C-F and C-H bonds are probably stronger than the double bond so that $:CF_2$ elimination is favored.

<u>Photolysis of 1,2-difluorochloroethylene</u>.

The following reaction scheme is proposed to account for the observed products.

[1] $C_2F_2HCl + h\nu \longrightarrow C_2F_2HCl^*$

[2] $C_2F_2HCl^* \longrightarrow C_2F_2H\cdot + Cl\cdot$

[3] $\longrightarrow :CFH + :CFCl$

[4] $\longrightarrow CFCl{=}C: + HF$

[5] $C_2F_2H\cdot + C_2F_2HCl \longrightarrow C_4F_4H_2Cl\cdot$

[6] $C_4F_4H_2Cl\cdot \longrightarrow C_4F_4H_2 + Cl\cdot$

[7] $C_4F_4H_2Cl\cdot + C_2F_2HCl \longrightarrow$ polymer

[8] $Cl\cdot + C_2F_2HCl \longrightarrow C_2F_2HCl_2\cdot$

[9] $C_2F_2HCl_2\cdot + C_2\ F_2HCl \longrightarrow$ polymer

[10] $:CFCl + C_2F_2HCl \longrightarrow C_3Cl_2F_2H^*$

[11] $C_3Cl_2F_2H^* \longrightarrow \text{polymer}$

[12] $+M \longrightarrow C_3Cl_2F_2H$

[13] $CFCl{=}C{:} + C_4H_{10} \longrightarrow C_6ClFH_{10}$

[14] $Cl\cdot + C_4H_{10} \longrightarrow C_4H_9\cdot + HCl$

[15] $C_4H_9\cdot + C_2F_2ClH \longrightarrow C_6ClF_2H_{10}\cdot$

[16] $C_6ClF_2H_{10}\cdot \longrightarrow C_6F_2H_{10} + Cl\cdot$

[17] $2C_4H_9\cdot \longrightarrow C_8H_{18}$

The reactions of the 1,2-difluorovinyl radical are similar to those of the 1,1-difluorovinyl and trifluorovinyl radicals in that it appears to add to the substrate with a resulting displacement of a Cl atom. The fate of the Cl atoms appears to be polymer formation by reaction with the substrate and the subsequent reaction of the radical formed in this process. Some of the higher molecular weight products may arise from reactions of the Cl atom. The cyclopropane formed by addition of :CFCl to the substrate was not found when C_2F_2ClH was photolysed alone. However, the pressures employed here were 20 torr so little or no stabilisation of the cyclopropane was occurring. It would probably decompose by loss of a Cl· atom the resulting fragments leading to polymer formation. When isobutane was added to the system the total pressure was greater than 200 torr so that stabilisation of the hot cyclopropane would occur more readily.

:CFH would be expected to add to the substrate. The resulting cyclopropane would be hot and would probably decompose even at high pressures. In the photolysis of trifluoroethylene (20) :CFH was formed. This added to the substrate and the resulting cyclopropane was only isolated at very high pressures. In the present instance decomposition by loss of a Cl· atom will probably be the fate of the cyclopropane and if there is sufficient excess energy generated in the reaction it may be impossible to stabilise the cyclopropane collisionally. Certainly there was no trace of any compound of molecular formula $C_3ClF_3H_2$ even in the presence of isobutane. The CFCl = C: radical was again found to react with isobutane. As in the case of the dichlorofluoroethylene no product attributable to reaction of CFCl = C: with the ethylene could be found. Again one would expect that decomposition of the adduct would occur by loss of a Cl atom and the resultant fragment would lead to formation of polymer. The formation of the product $C_6F_2H_{10}$ must be a radical process as it is a 1,2-difluoropentene and cannot be formed by an insertion process. Although this product decreased when NO was added to the system it was not completely eliminated. This was probably due to incomplete scavenging of the $C_4H_9\cdot$ radicals by NO.

Photolysis of 1,1-difluorochloroethylene

The following reaction scheme is proposed to account for the products observed.

[1] $C_2F_2HCl \quad + \quad h\nu \longrightarrow C_2F_2HCl^*$

[2] $C_2F_2HCl \longrightarrow C_2F_2H\cdot + Cl\cdot$

[3] $\longrightarrow :CF_2 + :CHCl$

[4] $\longrightarrow CF_2{=}C: + HCl$

[5] $Cl + C_2F_2HCl \longrightarrow C_2F_2HCl_2\cdot$

[6] $C_2F_2HCl_2\cdot + C_2F_2HCl \longrightarrow C_4F_4Cl_3H_2\cdot$

[7] $C_4F_4Cl_3H_2\cdot \longrightarrow C_4F_4Cl_2H_2 + Cl\cdot$

[8] $:CF_2 + C_2F_2HCl \longrightarrow C_3F_4HCl$

[9] $C_3F_4HCl \longrightarrow C_3F_4H\cdot + Cl\cdot$

[10] $C_3F_4H\cdot + C_2F_2HCl \longrightarrow C_5F_6H_2Cl\cdot$

[11] $C_5F_6ClH_2\cdot \longrightarrow C_5F_6H_2 + Cl\cdot$

[12] $:CF_2 + C_4H_{10} \longrightarrow C_5F_2H_{10}$

[13] $CF_2{=}C: + (CH_3)_3CH \longrightarrow (CH_3)_3C{-}CH{=}CF_2$

[14] $\longrightarrow (CH_3)_2CH{-}CH_2{-}CH{=}CF_2$

[15] $Cl\cdot + C_4H_{10} \longrightarrow C_4H_9^{\cdot} + HCl$

[16] $2\ C_4H_9^{\cdot} \longrightarrow C_8H_{18}$

In this system we find the same pattern of reaction as was found in the other systems. No products attributable directly to the reaction of the C_2F_2H radical were found. It would be expected by analogy with the vinylic radical reactions in the other systems that this would add to the substrate, the adduct then losing a Cl atom to form a butadiene. Either this does not occur in the present case or the butadiene formed was overlooked.

The reactions of $:CF_2$ in the present case are similar to those of the $:CF_2$ formed in the photolysis of C_2F_3Cl. Thus formation of hexafluoropentadiene in the present case parallels formation of perfluoropentadiene in the reaction of $:CF_2$ with C_2F_3Cl. When isobutane is added the $:CF_2$ reacts with it to form the same product as in the case of CF_2 formed by photolysis of C_2F_3Cl. Presumably this is again a direct insertion process. Although more energy will be required for the reaction.

$$CF_2{=}CHCl + h\nu \longrightarrow :CF_2 + :CHCl$$

than for the reaction

$$CF_2{=}CFCl + h\nu \longrightarrow :CF_2 + :CFCl$$

since $\Delta H_f(:CHCl)$ will probably be larger than $\Delta H_f(:CFCl)$, it appears that sufficient energy is absorbed to cause the $:CF_2$ formed in this reaction to also be very reactive in comparison to ground state $:CF_2$. Again in this instance

$:CF_2$ can be an electronically excited species or a highly vibrationally excited ground state. The similarity in reactivity of the $:CF_2$ from photolysis of both compounds would tend to indicate that both are in the same state. Since the energetics of each system is different this would tend to support the hypothesis that both are electronically excited rather than vibrationally excited since if vibrational excitation were involved, the amount of energy in the $:CF_2$ formed by photolysis of C_2F_3Cl would be greater than in CF_2 formed by photolysis of C_2F_2HCl. However, since the reactivities can be only qualitatively said to be the same then one cannot rule out the reactivity being due to vibrationally excited ground state species.

No product attributable to reaction of :CHCl in the present system was found. This is somewhat strange as one would expect this species to add readily to the double bond of the starting material. :CHCl has been generated in solution by thermolysis and photolysis of $CClHN_2$ (69). It was found to react with the double bonds of olefins producing cyclopropanes. In the absence of olefins it was found to insert into C-H bonds. However, the ratio k(insertion)/k(addition) was 0.01.

Tang and Rowland (70)) have generated :CHCl in the gas phase by elimination of hydrogen halide from a "hot" CHTClX (Where X is Cl or F), formed by reaction of recoil tritium atoms with CH_2ClX. The :CTCl reacted readily with ethylene to give chlorocyclopropane. No products attributable to insertion were found.

In the present case therefore if the :CHCl is in the same electronic state as the :CTCl in the above case one would not expect it to react with isobutane. If it does react with the olefinic double bond the resultant cyclopropane must be too hot to be deactivated collisionally and presumably loses a Cl atom while the remaining fragment reacts with the substrate to form polymer.

The reactivity of CF_2=C: formed in this system is similar to that formed in mercury photosensitization and photolysis of C_2F_3H (25). The CF_2=C: reacts three times faster with the tertiary C-H bond of isobutane than with the primary C-H bonds. This was evident in the present system from the ratio of the dimethylbutene to methylpentene when photolysis was carried out with added NO. NO prevents formation of octane which was not separable from dimethylbutene by gas chromatography and in these runs the ratio of butene to methylpentene was 1:3. This would indicate that CF_2=C: is in the same electronic state in all three cases. No product was found that could be attributed to reaction of CF_2=C: with the substrate. Again this is probably due to decomposition of the adduct by loss of a Cl atom for the reason discussed in the addition of CFCl=C: to dichlorofluoro and difluorochloroethylene.

Conclusions

In the case of the olefins discussed in this chapter in each case at least two primary processes were observed. Again as in the case of trifluorovinylchloride probably at least two excited states are responsible for the different decomposition modes. In the case of the difluorochloroethylenes where three decomposition processes are in evidence it is probable that three different excited states are being formed. It seems likely that these are not formed simultaneously and that either the state from which a Cl atom is lost or that from which hydrogen halide is eliminated will be the lowest lying. It is possible that two excited states are formed simultaneously. The first of these by a $\pi - \pi^*$ transition is probably that from which the carbon double bond fission is occurring. The other will be by $\pi - \sigma^*$ or $\sigma - \pi^*$ transitions (as mentioned in the case of the trifluorovinyl chloride) and from this Cl atom fission or hydrogen halide elimination can occur. One of these excited states can give rise to another excited state by non-radiative crossover and from this the third process, which does not occur from the initially formed excited states, can take place. Loss of a Cl atom may also be occurring from an excited state formed by an $n - \sigma^*$ transition where n is an unbonded Cl electron.

CHAPTER V

Results

1. Photolysis of 1,3-perfluorobutadiene

The photolysis of 1,3-perfluorobutadiene led to the formation of the following products. C_2F_4, perfluoropropyne, perfluorocyclopropene, 1,2-perfluorobutadiene, 2-perfluorobutyne and perfluorocyclobutene. C_2F_4 was identified by comparison of its retention time and mass spectrum with those of an authentic sample. Perfluoropropyne was identified by its mass and I.R. spectra. This compound has since been prepared by Stuckey and Heicklen (19) and its mass and I.R. spectra are the same as those found in the present experiment. Perfluorocyclopropene was also prepared by these workers and comparison of their data with that found in this work confirms the correctness of the assignment of the perfluorocyclopropene structure. Mass and I.R. spectral analyses were used to identify 1,2-perfluorobutadiene. The mass spectrum of this product showed its molecular formula to be C_4F_6. In I.R. analysis no absorption was detected in the region 1700 - 1800 cm^{-1} normally found for a perfluorovinyl group. However a strong absorption was found at 2042 cm^{-1} which is close to that found at 2065 cm^{-1} for perfluoroallene by Jacobs and Bauer (68). Thus, the 1,2-butadiene structure was assigned to this product. 2-Perfluorobutyne and perfluorocyclobutene were identified by comparison of their mass and I.R. spectra with those of authentic samples of these compounds.

The product yields were studied as a function of substrate pressure. The results are shown in Table 5. A plot of these results is shown in Figs. 7 and 8. A study was made of the change in product yields as a function of added CF_4 while the substrate pressure was maintained at 4 torr. The results are shown in Table 6. In Fig. 9 a plot of these results is shown. C_2F_4 could not be measured as it was impossible to separate it quantitatively from CF_4. The yields of 1,2-perfluorobutadiene and 2-perfluorobutyne were too small to measure accurately.

A mixture of 2.8 torr 1,3-perfluorobutadiene and 2.2 torr ethylene was photolysed but no new products were detected.

Photolysis with up to 3 torr of O_2 added had no effect on the product yields.

Photolysis of Perfluorocyclobutene

When perfluorocyclobutene was photolysed the products found were the same as those from the photolysis of 1,3-perfluorobutadiene with the exception that where perfluorocyclobutene was found in that case in the present instance 1,3-perfluorobutadiene was found as an isomeric product. This was identified by comparison of its mass spectrum and retention time with that of an authentic sample.

TABLE 5

Product yields as a function of substrate pressure in the photolysis of 1,3-perfluorobutadiene[(a)]

Pressure 1,3-BD[(b)] torr.	C_2F_4	$CF_3C{\equiv}CF$		1,2-BD[(c)]	Bu[(d)]	CB[(e)]
4	11.8	21.7	9.6	0.7	1.0	6.2
20	7.2	10.7	6.6	2.7	1.6	18.4
40	3.9	6.5	3.5	2.3	1.1	19.4
70	2.2	3.9	2.1	1.8	0.8	19.0

(a) All product yields in μmoles. All photolyses carried out for 60 mins.

(b) 1,3-perfluorobutadiene

(c) 1,2-perfluorobutadiene

(d) 2-perfluorobutyne

(e) perfluorocyclobutene

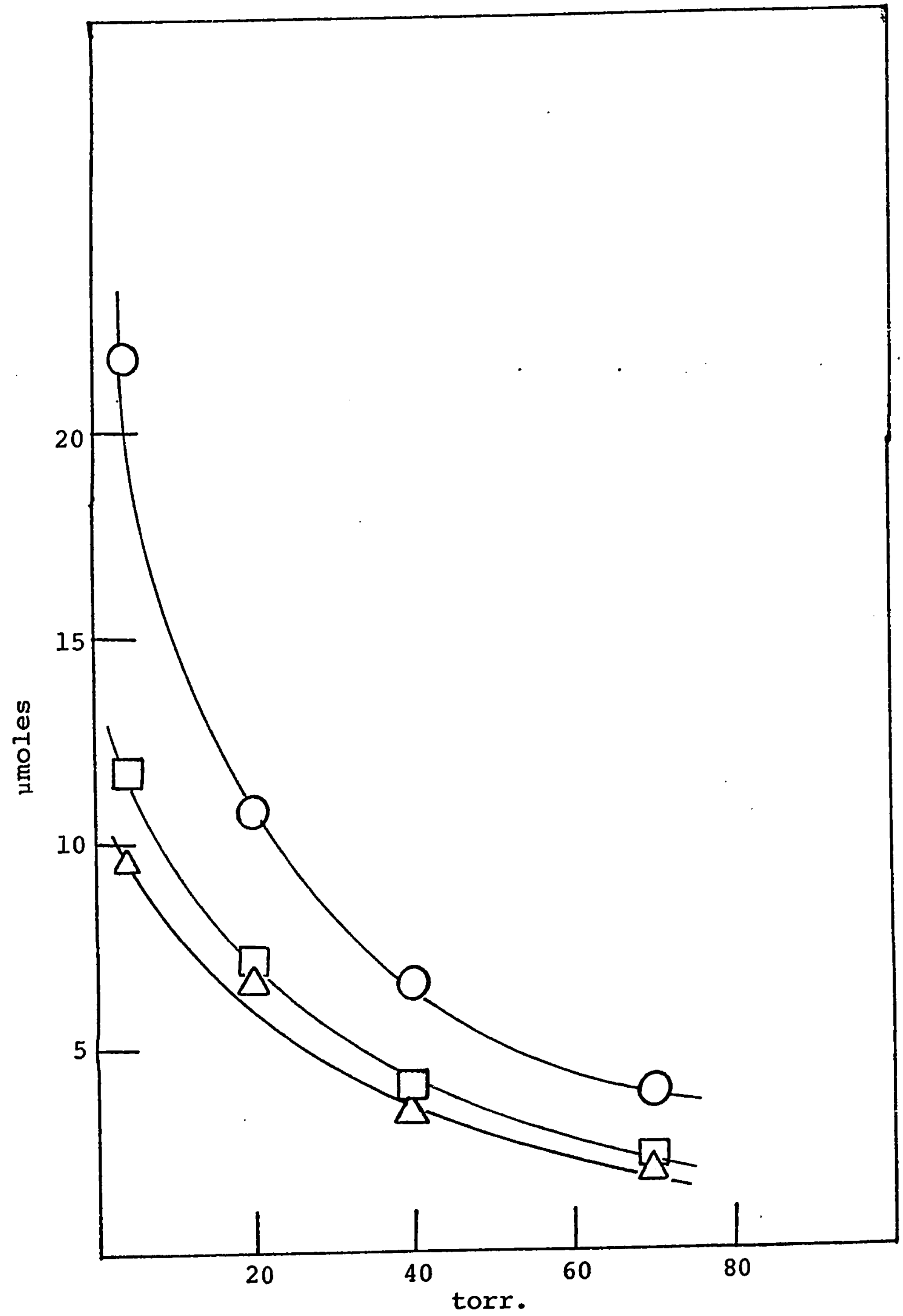


Fig. 7. Product yields as a function of substrate pressure in the photolysis of 1,3 perfluorobutadiene.

□ $CF_3C\equiv CF$ ○ C_2F_4 △

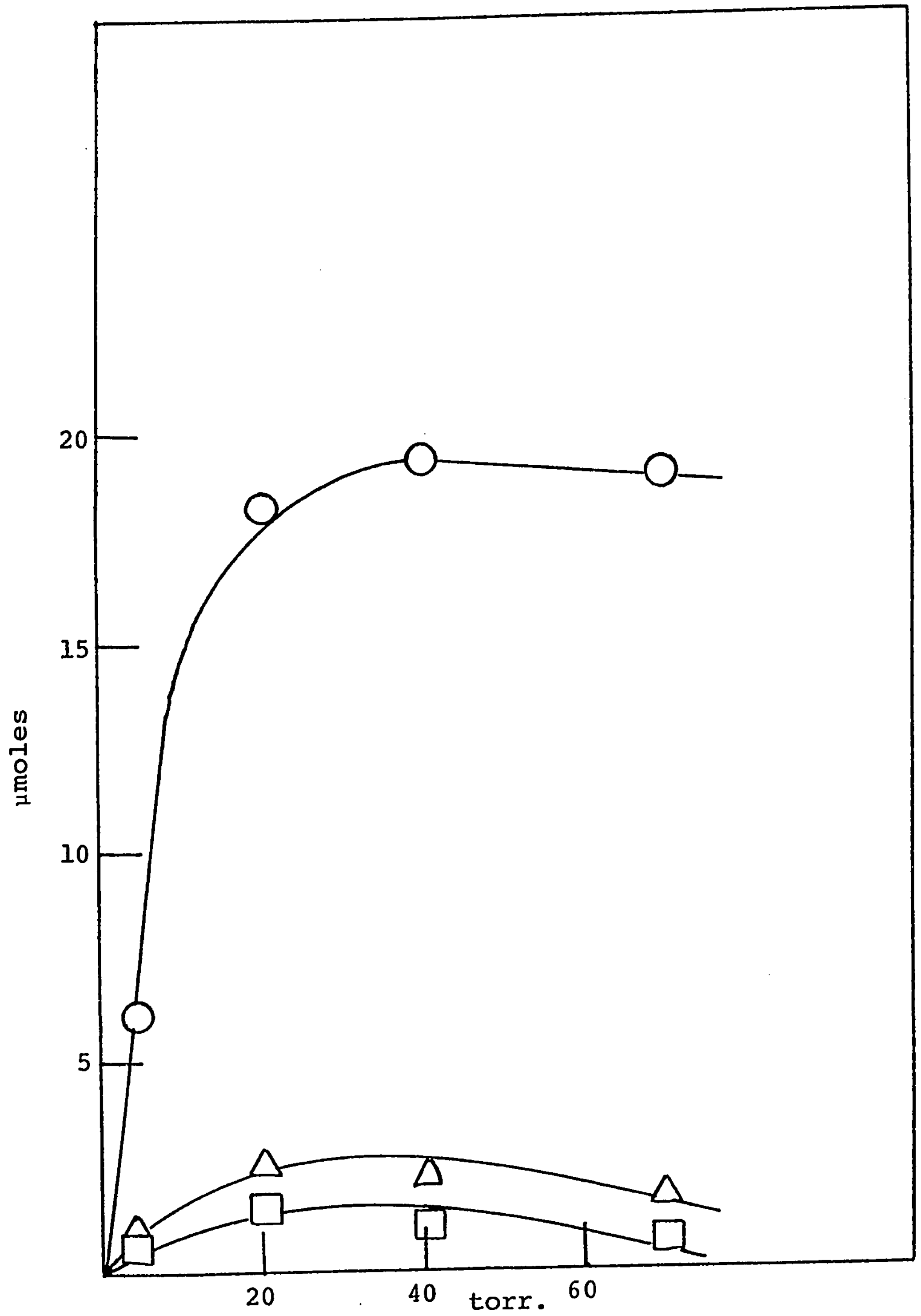
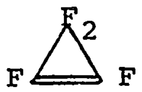
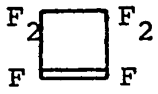


Fig. 8. Product yields as a function of substrate pressure in the photolysis of 1,3 perfluorobutadiene.

○ CB △ BD1,2 □ Bu

TABLE 6

Product yields as a function of added CF_4 pressure in the photolysis of 1,3-perfluorobutadiene[(a)]

Pressure CF_4 Torr	$CF_3C{\equiv}CF$ µmoles	 µmoles	 µmoles
0	21.2	9.6	6.2
200	3.4	1.6	12.5
340	1.8	1.4	11.0
570	1.3	1.4	9.0

(a) Pressure of 1,3-perfluorobutadiene = 4 torr.
All runs of sixty minutes duration.

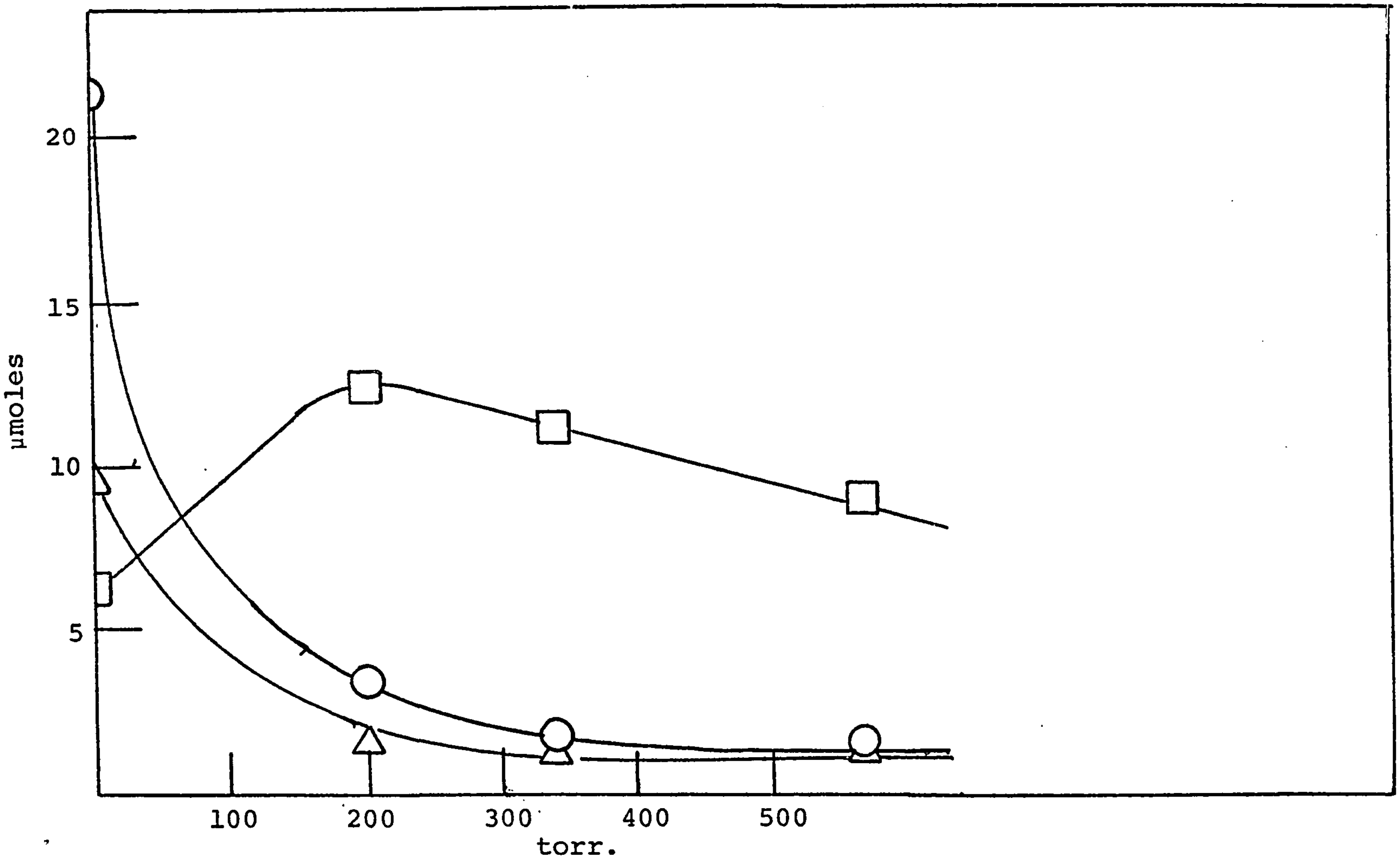
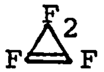


Fig. 9. Product yields as a function of added CF_4 pressure in the photolysis of 1,3-perfluorobutadiene.

○ $CF_3C\equiv CF$ △ 

□ perfluorocyclobutene

Product yields were studied as a function of substrate pressure and of the pressure of added CF_4. These are summarized in Tables 7 and 8. The results are plotted in Figs. 10 and 11. The isomeric products 1,2-perfluorobutadiene and 2-perfluorobutyne were too small (<.01 μmole) to be measured and as 1,3-perfluorobutadiene appeared after perfluorocyclobutene on the g.l.c. trace it could not be measured except at low pressure of perfluorocyclobutene.

Photolysis of 2-perfluorobutyne

The products produced by photolysis of 2-perfluorobutyne were the same as those found in the photolysis of the other isomers except that the isomeric products which were identified by comparison of their retention times with the authentic samples were 1,2-perfluorobutadiene, perfluorocyclobutene and 1,3-perfluorobutadiene.

Product yields were very small in the present case and not amenable to quantitative treatment.

DISCUSSION

Photolysis of 1,3-perfluorobutadiene

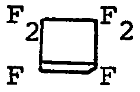
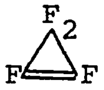
The following reaction scheme is proposed to account for the observed results.

[1] $BD + h\nu \longrightarrow BD^*$

[2] $BD^* \longrightarrow {:}CF_2 + C_3F_4$

TABLE 7

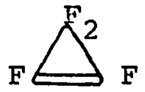
Product yields as a function of substrate pressure in the photolysis of perfluorocyclobutene(a)

 torr	C_2F_4 µmoles	$CF_3C{\equiv}CF$ µmoles	 µmoles
2.14	.11	.13	.09
5.26	.29	.30	.18
16.27	.41	.47	.20
21.60	.50	.51	.26

(a) All runs of 60 minutes duration except for that at 21.60 torr. Values of product yields in this case are 4/5ths of actual value found.

TABLE 8

Product yields as a function of added CF_4 in the photolysis of perfluorocyclobutene$^{(a)}$

Pressure CF_4 torr	$CF_3C{\equiv}CF$ µmoles	 µmoles	$CF_2{=}CF{-}CF{=}CF_2$ µmoles
0	0.47	0.175	very small
116	0.25	0.08	.04
219	0.22	0.08	.07

(a) Perfluorocyclobutene = 15.3 torr. All runs of sixty minutes duration.

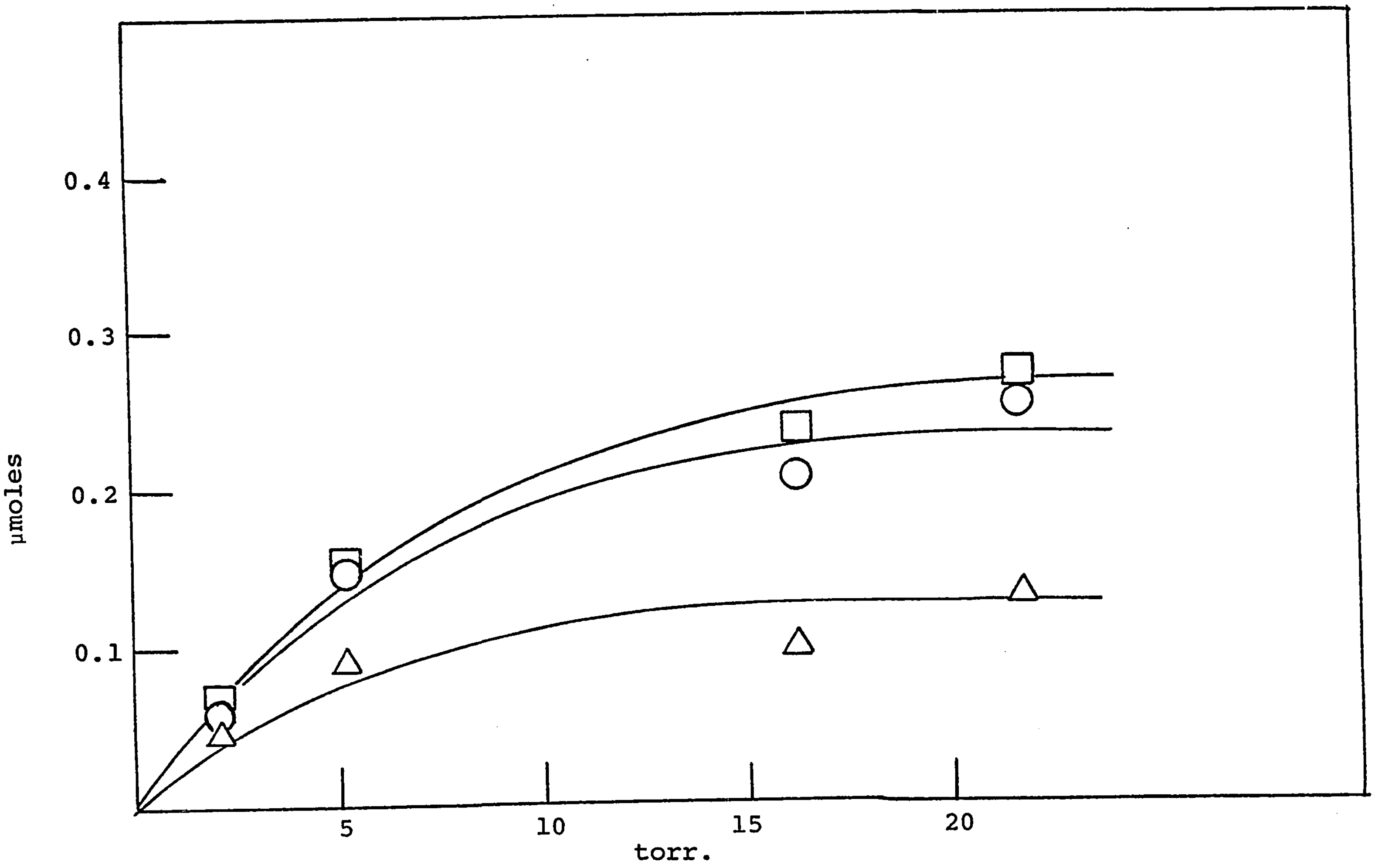


Fig. 10. Product yields as a function of substrate pressure in the photolysis of perfluorocyclobutene.

○ $CF_3C\equiv CF$ □ C_2F_4 △

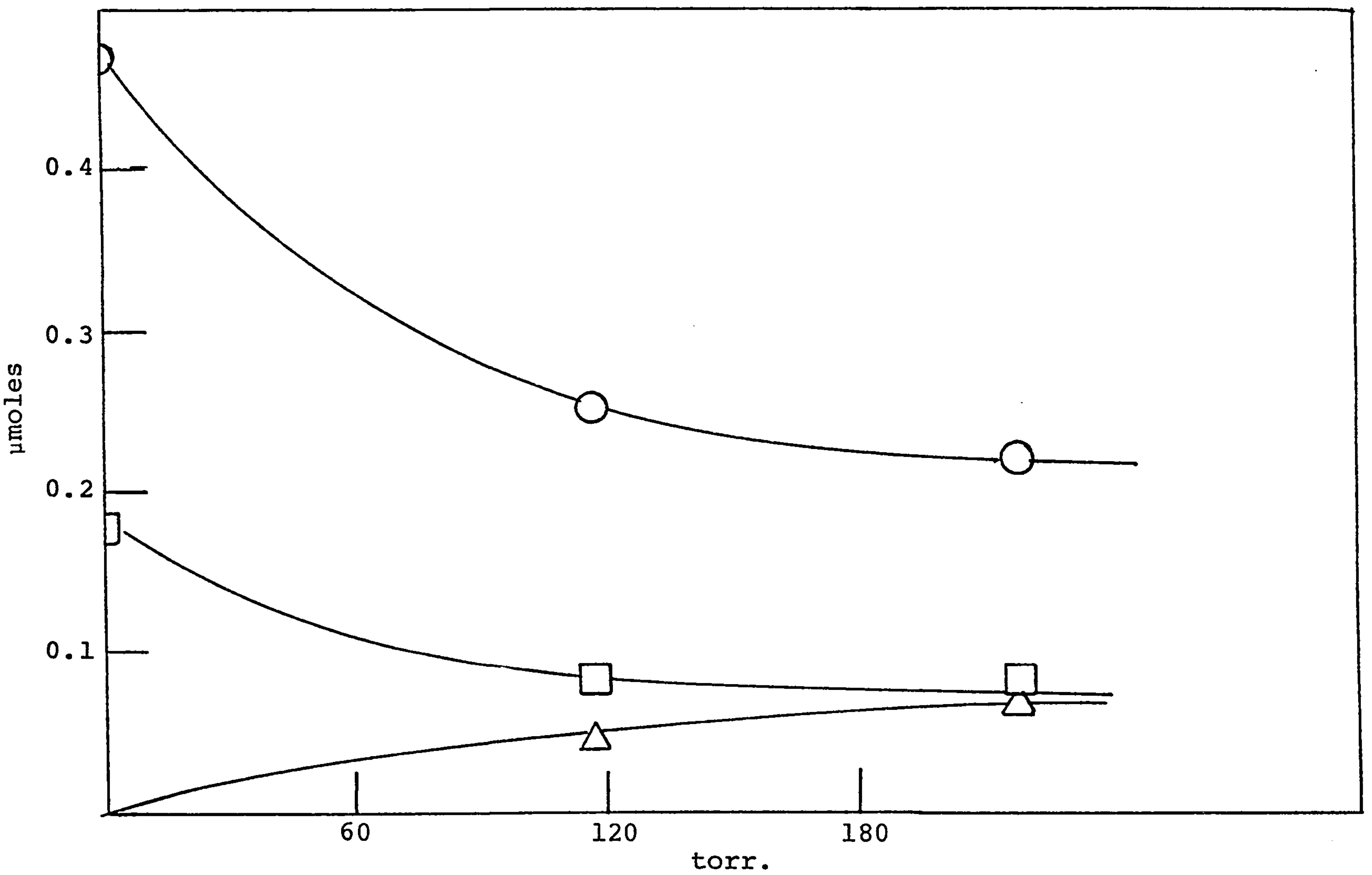
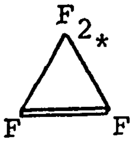
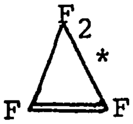
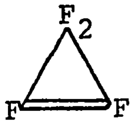


Fig. 11. Product yields as a function of added CF_4 pressure in the photolysis of perfluorocyclobutene.

○ $CF_3C \equiv CF$ □  △ 1,3-perfluorobutadiene

[3] $C_3F_4 \rightleftarrows$ 

[4] $\rightleftarrows CF_3C\equiv CF^*$

[5]  $+M \longrightarrow$ 

[6] $CF_3C \equiv CF^* + M \longrightarrow CF_3C \equiv CF$

[7] $BD^* \rightleftarrows CB^*$

[8] $\rightleftarrows BD^*1,2$

[9] $\rightleftarrows Bu^*$

[10 $CB^* + M \longrightarrow CB + M'$

[11] $BD^* 1,2 + M \longrightarrow BD + M'$

[12] $Bu^* + M \longrightarrow Bu + M'$

[13] $2{:}CF_2 \longrightarrow C_2F_4$

[14] $BD^* + M \longrightarrow BD + M'$

Where BD is 1,3-perfluorobutadiene, CB is perfluorocyclobutene and BD 1,2 is 1,2-perfluorobutadiene and Bu is 2-perfluorobutyne. On the basis of a steady state mechanism a relationship for $R_{C_3F_4}/R_{CB}$ can be derived.

$$R_{CB} = k_{10}[CB^*][M]$$

where R_{CB} is the rate of formation of perfluorocyclobutene.

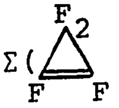
$$\frac{d[CB^*]}{dt} = -\frac{d[CB^*]}{dt}$$

$$k_7\ [BD^*] = k_{-7}[CB^*] + k_{10}[CB^*][M]$$

$$[CB^*] = k_7[BD^*] \Big/ k_{-7} + k_{10}\ [M]$$

$$\therefore R_{CB} = k_7k_{10}[BD^*][M] \Big/ k_{-7} + k_{10}[M]$$

$$R_{C_3F_4} = K_2[BD^*]$$

where $R_{C_3F_4}$ is the rate of formation of $\Sigma($  $+ CF_3C{\equiv}CF)$.

$$R_{C_3F_4} \Big/ R_{CB} = (k_2\ k_{-7}/k_7\ k_{10})\frac{1}{[M]} + k_2/k_7.$$

Thus a plot of $R_{C_3F_4}/R_{CB}$ vs $\frac{1}{[M]}$, where [M] is the pressure of BD, should yield a straight line. Such a plot is shown in Fig.12. From this plot we find

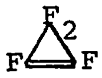
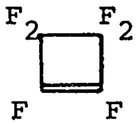
$$k_2/k_7 = .08$$

$$k_{-8}/k_{11} = 2.2 \times 10^2 \text{ torr}.$$

We can derive similar types of relationships for BD 1,2 and Bu.

TABLE 9

Product yields and ratios vs. pressure of substrate in the photolysis of 1,3-perfluorobutadiene[(a)]

[M]: pressure 1,3-perfluorobutadiene	1/[M] torr^{-1}	 + $CF_3C\equiv CF$		$R_{C_3F_4}/R_{CB}$ (b)
10	0.100	25.1	13.4	1.88
12.5	0.080	21.9	15.0	1.46
15	0.066	20.5	16.3	1.26
20	0.050	17.3	18.3	.94
30	0.033	13.0	19.2	.68
40	0.025	10.1	19.3	.52
50	0.020	8.2	19.2	.43
60	0.016	6.9	19.1	.36
70	0.014	6.0	19.0	.32

(a) Product yields derived from Figs. 7 and 8. All yields in μmoles.

(b) See text

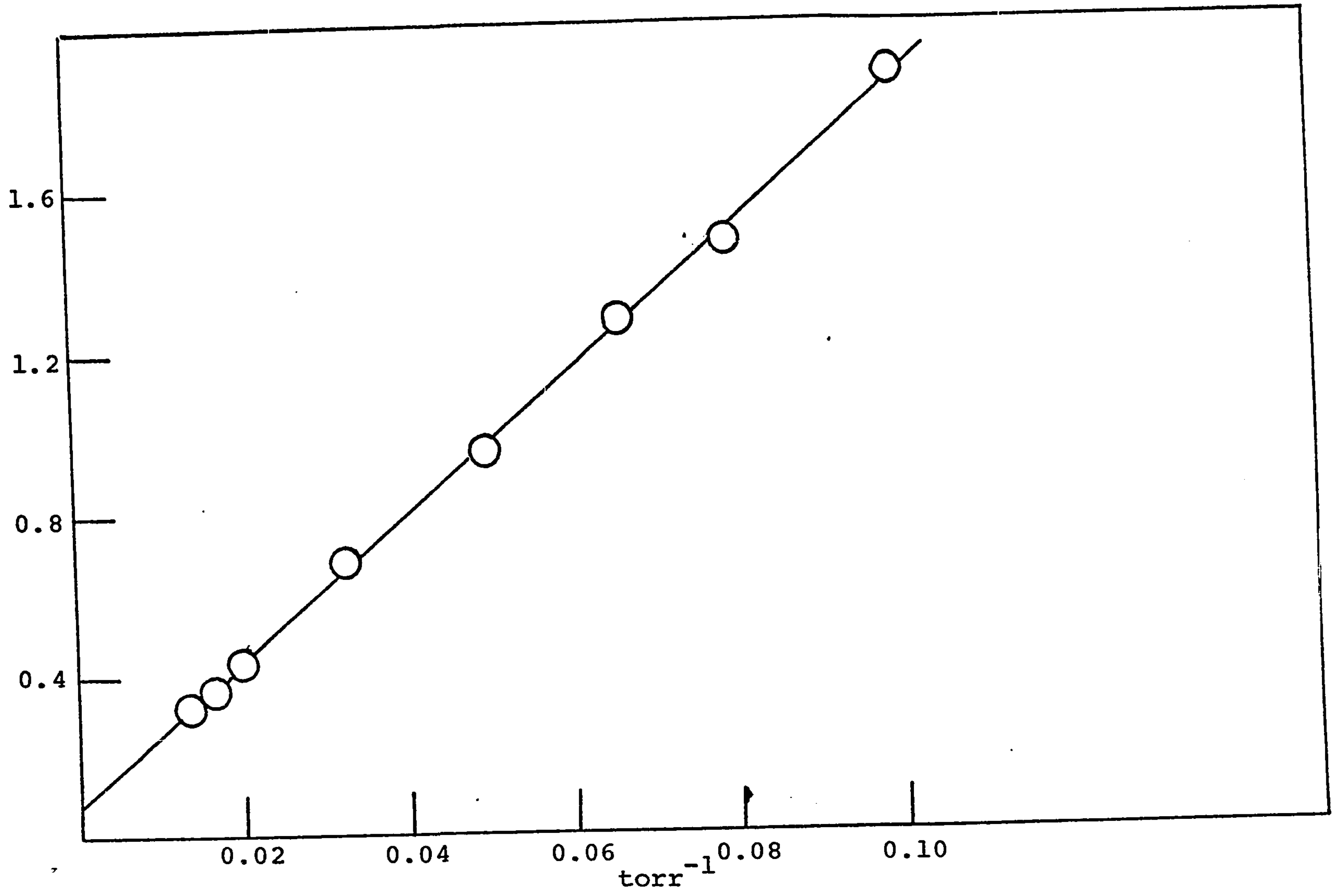


Fig. 12. A plot of $R_{C_3F_4}/R_{CB}$ vs. 1/[M].

Thus

$$R_{C_3F_4}/R_{BD1,2} = (k_2\ k_{-8}/k_{11}) \frac{1}{[M]} + k_2/k_8$$

and

$$R_{C_3F_4}/R_{Bu} = (k_2 k_{-9}/k_9 k_{12}) \frac{1}{[M]} + (k_2/k_9).$$ Plots of $R_{C_3F_4}/R_{Bu}$ and $R_{C_3F_4}/R_{BD1,2}$ vs $\frac{1}{[M]}$ are shown in Fig. 13. From these plots we find the relative rate constants shown in Table 11.

From these results, it can be seen that those isomerisation reactions which involve fluorine atom shifts will be considerably slower than reaction 7, in which no fluorine shift is involved.

The formation of excited 1,2-perfluorobutadiene, which involves only one fluorine migration is approximately four times faster than formation of excited 2-perfluorobutyne, which involves the migration of two fluorine atoms.

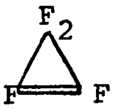
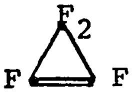
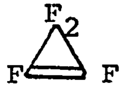
From the reaction scheme it can be seen that 2 x C_2F_4 should be equal to the sum of  and $CF_3C\equiv CF$. In Table 12 it can be seen that in fact the ratio $2C_2F_4/$ Σ  + $CF_3C\equiv CF$ = .79 ± .03. This implies that all of the $:CF_2$ is not appearing as C_2F_4. No product attributable to reaction of $:CF_2$ with the substrate was found. If it

Table 10

Product yields and ratios vs. substrate pressure in the photolysis of 1,3-perfluorobutadiene(a)

Pressure Perfluoro-butadiene 1,3 torr ([M])	$\frac{1}{[M]}$ torr^{-1}	 + $CF_3C\equiv CF$	Bu	BD 1,2	$R_{C_3F_4} \vert R_{Bu}$	$R_{C_3F_4} / R_{BD\ 1,2}$
10	0.100	25.1	1.55	2.0	16.2	12.55
12.5	0.080	21.9	1.6	2.3	13.7	9.5
15	0.066	20.5	1.6	2.5	12.8	8.2
20	0.050	17.3	1.6	2.7	10.8	6.4
30	0.033	13.0	1.4	2.6	9.3	5.0
40	0.0250	10.1	1.1	2.5	9.1	4.0
50	0.0200	8.2	1.0	2.2	8.2	3.7
60	0.0166	6.9	0.8	2.0	8.6	3.45
70	0.0143	6.0	0.7	1.8	8.5	3.33

(a) Product yields derived from curves in Figs. 7 and 8.

All yields in μmoles.

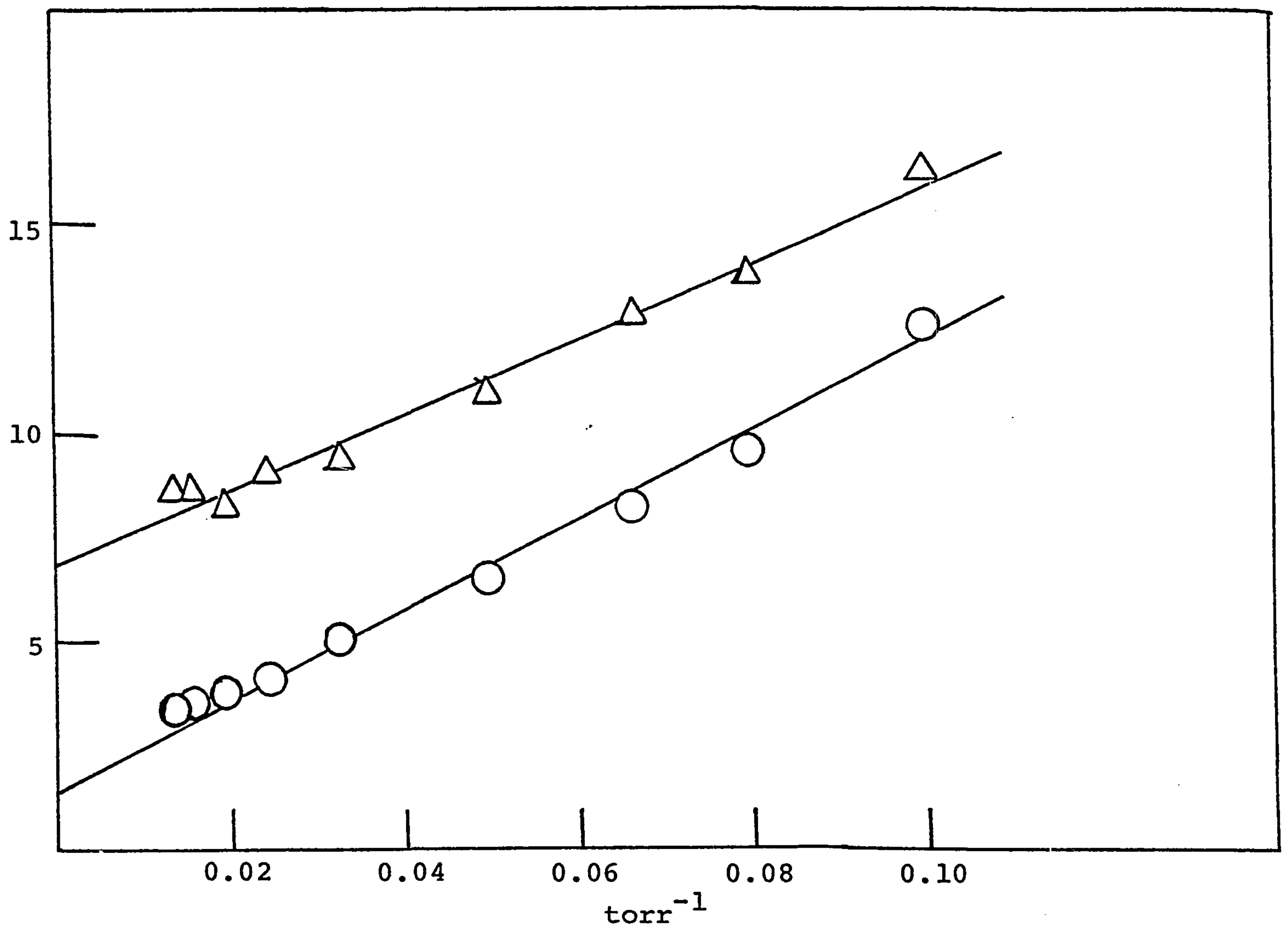


Fig. 13. $R_{C_3F_4}/R_{BD1,2}$ and $R_{C_3R_4}/R_{Bu}$ vs. 1/[M].

△ $R_{C_3F_4}/R_{Bu}$ ○ $R_{C_3F_4}/R_{BD1,2}$

TABLE 11

Relative rate constants

$k_2/k_8 = 1.6$

$k_{-8}/k_{11} = 6.4 \text{ X } 10 \text{ torr}$

$k_2/k_9 = 6.6$

$k_{-9}/k_{12} = 1.4 \text{ X } 10 \text{ torr}$

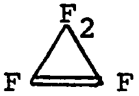
$k_2/k_7 = .08$

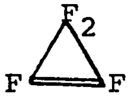
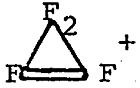
$\therefore \quad k_8/k_7 = .05$

$k_9/k_7 = .012$

$k_9/k_8 = .24$

TABLE 12

Ratio of C_2F_4 to  + $CF_3C{\equiv}CF$ as a function of pressure in the photolysis of 1,3-perfluorobutadiene

Pressure 1,3-Perfluorobutadiene torr	 + $CF_3C{\equiv}CF$ µmoles	C_2F_4 µmoles	$2 \times C_2F_4$ / ( + $CF_3C{\equiv}CF$)
5	30.2	11.6	.77
10	25.1	9.8	.78
15	20.5	8.4	.82
20	17.3	7.1	.82
25	14.9	6.1	.82
30	13.0	5.2	.80
40	10.1	3.9	.77
50	8.2	3.1	.76
60	6.9	2.6	.76

Values derived from curves in Fig. 7.

were in fact reacting with the substrate one would expect the above ratio to decrease linearly with increasing substrate pressure. The $:CF_2$ may be going to polymer. On the basis of steady state assumption the following may be derived.

$$R_C = k_5 [M][C^*]$$

$$\frac{d[C^*]}{dt} = - \frac{d[C^*]}{dt}$$

$$k_3[C_3F_4] = (k_{-3} + k_5[M])[C^*]$$

$$R_C = \frac{k_3k_5 [M][C_3F_4]}{k_{-3} + k_5[M]}$$

Where C is perfluorocyclopropene.

Similarly for perfluoropropyne

$$R_P = \frac{k_4k_6[M][C_3F_4]}{k_{-4} + k_6[M]}$$

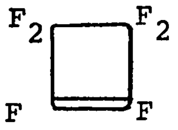
Thus

$$R_C/R_P = \frac{k_3k_5(k_{-4} + k_6[M])}{k_4k_6(k_{-3} + k_5[M])}$$

This predicts that a plot of R_C/R_P vs. pressure should be a smooth curve. In Table 13 values for R_C/R_P are given. It can be seen that this curve appears to go through a maximum. This implies that collisional deactivation is not directly proportional to pressure. One would expect the cyclopropene yield to be larger than the propyne yield if, as seems likely ring closure is more rapid than fluorine atom shift. However, if the cyclopropene contains a large amount of excess energy then ring opening will also be rapid. Several collisions may be necessary to stabilize the cyclopropene and thus, propyne formation will be favoured as it will be more easily stabilized. Also the variation in relative rates of formation as pressure increases will be complex. It can be seen that only at high pressures of added CF_4 is the yield of cyclopropene equal to that of propyne. This again shows that a large number of collisions must be necessary to deactivate the excited cyclopropene.

In their work on the thermal isomerisation of 1,3-perfluorobutadiene, Schlag and Peatman (71) have shown that the rate constant for the reaction

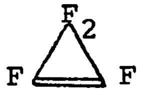
$$CF_2 = CF-CF=CF_2 \rightarrow$$



is equal to $10^{12.03}\ e^{-35,380\pm19/RT}$ sec^{-1}

TABLE 13

Relative rates of formation of perfluorocyclopropene and perfluoropropyne as a function of the pressure of 1,3-perfluorobutadiene

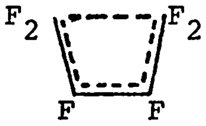
Pressure 1,3-perfluorobutadiene torr	 μmoles	$CF_3C{\equiv}CF$ μmoles	R_C/R_P (a)
10	8.3	16.6	.500
15	7.2	13.3	.54
20	6.3	11.1	.57
25	5.4	9.5	.57
30	4.7	8.3	.57
35	4.1	7.3	.56
40	3.6	6.5	.55
50	2.85	5.35	.53
60	2.4	4.55	.53
70	2.05	3.85	.53

(a) See text.

whereas for the reverse reaction

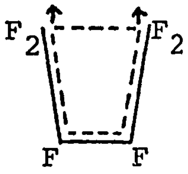
$$k = 10^{14.12} e^{-47,080\pm19/RT} \sec^{-1}.$$

Thus the cyclobutene is 11.7 kcal/mole more stable than the butadiene.

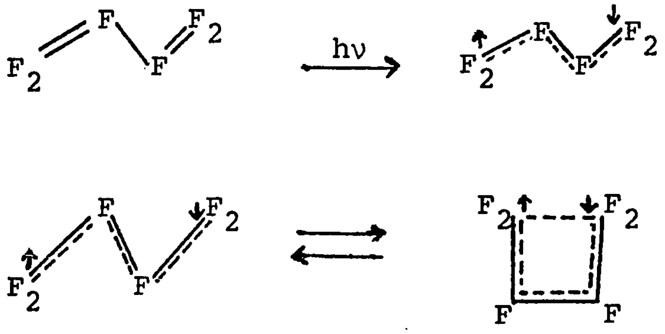
The authors proposed that isomerisation proceeds through an intermediate of the form 

Stuckey and Heicklen (33) have shown that mercury photosensitization of 1,3-perfluorobutadiene leads to isomerisation to perfluorocyclobutene. The reverse is found in the mercury photosensitization of perfluorocyclobutene. They proposed the following reaction scheme to account for the observed results.

[1] $B + Hg^* \rightarrow B^*$
[2] $B^* \rightarrow I$
[3] $I \rightarrow B$
[4] $I \rightarrow C$

Where B is 1,3-perfluorobutadiene, C is perfluorocyclobutene and I is an intermediate. A similar type of reaction scheme is postulated in the mercury photosensitization of perfluorocyclobutene. They found in both cases that $k_3/(k_3+k_4) = .86$. Thus the intermediate in this case preferentially reverts to the butadiene despite the greater stability of the cyclobutene. The triplet nature of the intermediate must be responsible for this. If we visualise the intermediate as  then there are two possible reaction paths. These are spin inversion to give cyclobutene or ring opening to give a biradical which on spin inversion gives butadiene. Since ring opening will presumably be faster than spin inversion the butadiene will be favored.

In the photolysis we can visualise the process on somewhat similar lines.

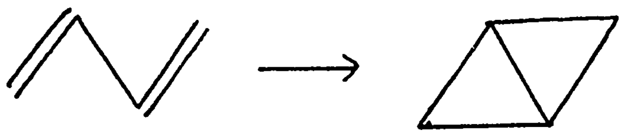


In this case the intermediate can either revert to the excited butadiene or be collisionally deactivated to yield cyclobutene. In the excited butadiene a 3,1 or 2,4 fluorine atom shift can yield an excited 1,2-perfluorobutadiene which can also revert to the excited butadiene or be collisionally deactivated. Similarly the shift of two fluorine atoms will be lead to formation of excited

2-perfluorobutyne. As decomposition from the butadiene also occurs the isomerisation should be favored at higher pressures as is found to be the case.

Photolysis of 1,3-butadiene in solution leads to formation of cyclobutene and bicyclo(1,1,0)butane (72). Cyclobutene was the predominant isomer despite the fact that one would expect the bicyclobutane to predominate due to the greater stability of the trans form of the butadiene from which the bicyclobutane would be formed.

Thus:



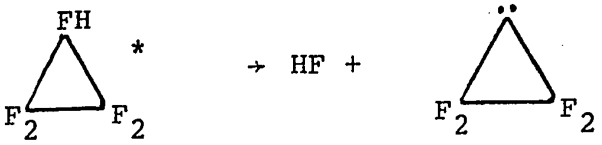
However due to ring strain in the bicyclic compound the cyclobutene will predominate.

In the present case no bicyclic isomer is found. This is to be expected as none was found in the gas phase photolysis of 1,3-butadiene.

Perfluorocyclopropene has been generated by reaction of O atoms with 1,3-perfluorobutadiene (19). No other isomers of C_3F_4 were found. On mercury photosensitization perfluorocyclopropene yielded perfluoropropyne and perfluoroallene. Thus the C_3F_4 formed in the present work must contain excess energy as it forms perfluoropropyne. The difference in reactivity of the C_3F_4 from photosensitization may be due to it being in a triplet state.

In the photolysis of trifluoroethylene (20), addition of $:CF_2$ to the substrate produced a cyclopropane which formed C_3F_4 by molecular elimination of HF. This species yielded perfluorocyclopropene or perfluoroallene. However the carbene formed in this case is probably in a different electronic state to that formed by decomposition of excited 1,3-perfluorobutadiene.

$$CF_2{=}CF{-}CF{=}CF_2^{*} \rightarrow :CF_2 + C_3F_4$$



The reactions of these two species are not directly comparable.

Since the C_3F_4 did not react with ethylene, isomerisation and ring closure must be fairly rapid. The failure of O_2 to produce any effect on the products implies that no triplet states are involved.

2. Photolysis of perfluorocyclobutene

A reaction scheme similar to that for the 1,3-perfluorobutadiene is to be expected in the photolysis of perfluorocyclobutene as the products obtained are the same. Insufficient data were obtained to confirm this by testing the mechanism on the basis of a steady state treatment. The overall product yields in the photolysis of perfluorocyclobutene were smaller by a factor of 20 than those found in the photolysis of 1,3-perfluorobutadiene. There are two possible explanations for this. Firstly, since perfluorocyclobutene is more stable than 1,3-perfluorobutadiene, a larger activation energy will be required for all steps leading to product formation. Thus, deactivation of the excited cyclobutene will be faster relative to product formation than in the case of the butadiene. Secondly, it seems probable that the amount of light absorbed will be smaller in the case of perfluorocyclobutene. The fact that the fragmentation product yields increase with increasing pressure of substrate shows that light absorption is decreased at lower pressures. This indicates a lower extinction co-efficient for perfluorocyclobutene than for 1,3-perfluorobutadiene where, as fragmentation product yields decrease with increasing substrate pressure, maximum light absorption at low pressures is indicated.

From Fig. 11 it can be seen that the yields of the products from the photolysis of perfluorocyclobutene vary with increasing pressure of CF_4. The fragmentation products decrease and the isomerization product increases as was found in the photolysis of 1,3-perfluorobutadiene in the presence of CF_4. This supports a similar reaction scheme for photolysis of both compounds.

In the photolysis of 2-perfluorobutene although similar products to the above cases were found, their yields were very small. This is to be expected since fluorine atom shifts will be necessary for both fragmentation and isomerization.

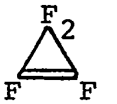
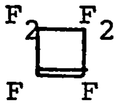
CHAPTER VI

Photolysis of Perfluorocyclopentene

The following products were formed in the photolysis of perfluorocyclopentene: C_2F_4, perfluoromethylacetylene, perfluoroallene, perfluorocyclopropene, perfluorocyclobutene and perfluorovinylcyclopropane. C_2F_4 was identified by comparison of its mass spectrum and retention time with that of an authentic sample. Perfluoroallene was identified by its mass and I.R. spectra which showed strong absorptions at 1040, 1240 and 2050 cm^{-1} compared to 1037, 1243 and 2065 cm^{-1} observed for an authentic sample (68). The other C_3F_4 isomers were identified by comparison of their mass and I.R. spectra with those of authentic samples of perfluoromethylacetylene and perfluorocyclopropene (19). Perfluorocyclobutene was identified by comparison of its mass spectrum and retention time with that of an authentic sample. Perfluorovinylcyclopropane was identified by its mass and I.R. spectrum which showed strong absorption at 1720 cm^{-1} attributable to CF_2=CF stretching and at 1050 cm^{-1} attributable to ring absorption. The product yields were studied both as a function of substrate pressure and of pressure of added CF_4. The results of these experiments are shown in Tables 14 and 15 and are plotted in Figs 14, 15, 16 and 17.

TABLE 14

Product yields as a function of pressure in the photolysis of perfluorocyclopentene[(a)]

Pressure C_5F_8 torr	C_2F_4 μmoles	$CF_2=C=CF$ μmoles	 μmoles	$CF_3C\equiv CF$ μmoles	 μmoles	PVC[(b)] μmoles
2.5	4.28		1.75	1.76	0.79	2.61
3.0	5.04	0.88	2.00	2.40	0.96	3.17
5	5.12	1.15	2.11	2.46	1.01	3.95
8.5	6.05	1.71	2.33	2.77	1.06	3.63
10.0	4.85	2.01	2.07	2.23	1.06	3.68
15.0	4.53	1.92	1.19	1.83	0.85	3.38
30.0	3.13	1.98	0.58	1.00	0.69	2.55
60.0	2.18	1.92	0.27	0.46	0.56	2.16

(a) All runs of sixty minutes duration.

(b) Perfluorovinylcyclopropane.

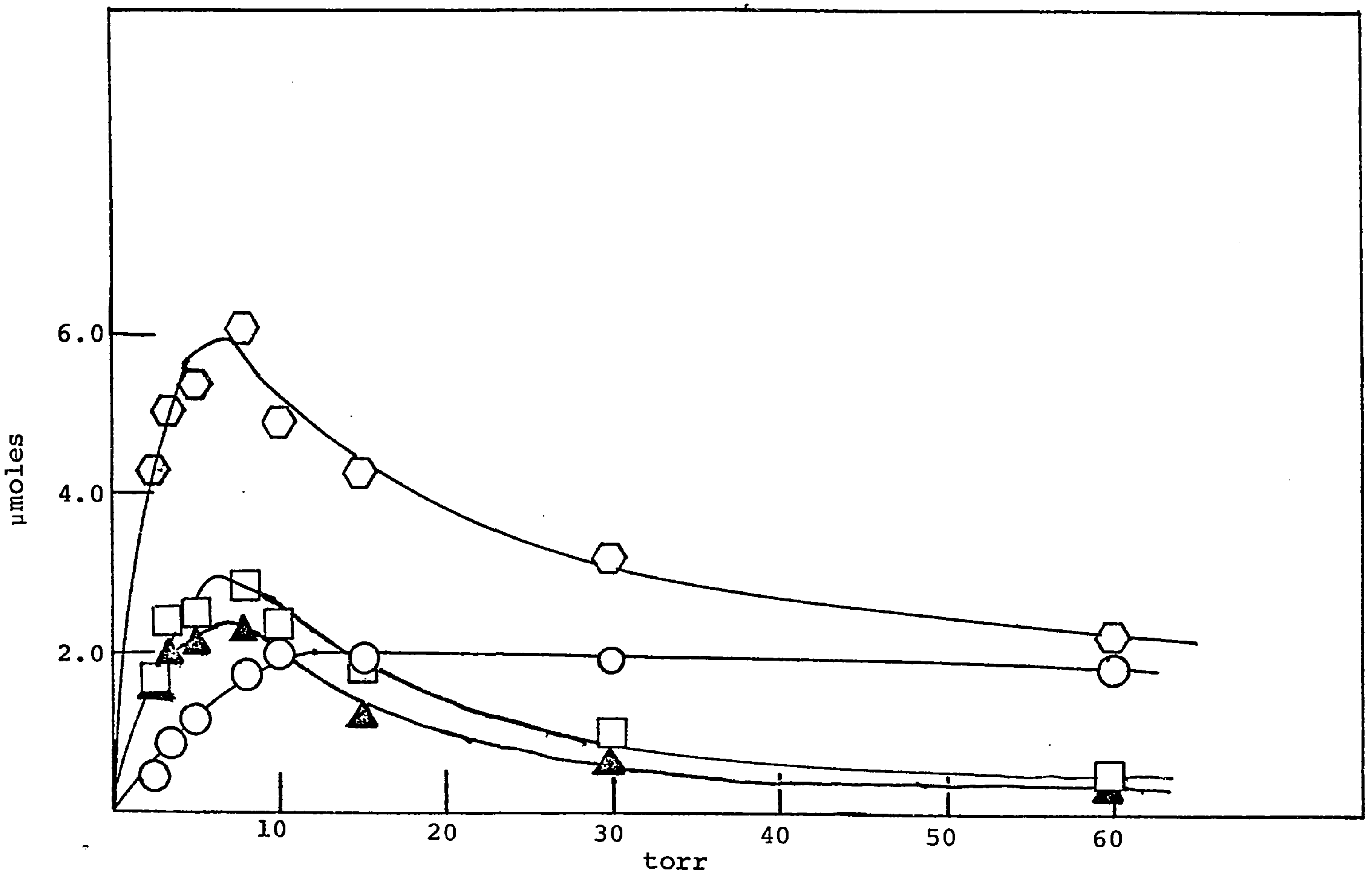
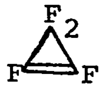


Fig. 14. Product yields as a function of pressure in the photolysis of perfluorocyclopentene.

⬡ C_2F_4 □ $CF_3C≡CF$ ▲



○ $CF_2=C=CF_2$

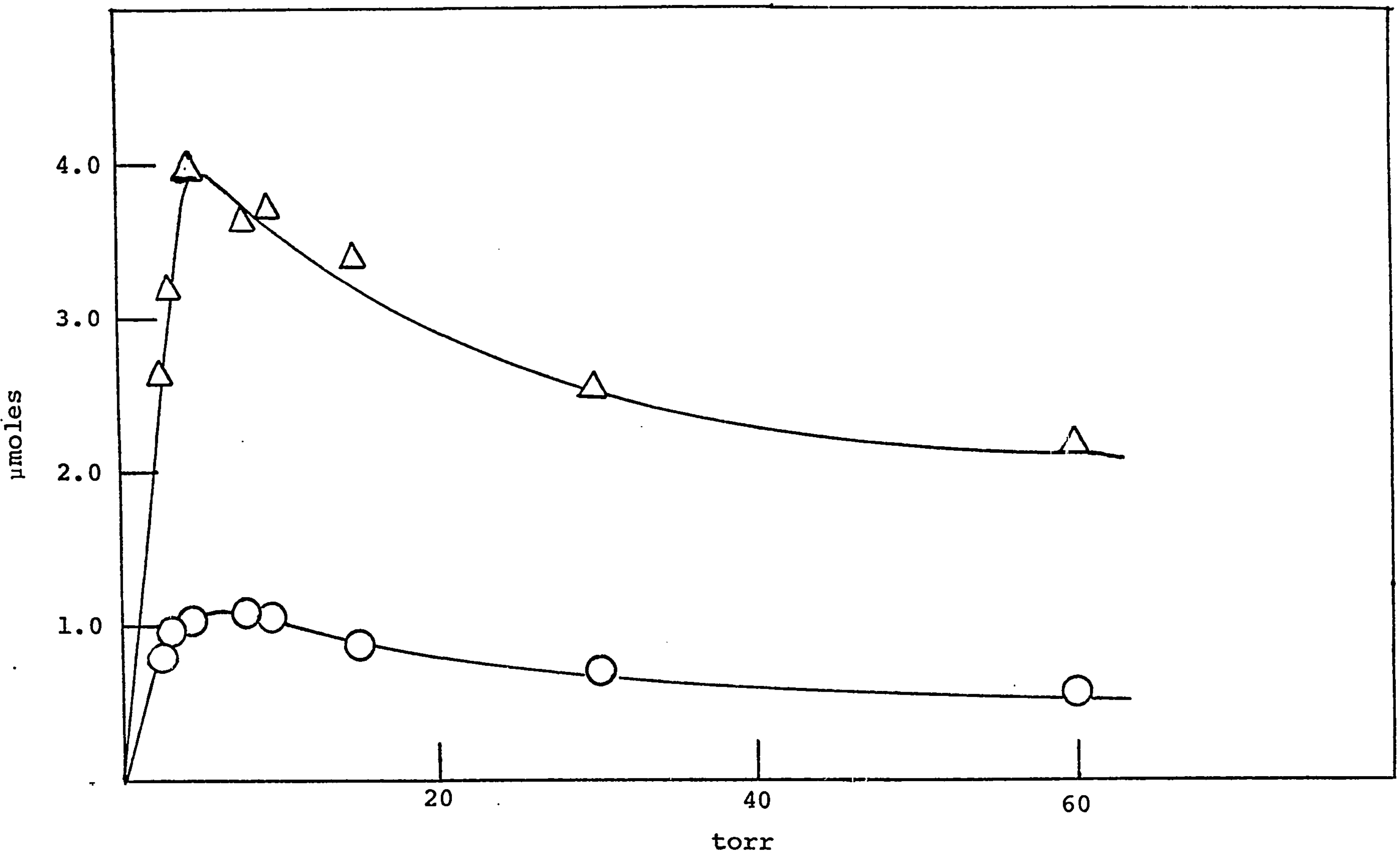


Fig. 15. Product yields as a function of pressure in the photolysis of perfluorocyclopentene.

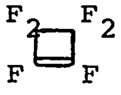
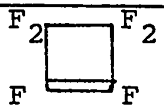
○  △ PVC

TABLE 15

Product Yields as a function of added CF_4 in the photolysis of perfluorocyclopentene$^{(a)}$

Pressure CF_4 torr	$CF_2=C=CF_2$ µmoles	 µmoles	$CF_3C\equiv CF$ µmoles	 µmoles	PVC µmoles
0	2.01	2.07	2.23	1.06	3.68
10	1.50	1.08	1.33	0.67	2.64
20	1.00	0.83	0.85	0.49	1.67
50	0.73	0.36	0.48	0.34	1.03
100	0.04	trace	trace	0.04	0.16

(a) Pressure perfluorocyclopentene = 10 torr
All runs were of 60 minutes duration.

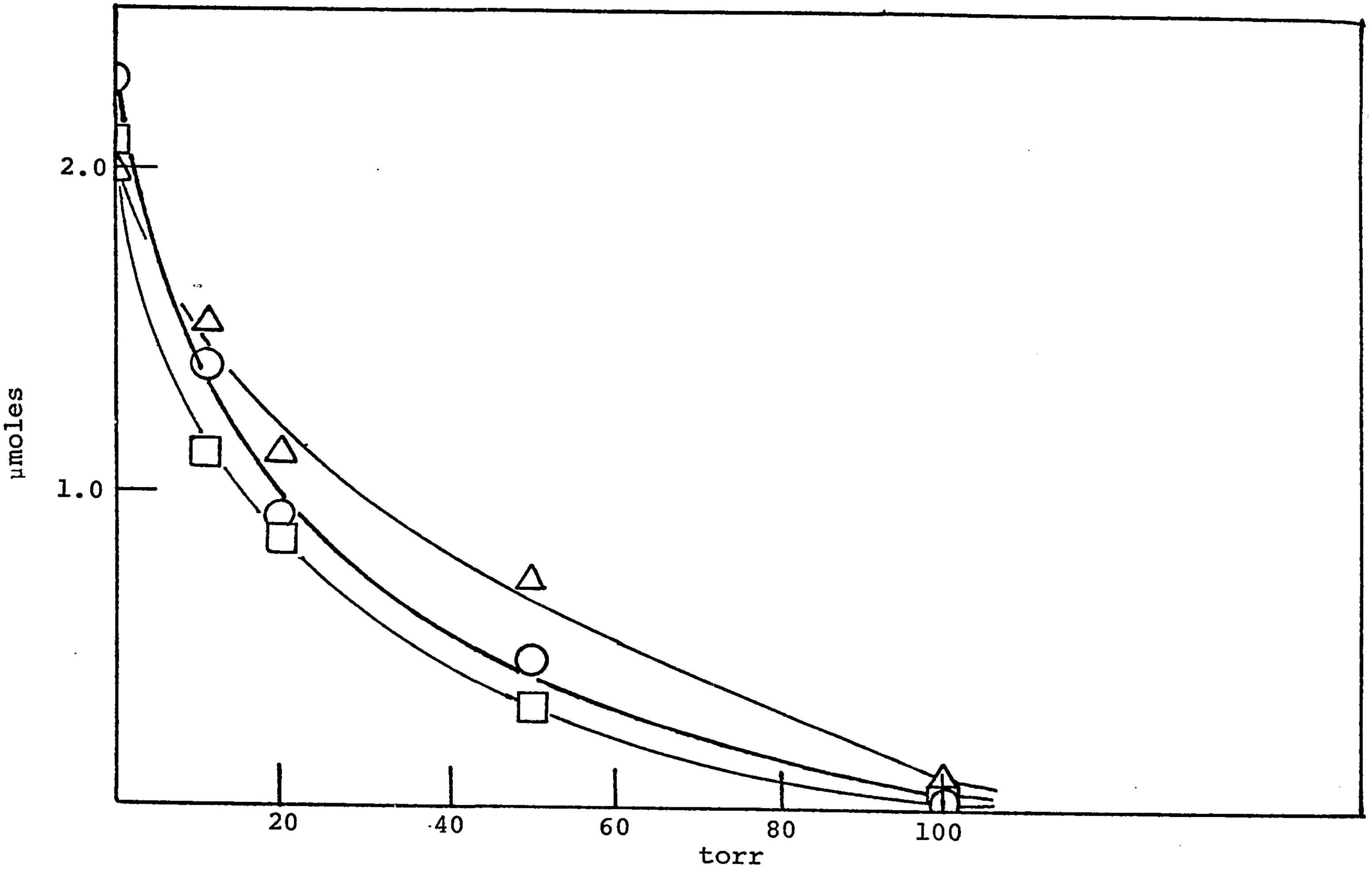


Fig. 16. Product yields as a function of added CF_4 in the photolysis of perfluorocyclopentene.

△ $CF_2=C=CF_2$ ○ $CF_3C\equiv CF$ □ 

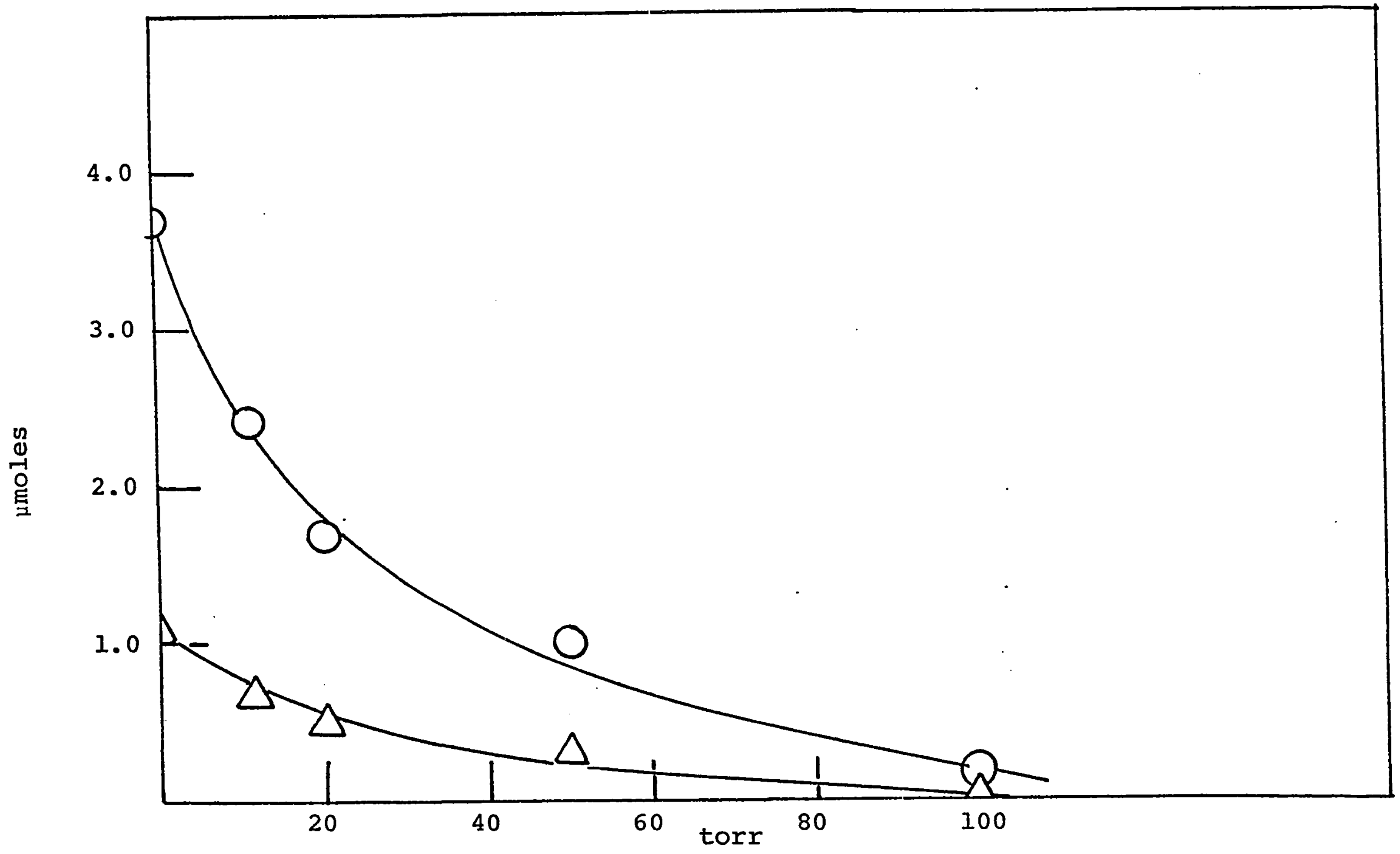
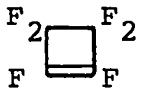


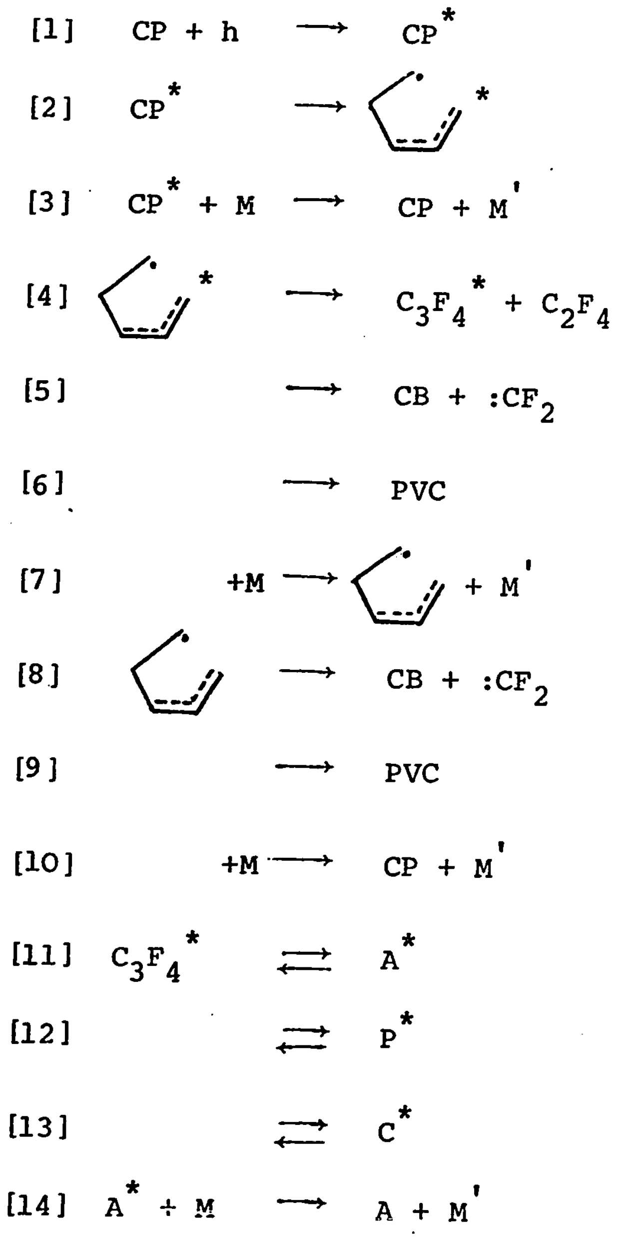
Fig. 17. Product yields as a function of added CF_4 in the photolysis of perfluorocyclopentene.

△ 

○ PVC

Discussion

The following reaction scheme is proposed to account for the observed products



[15] $P^* + M \rightarrow P + M'$

[16] $C^* + M \rightarrow C + M'$

[17] $2{:}CF_2 \rightarrow C_2F_4$

where CP is perfluorocyclopentene, CB is perfluorocyclobutene, PVC is perfluorovinylcyclopropane, A is perfluoroallene P is perfluoropropyne and C is perfluorocyclopropene.

On the basis of a steady state mechanism the following relationship can be derived.

$$R_{CB} = k_4[B^*] + k_8[B]$$

where B is the biradical

$$\frac{d[B]}{dt} = -\frac{d[B]}{dt}$$

$$k_7[B^*][M] = \left(k_8 + k_9 + k_{10}[M]\right)[B]$$

$$[B] = \frac{k_7 \; [B^*][M]}{k_8 + k_9 + k_{10}[M]}$$

$$R = \left(k_5 + \frac{k_7 \; k_8 [M]}{k_8 + k_9 + k_{10}[M]} \right)[B^*]$$

$$R_{PVC} = \left(k_6 + \frac{k_7 k_9 [M]}{k_8 + k_9 + k_{10} [M]} \right) [B^*]$$

$$R_{CB}/R_{PVC} = \frac{k_8 \left({}^{k_5}/_{k_8} + \frac{k_7 [M]}{k_8 + k_9 + k_{10} [M]} \right)}{k_9 \left({}^{k_6}/_{k_9} + \frac{k_7 [M]}{k_8 + k_9 + k_{10} [M]} \right)}$$

It can be seen from Tables 16 and 17 that R_{CB}/R_{PVC} is invariant with both substrate and added CF_4 pressure. There are two possible explanations for this. The first is to assume that $k_8 + k_9 << k_{10} [M]$ and so the equation above reduces to

$$R_{CB}/R_{PVC} = \frac{k_5 k_{10} + k_7 k_8}{k_6 k_{10} + k_7 k_9}$$

which is constant. The second possible explanation is

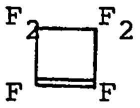
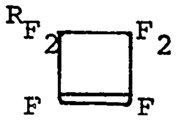
that if $k_5/k_8 = k_6/k_9$

then $R_{CB}/R_{PVC} = k_8/k_9 = k_5/k_6$.

For this to be so the A-factors for isomerisation and decomposition for both the ground state and vibrationally excited biradical must be the same. It is of interest to consider this possibility since it allows us to derive $k_5/k_6 = 0.27$. It has been shown in the previous chapter that for 1,3-perfluorobutadiene $k_{dissosciation}/k_{isomerisation} = 0.08$, where isomerisation is to perfluorocyclobutene.

Table 16

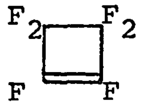
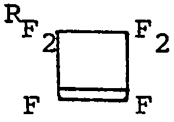
Relative rates of formation of perfluorocyclobutene and perfluorovinylcyclopropane as a function of substrate pressure in the photolysis of perfluorocyclopentene(a)

Pressure perfluorocyclopentene torr	 µmoles	PVC µmoles	 / R_{PVC}
7.5	1.07	3.79	.28
10	1.04	3.61	.29
15	0.90	3.27	.28
20	0.80	2.96	.27
25	0.74	2.72	.27
30	0.68	2.54	.27
40	0.61	2.32	.26
50	0.57	2.21	.26
60	0.55	2.16	.26

(a) Product yields from Fig. 15.

Table 17

Relative Rates of formation of perfluorocyclobutene and perfluorovinylcyclopropane as a function of CF_4 pressure in the photolysis of perfluorocyclopentene(a)

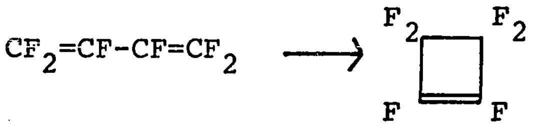
Pressure CF_4 torr	 µmoles	PVC µmoles	R  / R_{PVC}
10	0.73	2.50	.29
20	0.51	1.70	.30
30	0.40	1.38	.29
40	0.32	1.16	.28
50	0.25	0.96	.26
60	0.20	0.78	.26
70	0.15	0.60	.25
80	0.11	0.43	.26

(a) Product yields from Fig. 18.

Thus $k_{dissociation}/k_{isomerisation}$ is ∿ 3 times larger in the present instance. Two explanations for this are possible. If we consider the intermediates involved

it can be seen that $:CF_2$ elimination from perfluorobutadiene involves breaking a partially formed double bond in contrast to the present case where only a C-C single bond has to be broken to eliminate $:CF_2$. Thus $k_{dissociation}/k_{isomerisation}$ would be expected to be larger in the case of cyclopentene.

The thermal isomerisation of perfluorovinylcyclopropane to perfluorocyclopentene has been studied by Mitch and Neuvar (73)) and they have shown the activation energy to be = 34.6 kcal/mole. The activation energy for the reverse reaction would be expected to be larger due to decreased stability in the smaller ring compound. Now E_a = 35.4 for the reaction



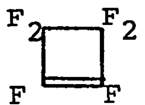
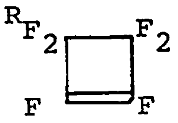
Thus, the activation energy for isomerisation of perfluorocyclopentene will be larger than that above for perfluorobutadiene, as the former activation energy will be equal to (34.6 + A) kcal/mole, where A is the difference between the heats of formation of perfluorovinylcyclopropane and perfluorocyclopentene, and A will probably be >10 kcal/mole. If this is true for isomerisation from the excited state then $k_{isomerisation}$(perfluorocyclopentene) will be smaller than $k_{isomerisation}$(perfluorobutadiene). Coupled with the effect discussed above this will produce a higher $k_{dissociation}/k_{isomerisation}$ for perfluorocyclopentene.

The formation of C_3F_4 and C_2F_4 from a hot biradical is postulated because of the overall decrease in the yield of ΣC_3F_4 relative to that of perfluorocyclobutene with increasing pressure of perfluorocyclopentene as can be seen in Table 18. However no variation of the ratio ΣC_3F_4 to perfluorocyclobutene is found with increasing pressure of CF_4 as can be seen in Table 19. Thus CF_4 appears to be very ineffective in removing excess vibrational energy from the biradical. It may be that the biradical is vibrationally excited and requires a very large number of collisions with CF_4 to deactivate it in a stepwise manner, whereas perfluorocyclopentene may be able to deactivate the vibrationally excited biradical to the ground vibrational state in one collision.

The C_3F_4 formed in the present instance differs from that formed in the photolysis of 1,3-perfluorobutadiene in that it forms perfluoroallene. It may be that formation of perfluoroallene from C_3F_4 requires a greater activation

Table 18

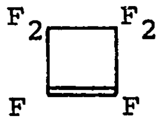
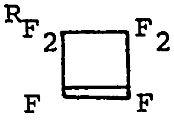
Relative rates of formation of C_3F_4 isomers and perfluorocyclobutene
as a function of substrate pressure
in the photolysis of perfluorocyclopentene[a]

Pressure perfluorocyclopentene torr	C_3F_4 µmoles	 µmoles	$R_{\Sigma C_3F_4}$ / R 
7.5	6.15	1.07	5.75
10	6.45	1.04	6.20
15	5.15	0.90	5.72
20	4.25	0.80	5.31
30	3.3	0.68	4.85
40	2.7	0.61	4.42
50	2.45	0.57	4.30
60	2.15	0.55	3.91

(a) Product yields derived from Figs. 14 and 15.

Table 19

Relative rates of formation of C_3F_4 isomers and perfluorocyclobutene as a function of CF_4 pressure in the photolysis of perfluorocyclopentene[(a)]

Pressure CF_4 torr	C_3F_4 µmoles		$R_{\Sigma C_3F_4}$ / R 
10	3.99	0.73	5.47
20	2.87	0.51	5.63
30	2.19	0.40	5.48
40	1.64	0.32	5.13
50	1.39	0.25	5.56
60	1.09	0.20	5.45
70	0.80	0.15	5.33
80	0.53	0.11	4.82

(a) Product yields, derived from curves in Figs. 16 and 17, in µmoles energy than formation of the other isomers. If the C_3F_4 in the present instance is formed with excess energy compared to that in the case of the butadiene then allene formation will be possible.

As can be seen from Fig. 18 the ratio of $CF_2=C=CF_2$ to perfluorocyclopropene increases with substrate pressure. Using the steady state assumption we can derive the following relation.

$$R_A = k_{14}[M][A^*]$$

$$-\frac{dA^*}{dt} = \frac{dA^*}{dt}$$

$$k_{-11} + k_{14}[M] \quad [A^*] = k_{11}[C_3F_4]$$

$$[A^*] = k_{11}[C_3F_4] / (k_{-11} + k_{14}[M])$$

$$R_A = k_{11}\, k_{14}\, [M][C_3F_4] / (k_{-11} + k_{14}[M])$$

similarly

$$R_C = k_{13}\, k_{16}[M][C_3F_4] / (k_{-13} + k_{16}[M])$$

R_A is the rate of formation of perfluoroallene and R_C is the rate of formation of perfluorocyclopropene

Thus $$R_A/R_C = \frac{k_{11}\, k_{14}\, (k_{-13} + k_{16}[M])}{k_{13}\, k_{16}\, (k_{-11} + k_{14}[M])}$$

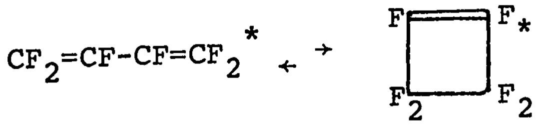
This predicts a non-linear relationship between R_A/R_C and substrate pressure. This can be rewritten as

$$R_A/R_C = \frac{k_{11}\ (k_{-13}/k_{16} + [M])}{k_{13}\ (k_{-11}/k_{14} + [M])}$$

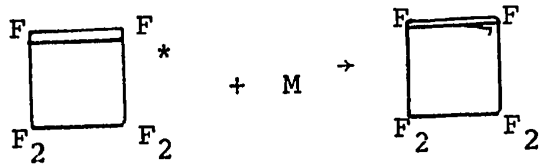
This ratio should become constant when

$$M \gg k_{-13}/k_{16} \text{ and } k_{-11}/k_{14}.$$

In the previous chapter it was shown that for the reactions



[1]



[2]

$$k_{-1}/k_2 = 2.2 \times 10^2 \text{ torr.}$$

If in the present case the ratios k_{-13}/k_{16} and k_{-11}/k_{14} are of the same order of magnitude the ratio R_A/R_C will not reach a constant value until a very high pressure of perfluorocyclopentene is present.

Since the constant value will be greater than 1 this means that $R_{11} > k_{13}$. Also since R_A/R_C is less than $k_{11} > k_{13}$

at lower pressures this implies that $k_{-13}/k_{16} < k_{-11}/k_{14}$. A similar type of relationship can be derived for the ratio of R_A to R_P, where R_P is the rate of formation of perfluoropropyne

Thus $$R_A/R_P = \frac{k_{11}\ (k_{-12}/k_{15} + [M])}{k_{12}\ (k_{-11}/k_{14} + [M])}$$

As can be seen in Fig. 17 this plot is similar to that of R_A/R_C vs pressure but it appears that the final constant value will be smaller than that for R_A/R_C.

Thus $$k_{11} > k_{12}$$

and $$k_{12} > k_{13}.$$

Also $$k_{-11}/k_{14} > k_{-12}/k_{15}$$

From the above results it can be seen that the C_3F_4 formed by photolysing perfluorocyclopentene must differ radically from that formed in the case of 1,3-perfluorobutadiene. The fact that k_{11} is greater than both k_{12} and k_{13} would suggest that the C_3F_4 is of the form

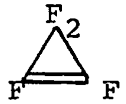
$$\dot{\mathrm{C}}\mathrm{F}_2 \overset{-\,-}{=} \mathrm{C} = \dot{\mathrm{C}}\mathrm{F}_2$$

rather than

$$\dot{\mathrm{C}}\mathrm{F} = \mathrm{CF} - \dot{\mathrm{C}}\mathrm{F}_2$$

Table 20

Relative rates of formation of perfluorocyclopropene, perfluoropropyne and perfluoroallene as a function of substrate pressure in the photolysis of perfluorocyclopentene[(a)]

Pressure perfluoro-cyclopentene torr	 µmoles	$CF_3C\equiv CF$ µmoles	$CF_2=C=CF_2$ µmoles	$R_{CF_2=C=CF_2}/R_C$[(b)]	$R_{CF_2=C=CF_2}/R_{CF_3C\equiv CF}$
10	1.95	2.55	1.95	1.0	.76
15	1.30	1.85	2.0	1.54	1.08
20	0.90	1.40	1.95	2.17	1.39
25	0.70	1.05	1.90	2.71	1.81
30	0.60	0.80	1.85	3.08	2.31
35	0.50	0.65	1.75	3.50	2.69
40	0.45	0.55	1.65	3.67	3.00
45	0.40	0.52	1.60	4.00	3.08
50	0.38	0.50	1.55	4.08	3.10
55	0.35	0.48	1.50	4.29	3.13

(a) Product yields from Fig. 14.

(b) R_C is the rate of formation of perfluorocyclopropene.

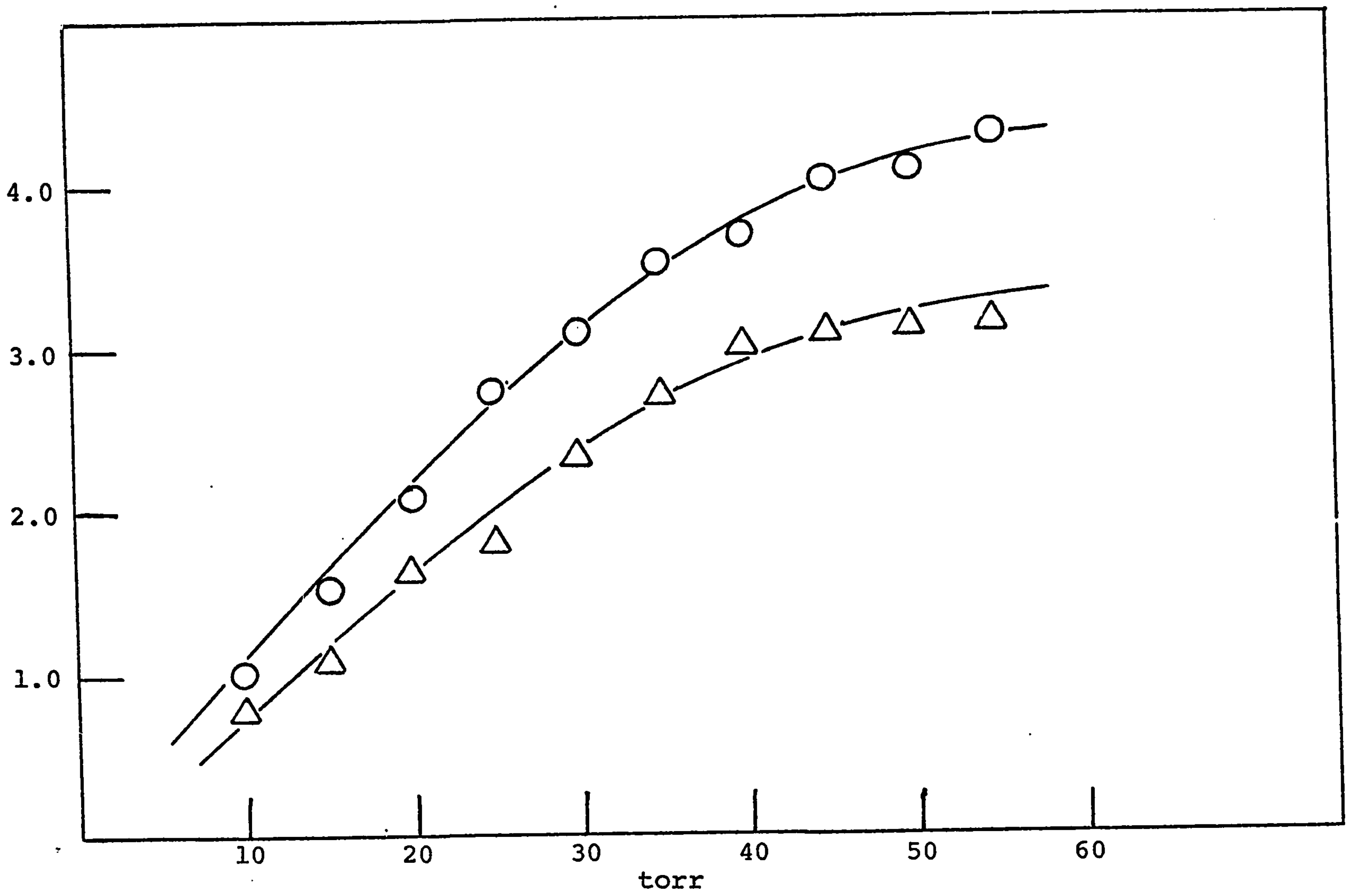
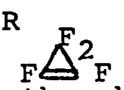
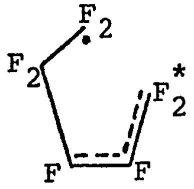


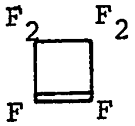
Fig. 18. $R_{CF_2=C=CF_2}/R$  and $R_{CF_2=C=CF_2}/R_{CF_3C\equiv CF}$ as a function of substrate pressure in the photolysis of perfluorocyclopentene.

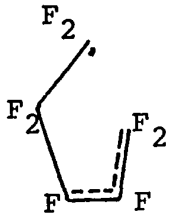
○ $R_{CF_2=C=CF_2}/R$  △ $R_{CF_2=C=CF_2}/R_{CF_3C\equiv CF}$

This implies that the dissociation of the biradical



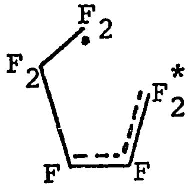
is preceded by or coincident with a fluorine shift from carbon 2 to carbon 3. This would explain the necessity for excess energy in the biradical for formation of C_3F_4 and C_2F_4.

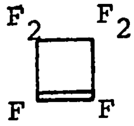
In Table 21 the ratio of $C_2F_4/\left(\Sigma C_3F_4 + \frac{1}{2}\right.$  $\left.\right)$ is shown. As can be seen this ratio approaches unity at high pressures showing that mass balance is obtained. It would seem that at lower pressures some of the C_2F_4 is being lost. If in the reaction

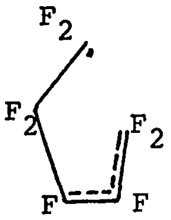
 $\rightarrow C_3F_4 + C_2F_4$

the $^{*}C_2F_4$ is formed with some excess energy then this can polymerise if it is not collisionally deactivated. Some polymer formation was observed.

Alternatively, some secondary photolysis of C_2F_4 may be taking place although this is unlikely as other species present would be expected to absorb more strongly.

This implies that the dissociation of the biradical  is preceded by or coincident with a fluorine shift from carbon 2 to carbon 3. This would explain the necessity for excess energy in the biradical for formation of C_3F_4 and C_2F_4.

In Table 21 the ratio of $C_2F_4/\Big(\Sigma C_3F_4 + \frac{1}{2}$  $\Big)$ is shown. As can be seen this ratio approaches unity at high pressures showing that mass balance is obtained. It would seem that at lower pressures some of the C_2F_4 is being lost. If in the reaction



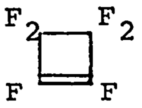
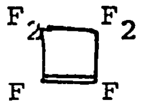
$$\rightarrow C_3F_4 + C_2F_4$$

the C_2F_4 is formed with some excess energy then this can polymerise if it is not collisionally deactivated. Some polymer formation was observed.

Alternatively, some secondary photolysis of C_2F_4 may be taking place although this is unlikely as other species present would be expected to absorb more strongly.

Table 21

Ratio of C_2F_4 to the sum of the C_3F_4 isomers plus 1/2 cyclobutene as a function of substrate pressure in the photolysis of perfluorocyclopentene[(a)]

Pressure perfluorocyclopentene torr	C_2F_4	ΣC_3F_4	$\frac{1}{2}$ 	$C_2F_4 / \Sigma C_3F_4 + \frac{1}{2}$ 
10	5.0	6.45	.52	.72
15	4.25	5.15	.45	.76
20	3.80	4.25	.40	.82
25	3.45	3.7	.36	.85
30	3.20	3.3	.34	.88
40	2.85	2.17	.305	.95
50	2.40	2.45	.285	.88
60	2.20	2.15	.275	.90

(a) Product yields, in μmoles, from curves in Figs. 14 and 15.

CHAPTER VII

SUMMARY AND CONCLUSIONS

The photolysis of trifluorovinylchloride led to its decomposition by two different modes. The first of these led to formation of trifluorovinyl radicals and chlorine atoms. These reacted with the substrate leading to formation of products such as 4,4,-dichloroperfluoro-1-butene. Both of the above radicals were probably responsible for polymer formation.

The second mode of decomposition was by fission of the double bond, leading to formation of :CFCl and $:CF_2$ radicals. The :CFCl was found to react with the substrate, producing 1,2-dichloroperfluorocyclopropane and 1,1-dichloroperfluoro-1-propene. It did not, however, react with isobutane.

The $:CF_2$, produced by the photolysis of C_2F_3Cl, proved to be reactive, in contrast to most previous work in which it was found to be relatively inert. Two products, attributable to reaction of $:CF_2$, were found when the substrate was photolysed alone. These were 1,4-perfluoropentadiene and tetrafluoroethylene. When photolysis of C_2F_3Cl was carried out in the presence of isobutane, a product, of molecular formula $C_5F_2H_{10}$, was found which was attributed to reaction of $:CF_2$ with isobutane. It was proposed that the latter reaction was a direct insertion similar to the reaction of $:CH_2$ with carbon hydrogen bonds. If so, this is the first known case of direct insertion into a carbon hydrogen bond by $:CF_2$. The reactivity of $:CF_2$ in the present instance can be attributed to its being either in an electronically excited state or a vibrationally excited ground state. It could not be decided from the present work which of the above was the case.

The photolysis of three other chlorofluoroethylenes was also carried out. All these systems were very complex.

Photolysis of 1,2-dichlorofluoroethylene led to its decomposition. It appeared that most of the decomposition was by carbon chlorine bond fission. The radicals produced seemed to produce primarily polymer. Some evidence was found for formation of CFCl=C:. When photolysis of the substrate was carried out in the presence of isobutene one product mixture showed a peak corresponding to m/e = 136. This could be attributed to a compound of molecular formula C_6ClFH_{10}, a product which could arise by insertion of CFCl=C: into a carbon hydrogen bond of isobutane. The latter reaction would be analagous to the reactions of CF_2=C: with carbon hydrogen bonds.

In the photolysis of 1,2-difluorochloroethylene evidence for the formation of five radical species was found. The species were $\cdot C_2F_2H$, $\cdot Cl$, $:CFCl$, $:CFH$ and $CFCl{=}C:$.

The photolysis of 1,1-difluorochloroethylene led to its decomposition by three primary processes with the formation of the radicals $\cdot C_2F_2H$, $\cdot Cl$, $:CF_2$, $:CHCl$ and $CF_2{=}C:$.

A product, of molecular formula $C_5F_6H_2$, was attributed to reaction of $:CF_2$ with the starting material. This reaction would be analogous to that whereby C_5F_8 was produced, in the reaction of $:CF_2$ with C_2F_3Cl. When the substrate was photolysed in the presence of isobutane a product of molecular formula $C_5F_2H_{10}$ was found. This was the same product as that found in the reaction of $:CF_2$, generated by photolysis of C_2F_3Cl, with isobutane. It would indicate that photolysis of 1,1-difluorochloroethylene also leads to reactive $:CF_2$ which can insert into carbon hydrogen bonds.

The $CF_2{=}C:$ was found to react with carbon hydrogen bonds by an insertion process. This is similar to the reactions of $CF_2{=}C:$ produced by Hg photosensitization or photolysis of trifluoroethylene (20,25). The same degree of discrimination between primary and tertiary bonds was found in the present work as in the latter two cases.

The photolysis of the isomers, 1-3 perfluorobutadiene, perfluorocylcobutene and 2-perfluorobutyne led to similar types of products in all three cases. Two types of processes were found. The first of these was decomposition to $:CF_2$ and C_3F_4. The $:CF_2$ was unreactive and formed only C_2F_4. The C_3F_4 was found as perfluorocyclopropene and perfluoropropyne.

The second process was isomerisation. The isomers found in the case of 1,3-perfluorobutadiene were 1,2-perfluorobutadiene, 2-perfluorobutyne and perfluorocyclobutene. The analogous isomers were found in the photolysis of the other isomers.

The photolysis of perfluorocyclopentene was also studied. In this case three types of reaction were found. The first of these was formation of tetrafluoroethylene and perfluoroallene. It was proposed that this process is occurring from a vibrationally excited biradical. The other two processes which occurred were, (1) formation of $:CF_2$ and perfluorocyclobutene and (2) isomerisation to perfluorovinylcyclopropane. In the case of these reactions, it was proposed that they were taking place from both the vibrationally excited and the thermally equilibrated biradical.

BIBLIOGRAPHY

(1) P. Ausloos and R. Gorden, J. Chem. Phys. 36, 5 (1962).

(2) H. Okabe and J. R. McNesby, J. Chem. Phys. 36, 601 (1962).

(3) R. Gorden and P. Ausloos, J. Chem. Phys. 44, 1803, (1966).

(4) A. B. Callear and R. J. Cvetanovic, J. Chem. Phys. 24, 873 (1965).

(5) D. W. Setser, B. S. Rabinovitch and D. W. Placzek, J. Am. Chem. Soc. 85, 862 (1963).

(6) R. F. Hampson and J. R. McNesby, J. Chem. Phys., 43, 3592, (1965).

(7) T. Teras, S. Kirokami, S. Sato and R. J. Cvetanovic, Can. J. Chem., 44, 2173 (1966).

(8) H. E. Hunziker, J. Chem. Phys., 50, 1288 (1969).

(9) C. R. Patrick, Advances in Fluorine Chemistry Vol. 2, Butterworths 1961, I.

(10) L. Pauling, The Nature of the Chemical Bond. Cornell University Press, 1960, p. 314.

(11) D. Peters, J. Chem. Phys., 38, 561 (1963).

(12) C. R. Patrick, Tetrahedron, 4, 26 (1958).

(13) H. E. O'Neal and S. W. Benson, J. Phys. Chem., 72, 1866 (1968).

(14) F. Casas, J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc., 1141 (1965).

(15) R. P. Buckley and M. Szwarc, J. Am. Chem. Soc., 78, 5696 (1956).

(16) H. H. Jaffe and M. Orehin, Theory and Applications of Ultraviolet Spectroscopy. Wiley and Sons, Inc. 1962, p. 175.

(17) R. Fields and R. N. Haszeldine, J. Chem. Soc., 1881 (1964).

(18) D. M. Gale, W. J. Middleton and C. G. Krespan, J. Am. Chem. Soc., 88, 3617 (1967).

(19) W. Stuckey and J. Heicklen, J. Am. Chem. Soc., 90, 3952 (1968).

(20) J. L. W. Jones, O. P. Strausz and H. E. Gunning, to be published.

(21) D. C. Phillips and A. F. Trotman-Dickenson, J. Chem. Soc., (A), 1144 (1968).

(22) B. Atkinson and D. McKeagan., Chem. Comm., 189 (1966).

(23) J. M. Birchall, R. N. Haszeldine and D. W. Roberts, Chem. Comm., 287 (1967).

(24) N. L. Craig, Tai-na Hu and P. H. Martyn, J. Phys. Chem., 72, 2234 (1968).

(25) R. Norstrom, Ph.D. Thesis University of Alberta (1966).

(26) K. Bayes, J. Am. Chem. Soc., 85, 1730 (1963).

(27) Y. N. Tang and F. S. Rowland, J. Am. Chem. Soc., 89, 6420 (1967).

(28) W. Kirmse, Carbene Chemistry, Academic Press 1964, p. 145 and ff.

(29) R. A. Moss and R. Gerstl, J. Org. Chem., 32, 2268 (1967).

(30 R. A. Mitsch, J. Am. Chem. Soc., 87, 758 (1965).

(31) J. Heicklen and V. Knight, J. Chem. Phys., 42, 221 (1965).

(32) J. Heicklen and V. Knight, J. Phys. Chem., 69, 3600 (1965).

(33) W. Stuckey and J. Heicklen, Can. J. Chem., 46, 1361 (1968).

(34) Advances in Fluorine Chemistry. Butterworths. Vol. 4, 1965 p. 263.

(35) Advances in Fluorine Chemistry. Butterworths. Vol. 4, 1965 p. 268.

(36) V. A. Slabey, J. Am. Chem. Soc., 76, 3604 (1954).

(37) S. W. Tobey and R. West, J. Amer. Chem. Soc., 88, 2481 (1966).

(38) R. A. Mitsch, J. Heterocyclic Chem., 1, 272 (1965).

(39) M. G. Bellas, J. K. S. Wan, O. P. Strausz and H. E. Gunning, J. Phys. Chem., 68, 2170 (1964).

(40) W. Kirmse, Carbene Chemistry, Academic Press. 1964 p. 39.

(41) P. S. Skell and R. C. Woodworth, J. Am. Chem. Soc., 78, 4496 (1956).

(42) R. J. Cvetanovic, H. E. Avery and R. S. Irwin, J. Chem. Phys., 46, 1993 (1967).

(43) R. Hoffmann, J. Am. Chem., Soc. 90, 1475 (1968).

(44) R. A. Moss and R. Gerstl, Tetrahedron, 23, 2549 (1967).

(45) P. Ventaskewarhr, Phys. Rev., 77, 676 (1950).

(46) D. E. Mann and B. A. Thrush, J. Chem. Phys., 33, 1732 (1960).

(47) C. W. Matthews, J. Chem. Phys., 45, 1068 (1966).

(48) J. Simons, Nature, 205, 1308 (1965).

(49) J. Simons, J. Chem. Soc., 5406 (1965).

(50) B. Atkinson, J. Chem. Soc., 2684 (1952).

(51) N. Cohen and J. Heicklen, J. Chem. Phys., 43, 871 (1965).

(52) F. W. Dalby, J. Chem. Phys., 41, 2297 (1964).

(53) L. Elias and H. Schiff, Can. J. Chem. 38, 1657 (1960).

(54) E. M. Lown, H. A. Wiebe, W. B. O'Callaghan, O. P. Strausz and H. E. Gunning, to be published.

(55) A. B. Callear and W. J. R. Tyerman, Trans. Far. Soc., 62, 371 (1966).

(56) R. Hoffmann, G. D. Zeiss and G. W. Van Dine, J. Am. Chem. Soc., 90, 1485 (1968).

(57) J. W. Edwards and P. A. Small, Nature, 202, 1329 (1964).

(58) W. Mahler, Inorg. Chem., 2, 230 (1963).

(59) H. C. Clark and C. J. Willis, J. Am. Chem. Soc., 82, 1888 (1960).

(60) P. B. Ayscough and H. J. Emelews, J. Chem. Soc., 3381 (1954).

(61) S. Andreades, Chem. and Ind. (London), 782 (1962).

(62) R. F. Pottie, J. Chem. Phys., 42, 2606 (1965).

(63) F. P. Lossing, J. Phys. Chem., 72, 1552 (1968).

(64) C. R. Patrick, Advances in Fluorine Chemistry, Butterworths, Vol. 2, p. 27 (1961).

(65) R. S. Berry, J. Chem. Phys., 38, 1934 (1963).

(66) M. B. Robin, R. B. Hart and N. A. Kueblar, J. Chem. Phys., 44, 1803 (1966).

(67) M. H. Wijnen, J. Am. Chem. Soc., 41, 2297 (1964).

(68) T. L. Jacobs and R. S. Bauer, J. Am. Chem. Soc., 78, 4815 (1956).

(69) G. L. Closs and J. J. Cogle, J. Am. Chem. Soc., 84, 4350 (1962).

(70) Y. N. Tang and F. S. Rowland, J. Am. Chem. Soc., 87, 1625 (1965).

(71) E. W. Schlag and W. B. Peatman, J. Am. Chem. Soc., 86, 1676 (1964).

(72) I. Haller and R. Sornwascin, J. Chem. Phys., 40, 1992 (1964).

(73) R. A. Mitsch and E. W. Newman, J. Phys. Chem., 70, 546 (1966).

APPENDIX

Mass and I.R. Spectra

TABLE 22

Mass Spectrum of 1,2 dichloroperfluorocyclopropane

M/e	relative intensity	M/e	relative intensity
31	38.5	97	7.5
35	2.4	99	2.4
37	0.8	101	7.6
43	1.7	103	5.0
49	5.0	112	2.3
50	3.0	116	27.5
55	1.9	118	9.1
62	3.8	131	4.8
66	15.1	132	43.5
68	4.9	134	28.1
74	3.4	136	4.9
78	4.1	147	100
80	1.4	149	33.9
82	21.1	151	3.9
84	13.6	153	2.6
85	32.4	155	0.7
87	10.6	182	1.7
93	36.6	184	0.9
		186	0.16

TABLE 23

Mass Spectrum of 3,3-dichloroperfluoropropene

M/e	relative intensity	M/e	relative intensity
31	32.6	118	12.2
47	3.5	147	26.6
49	1.1	149	8.5
66	4.6	151	24.4
68	1.6	153	15.2
69	36.0	155	3.05
85	100	163	6.4
87	33.3	165	4.3
109	7.8	167	0.6
111	2.6	182	2.8
112	4.0	184	1.6
116	36.6	186	0.4

TABLE 24

Mass Spectrum of $C_5F_2H_{10}$ (a)

M/e	relative intensity	M/e	relative intensity
27	16.9	57	100
29	42.2	65	55.8 (b)
39	21.2	69	2.9
41	71.3	73	4.3
47	15.7	77	7.3
50	1.7	92	2.6
51	12.2	93	6.8
53	6.9		

(a) This spectrum was recorded on an AEl model MS9 high resolution mass spectrometer.

(b) An accurate mass count showed this peak to be $C_2F_2H_3^+$.

TABLE 25

Mass Spectrum of 4,4,–dichloroperfluoro-1-butene

M/e	relative intensity	M/e	relative intensity
31	11.1	132	4.9
69	23.9	134	2.3
85	21.1	136	0.3
87	6.7	147	14.9
93	10.0	149	4.4
101	3.3	163	1.6
103	2.1	165	1.1
105	0.4	167	0.2
116	5.7	197	3.5
118	1.9	199	1.2
131	100		

TABLE 26

Mass Spectrum of C_4F_6ClH

M/e	relative intensity	M/e	relative intensity
31	15.3	117	51.1
51	11.1	119	16.2
<u>67</u>	<u>100</u>	129	7.8
69	42.2	131	75.6
85	28.9	152	4.4
87	9.8	154	2.7
101	7.8	198	5.4
113	15.6	200	1.8

Mass Spectrum of perfluorovinylcyclopropane

M/e	relative intensity	M/e	relative intensity
212	1.6	74	19.8
193	2.7	69	9.2
162	3.5	62	9.3
143	12.7	55	9.2
124	8.0	50	7.5
112	16.6	31	35.4
93	100		

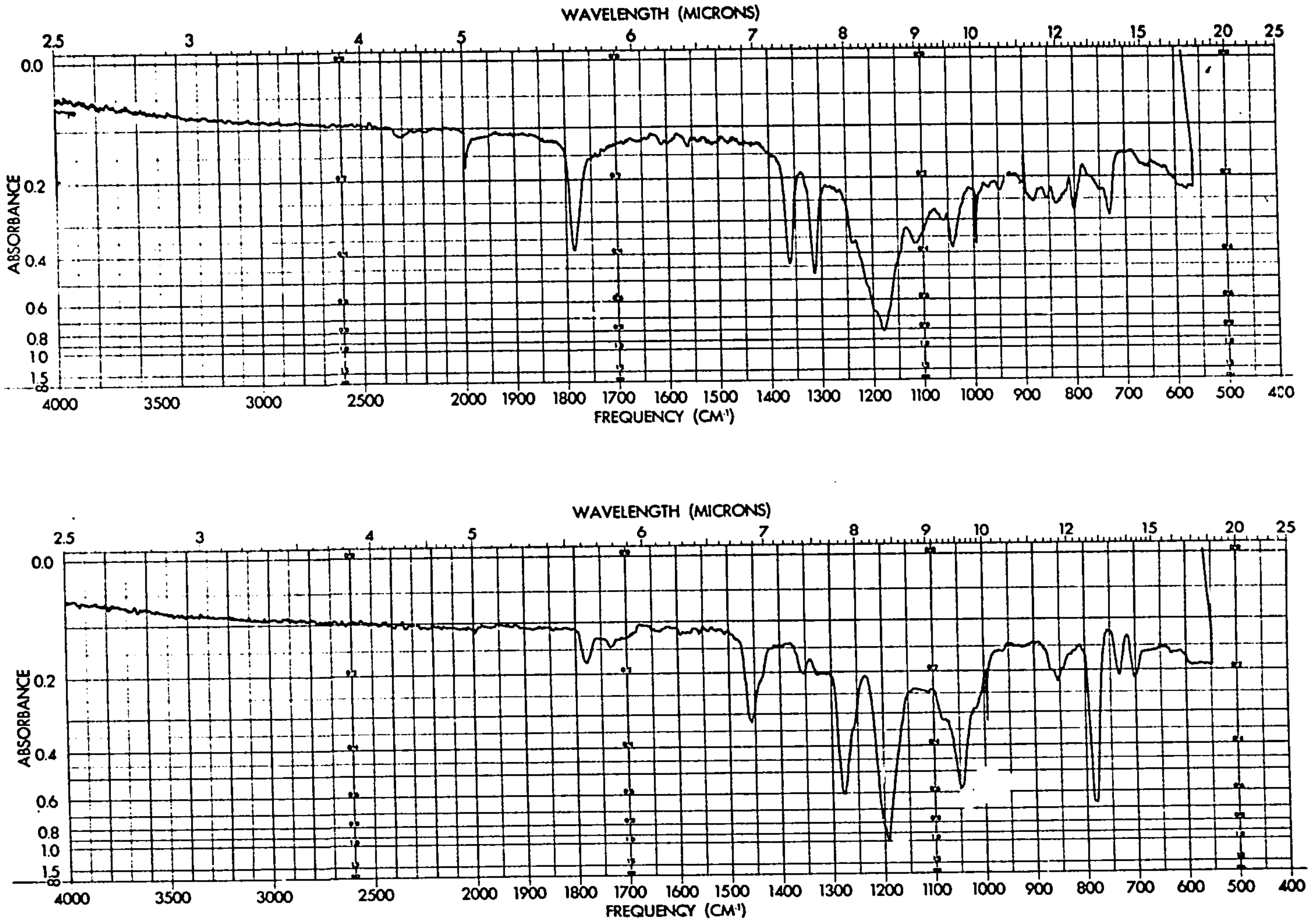


Fig. 19. I.R. Spectra of CF_2=CF-$CFCl_2$ (upper) and

(lower).

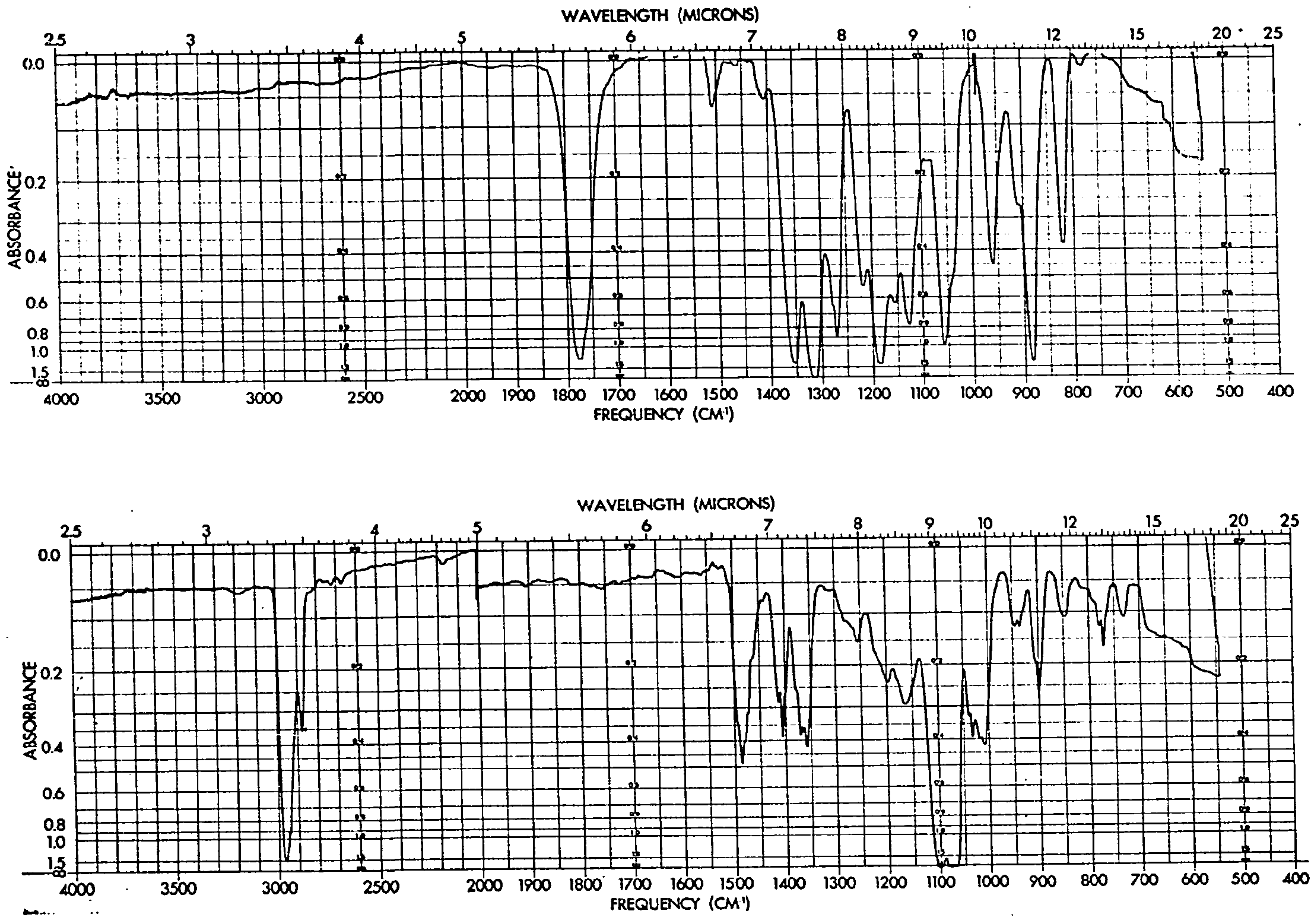


Fig. 20. I.R. Spectra of 1,4-perfluoropentadiene (upper) and $C_5F_2H_{10}$ (lower).

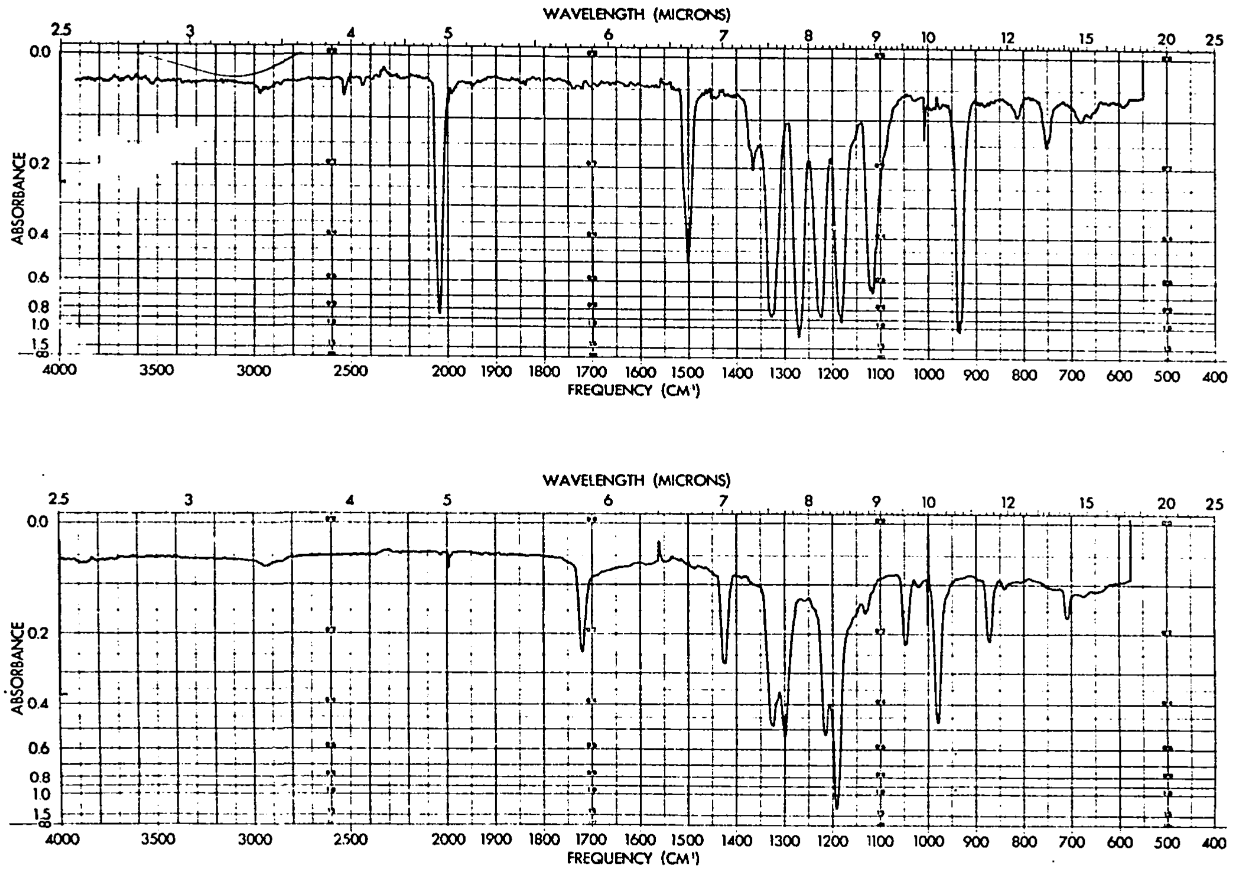


Fig. 21. I.R. Spectra of 1,2-perfluorobutadiene (upper) and perfluorovinylcyclopropane (lower).