THE REACTIONS OF OXYGEN ATOMS AND MONOFLUOROMETHYLENE RADICALS WITH FLUORINATED ETHYLENES IN THE GAS PHASE

By

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TO

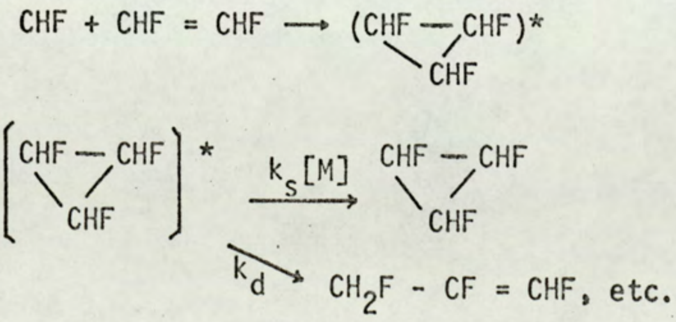
MY MOTHER AND FATHER

SUMMARY

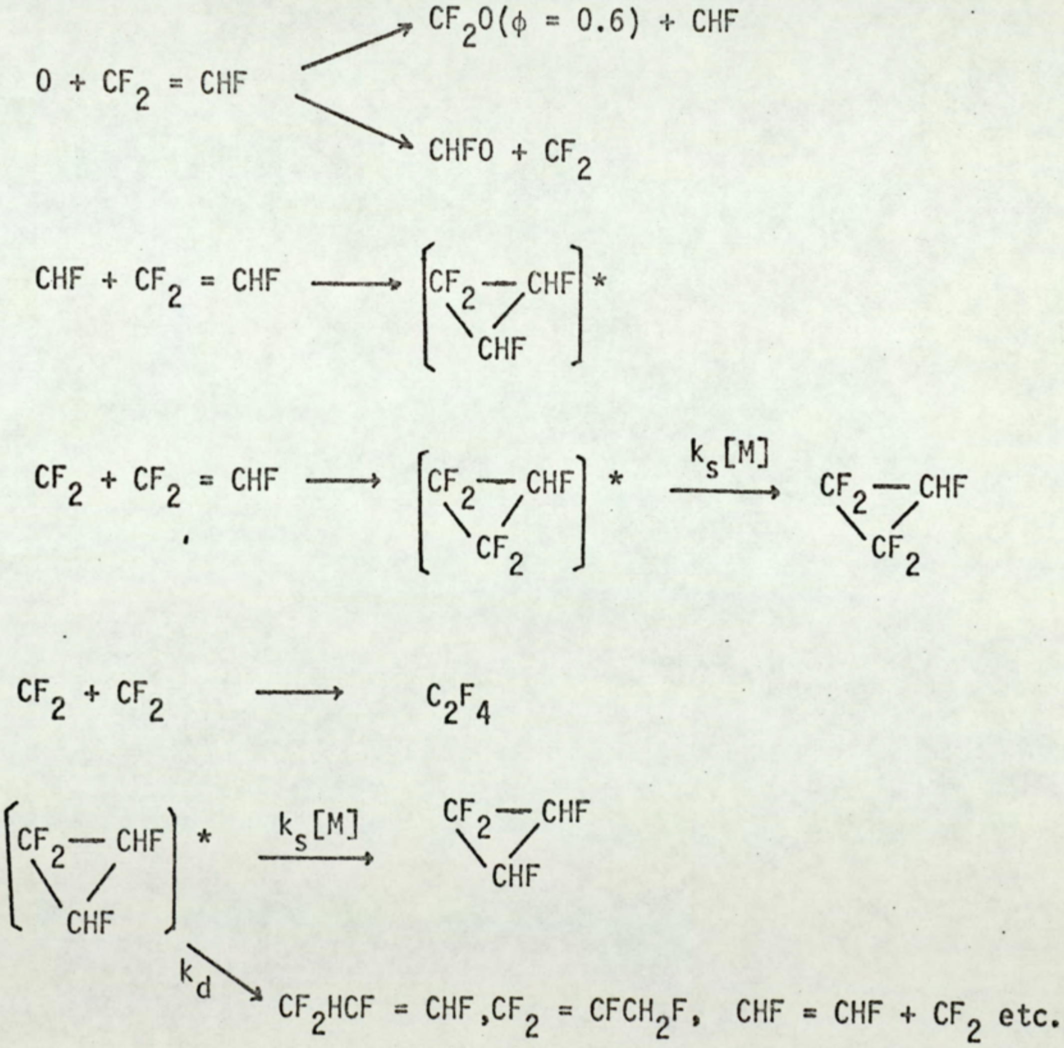
Oxygen atoms generated in a mercury photosensitized decomposition of nitrous oxide were reacted with 1,2-difluoroethylene and trifluoroethylene and observed to form mainly monofluoromethylene (CHF) radicals and carbonyl fluoride. The CHF radicals then added to fluoroethylene to form "hot" fluorocyclopropanes which could be stabilized by collision (or isomerize or fragment). The mechanism of these reactions have been studied in detail.

The main products of the reaction of CHF radical with trans-1,2-difluoroethylene were found to be trans- 1,2,3-trifluorocyclopropane, cis- and trans- 1,2,3-trifluoropropylene whereas the reaction with cis- 1,2-difluoroethylene gave both cis- and trans- 1,2,3-trifluorocyclopropane, cis- and trans- 1,2,3-trifluoropropylene. The electronic state of CHF radical was believed to be singlet according to the stereospecific addition reaction and the lack of change in the products yield in the presence of small amount of molecular oxygen. The exothermicity of the addition reaction was estimated as 286 kJ mol^{-1}.

$$O + CHF = CHF \longrightarrow CHFO + CHF \quad (\phi \sim 1)$$



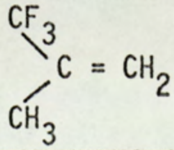
The reaction products of the reaction of CHF radical with trifluoroethylene were cis- and trans- 1,2,3,3-tetrafluorocyclopropane, cis- and trans- 1,2,3,3-tetrafluoropropylene, 1,1,2,3-tetrafluoropropylene, cis- and trans- 1,2-difluoroethylene, tetrafluoroethylene and pentafluorocyclopropane. Some CF_2 elimination from "hot" cyclopropane occurred even at atmospheric pressure. The pentafluorocyclopropanes were formed by addition of CF_2 to the trifluoroethylene. Principal features of the mechanism are shown in the following scheme:



Following the detailed studies of the reaction, the systems were used to determine relative reactivities of CHF radicals with all the fluorinated ethylenes. Relative rate constants for the reaction with propylene and fluoroethylenes were measured by a competitive method at 23 ± 2^{o}C. The results are summarized below

OLEFIN	$K_{OLEFIN}/K_{C_2H_4}$
$CH_2 = CH_2$	1.00
$CH_2 = CHF$	0.42
$CH_2 = CF_2$	0.16_5
trans-CHF = CHF	0.17, 0.20
cis-CHF = CHF	0.09, 0.11
$CF_2 = CHF$	0.11
$CF_2 = CF_2$	0.03
CH_3-CH=CH_2	2.51

The relative rate constants for the reaction of fluoroethylenes with CHF radicals produced from different sources are in good agreement.

Reference	$\frac{K_{CH_2 = CHF}}{K_{CH_2 = CH_2}}$	Reference	$\frac{K_{CIS-CHF = CHF}}{K_{TRANS-CHF = CHF}}$
cis-CHF = CHF	0.34_4	$CH_2 = CHF$	0.54
trans-CHF = CHF	0.34_1	$CH_2 = CH_2$	0.53_3
$CF_2 = CHF$	0.41_8	 $(CF_3)(CH_3)C = CH_2$	0.53_2

This work was carried out between 1970 and 1973 at The University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

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CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 MERCURY PHOTOSENSITIZATION

Photosensitization was first discovered by Cario and Franck$^{(1)}$. This process involves the absorption of light energy by a strongly absorbing substance, the "sensitizer", and transfer of this energy by collision to another substance, the "quencher", which does not absorb or only very weakly in the spectral region employed. The process whereby light energy is absorbed by sensitizer and dissipated by collision with another molecule is known as "quenching".

Several substances have been used as sensitizers, including some metals e.g. mercury, cadmium and zinc$^{(2)}$ and aromatic hydrocarbons in the gas phase. Mercury is particularly useful as a sensitizer for a number of reasons. Firstly, it is not very reactive and hence does not usually react chemically with other molecules in the system. Secondly, the vapour pressure is measurably large at room temperature (1.5×10^{-3} mm at $23^{o}C$). Thirdly, it has a low lying triplet state $6(^3P_1)$ 469.5 KJ mol^{-1} above the ground state, (see Fig. 1.1) which has sufficient energy to induce many chemical reactions.

A low pressure mercury lamp emits mainly unreversed 253.7 nm radiation corresponding to the transition:

$$Hg\ 6(^3P_1) \leftrightarrow Hg\ 6(^1S_0)$$

which is spin forbidden (triplet-singlet transition). Mercury is a

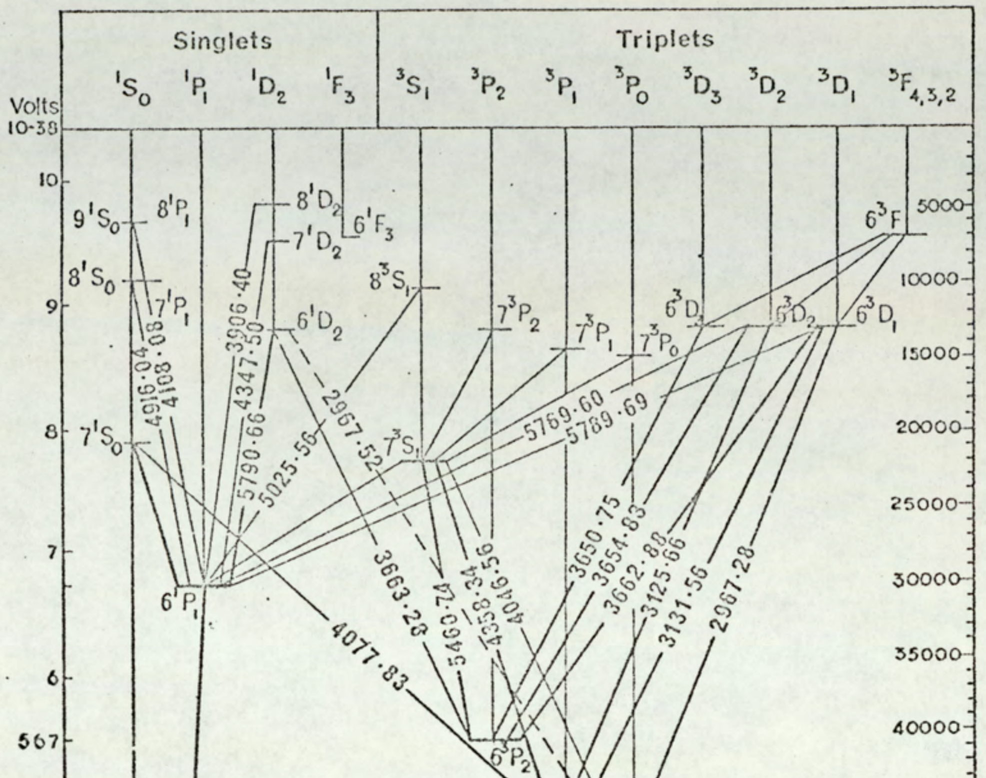


Fig. 1.1 ENERGY LEVELS OF MERCURY

heavy atom, the resonance line is fairly strong because of the breakdown of the selection rule ($\Delta S = 0$). Radiation at 184.9 nm, due to the transition:

$$\mathrm{Hg}\ 6(^{1}\mathrm{Pi}) \leftrightarrow \mathrm{Hg}\ 6(^{1}\mathrm{So})$$

is also emitted by the low pressure mercury lamp, but is absorbed strongly by ordinary quartz and atmospheric oxygen.

Mercury photosensitized reactions are widely used as a convenient source of free radicals and atoms and were reviewed by Cvetanovic(3). He concluded three basic types of quenching of triplet excited mercury atoms, $\mathrm{Hg}\ 6(^{3}\mathrm{Pi})$, as follows.

1. Quenching to metastable state, $\mathrm{Hg}\ 6(^{3}\mathrm{Po})$ with transfer of only about 21 KJ mol^{-1} to the quenching gas.

2. Formation of electronically excited molecules of the quenching gas.

3. One-step dissociation of the quenching gas.

This conclusion may be represented by the following equations

$$\mathrm{Hg}\ 6(^{3}\mathrm{Pi}) + Q \rightarrow \mathrm{Hg}\ 6(^{3}\mathrm{Po}) + Q^{+}$$

$$\mathrm{Hg}\ 6(^{3}\mathrm{Pi}) + Q \rightarrow \mathrm{Hg}\ 6(^{1}\mathrm{So}) + Q^{*}$$

$$\mathrm{Hg}\ 6(^{3}\mathrm{Pi}) + Q \begin{array}{l} \nearrow \ \mathrm{Hg}\ 6(^{1}\mathrm{So}) + Q_1 + Q_2 \\ \searrow \ \mathrm{Hg}\,Q_1 + Q_2 \end{array}$$

where Q is the ground state quenching molecule.

Q^+ is the quenching gas with 21 KJ mol^{-1} excess energy.

Q* is the electronically excited quencher (469.5 KJ mol^{-1} above the ground state).

Q_1 and Q_2 are fragments formed from Q.

These three modes of quenching will be described in detail.

1. Quenching to a metastable state

This step involves the quenching of the triplet mercury state ($^3P_1$) to the metastable state ($^3P_0$). The metastable state ($^3P_0$) is the lowest level of atomic mercury (see Fig. 1.1). It lies only 21 KJ $mole^{-1}$ below the $^3P_1$ state and this energy is transferred to the quenching molecule. In this case therefore, no chemical reaction occurs. The controversy about the extent of metastable quenching by various gases has been due mainly to the difficulty in monitoring the metastable population levels quantitatively. The work of Messanger(4) and Coulliette(5) has been shown that Hg ($^3P_0$) atoms can be detected and their concentration measured by the fact that they induce the emission of electrons from a metal surface. More recent work using this method has been studied by Darwent and Hurtubise(6) who found that metastable atoms can be detected with nitrogen, hydrogen, ethylene and ethane based on their ability to induce the emission of electrons from a nickel surface. Recently metastable atoms were detected in mixtures of mercury vapour with gases nitrogen, water, carbon monoxide and argon (very weakly). This work has been done by Callear and Norrish(7) using the flash photolysis technique. The more reliable work has been carried out by Callear and Hedges(8) by using flash photolysis method with the special lamp constructed to produce an intense flash of mercury resonance radiation. They found that the significant yields of Hg (^{3}Po) were observed with N_2, CH_4, C_3H_8 and CO. It is suggested that this new technique is capable of achieving an analysis of essentially the complete role of metastable atoms in mercury photosensitized reaction.

2. Quenching to the Ground State

This step is direct quenching of Hg (^{3}Pi) to the ground state Hg (^{1}So) and energy of 469 KJ mol^{-1} was transferred to the quenching molecule. This energy raises the quenching molecule to an electronic excited state.

3. One-step Dissociation of the Quenching Gas

This step involves the quenching of Hg (^{3}Pi) to the ground state and again with energy transfer to the quenching molecule but in this case the quenching molecule fragments. An example of this step is the quenching by hydrocarbon molecules in which the energy is sufficient to break the C-H bond and form a hydrogen atom and alkyl radical

$$\text{Hg } (^3\text{P}_1) + \text{RH} \longrightarrow \text{Hg } (^1\text{So}) + \text{H} + \text{R.}$$

It is possible for one of the fragments to form a complex with the mercury atom.

$$\text{Hg } (^3\text{P}_1) + \text{RH} \longrightarrow \text{Hg H} + \text{R}$$

Callear and Hedges(9) have observed the formation of Hg H in the mercury flash-photosensitized decomposition reaction of Hg ($^3P_1$) with H_2. Hg H was also detected in a flashed mixture of Hg ($^3P_0$) and C_2H_2.

1.1.1 Quenching Cross Sections

The efficiency of the quenching reactions of triplet excited mercury can be measured in two ways.

a) Physical method

b) Chemical method

a) Physical method

The three general types of primary processes found in quenching experiments with Hg ($^3P_1$) atoms are

1. $Hg\ (^1S_0) + h\nu\ (253.7\ nm) \longrightarrow Hg\ (^3P_1)$

2. $Hg\ (^3P_1) \xrightarrow{k_f} Hg\ (^1S_0) + h\nu\ (253.7\ nm)$

3. $Hg\ (^3P_1) + Q \xrightarrow{k_q} Hg\ (^1S_0) + Q^1$

Steady state considerations, the following equation was obtained

$$\underline{R_f^o/R_f = 1 + \tau\, k_q\, [Q]}$$

where R_f is the rate of the fluorescence reaction

R_f^o is the rate of the fluorescence reaction in the absence of Q

k_q is the quenching rate constant

τ is the mean lifetime of $Hg(^3P_1) = 1/K_f$

From this Stern-Volmer equation the quenching rate constant, k_q, can be evaluated by measuring the intensity of fluorescence in the presence and absence of a quenching gas. The mean life-time of Hg ($^3P_1$) in the system must be known. This k_q is related to the quenching cross section, δ_q^2, by the following equation

$$k_q = \delta_q^2 \left[8\pi RT \left(\frac{M_{Hg} + M_Q}{M_{Hg} \cdot M_Q} \right) \right]^{\frac{1}{2}}$$

Unfortunately there is a great deal of uncertainty in the values of quenching cross sections. The difficulty is the uncertainty in the apparent life time of the triplet excited state of mercury atom, because of the effect of "imprisonment" of 253.7 nm resonance radiation in mercury photosensitized reactions(10-13). The phenomenon of imprisonment occur many times in a reaction cell and prolong the apparent life time of Hg ($^3P_1$).

Several theories have been advanced to treat radiation imprisonment and the resulting theoretical τ is then used to evaluate k_q from quenching data(15). Kang Yang(16) has eliminated the effect of imprisonment of resonance radiation by noting the effect of increasing mercury vapour pressure on the value of τk_q. He found that τk_q varies linearly with mercury vapour pressure. The value of τk_q was obtained by extrapolating to zero pressure of mercury. He also estimated the quenching rate constant (k_q) for ethylene by substituting the known τ_o value (where τ_o is the mean life of an isolated Hg(^{3}Pi) atom), = 1.08 x 10^{-7} sec, into the extrapolated value obtained of τ_o k_q From the above equation, k_q for the reaction Hg(^{3}Pi)+ $C_2H_4 \rightarrow$ Hg(^{1}So) + C_2H_4* at 25^{0}C was estimated to be 4.61 x 10^{11} ℓ.mol^{-1}.sec^{-1}, then δ_q^2 = 48.2 nm².

(b) Chemical method

The chemical methods are based on competitive quenching processes and therefore provide only relative values of quenching cross sections. The advantages of this method are as follows:

a) They are independent of such effects as radiation imprisonment.

b) The experiments can be performed under conditions normally employed in mercury photosensitized studies.

In 1955, Cvetanovic studied mercury photosensitized decomposition of nitrous oxide$^{(17)}$ and mixtures of nitrous oxide with some hydrocarbons$^{(18)}$. He found that triplet mercury atoms react with nitrous oxide to form molecular nitrogen and oxygen atoms. The nitrogen formed can be measured quantitatively. The competitive reaction scheme can be written as follows:

1. $\mathrm{Hg} + h\nu \xrightarrow{253.7\ \mathrm{nm}} \mathrm{Hg}^*$ Rate = Ri
2. $\mathrm{Hg}^* + \mathrm{N_2O} \xrightarrow{k_{N_2O}} \mathrm{Hg} + \mathrm{N_2} + \mathrm{O}\ (^3\mathrm{Pi})$
3. $\mathrm{Hg}^* + \mathrm{RH} \xrightarrow{k_{RH}} \mathrm{Hg} + \mathrm{Products}$

where Hg* represents Hg(^{3}Pi)

Consideration of the above competitive reaction scheme if the rate of reactions 2) and 3) are R_{N_2O} and R_{RH} respectively, then

$$R_i = R_{N_2O} + R_{RH}$$

In the absence of hydrocarbon

$$R_i = R^{o}_{N_2O} \overset{=}{\cancel{+}} R^{o}_{N_2} \quad \text{(rate of nitrogen formation)}$$

$$R^{\cancel{o}}_{N_2} = k_{N_2O}[Hg^*][N_2O] + k_{RH}[Hg^*][RH] = R_i$$

$$R^{o}_{N_2} = k_{N_2O}[Hg^*][N_2O]$$

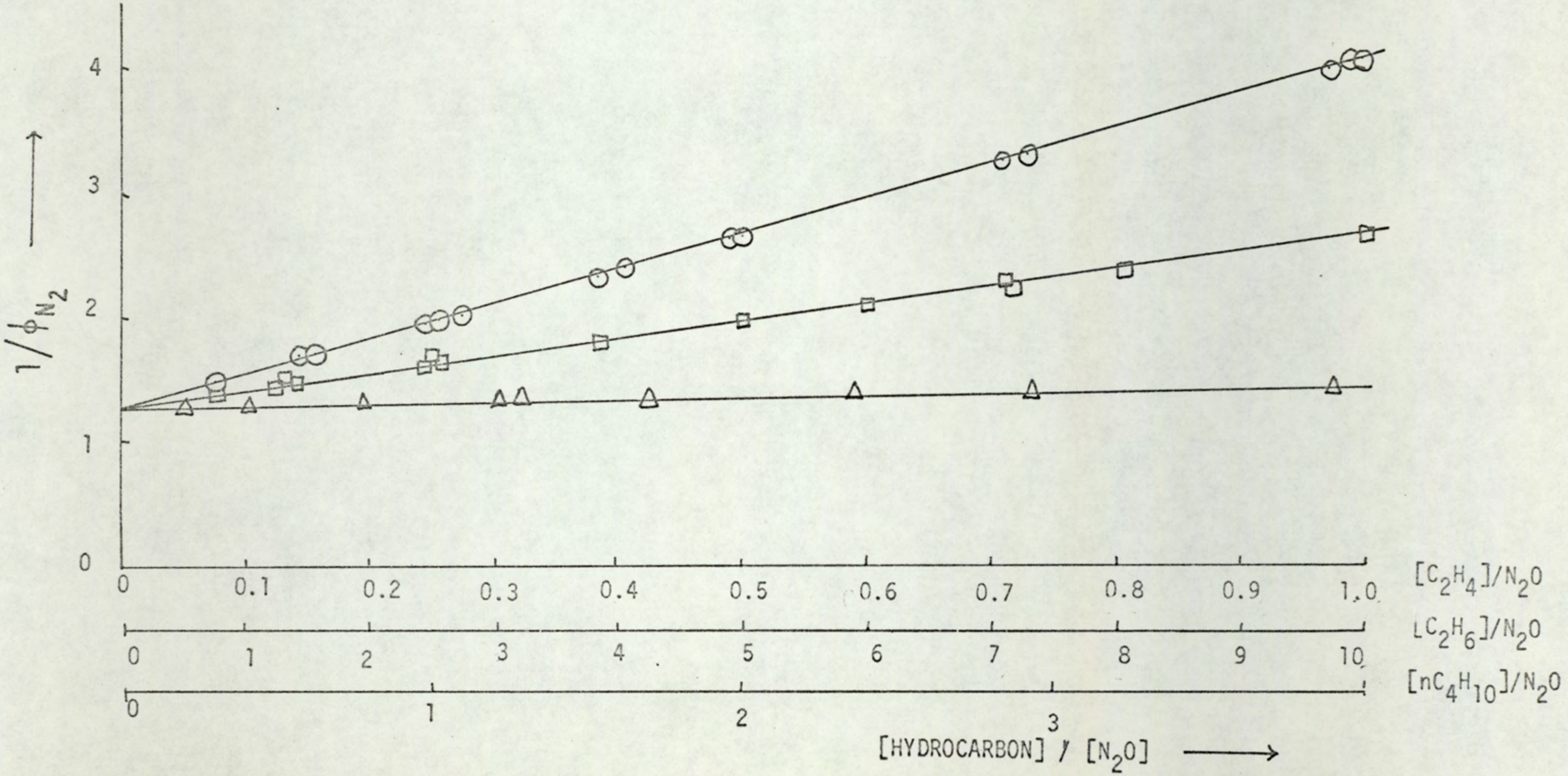
$$R^{o}_{N_2}/R_{N_2} = 1 + k_{RH}[RH]/k_{N_2O}[N_2O] = 1/\phi_{N_2}$$

A plot of $1/\phi_{N_2}$ VS $[RH]/[N_2O]$ should give a straight line with slope $= k_{RH}/k_{N_2O}$, which is the quenching rate constant of the hydrocarbon relative to nitrous oxide. Cvetanovic's results (as shown in Fig. 1.2) for ethane, ethylene and n-butane showed that this relationship agrees well in practice.

Payette, Bertrand and Rousseau(44) have recently observed that the quenching cross sections obtained by the chemical method (nitrous oxide method) in some cases, e.g. n-butane and propylene are dependent upon the incident light intensity. The plot of $1/\phi_{N_2}$ VS $[RH]/[N_2O]$ showed that for a change of incident light intensity of 10^3, the slope of the straight line varies by a factor of 4.7 for n-butane and 1.3 for propylene. This indicated that δ_q^2 increase

FIG. 1.2 PLOTS OF $1/\phi_{N_2}$ [HYDROCARBON] / [N_2O] FOR ETHYLENE, nBUTANE AND ETHANE

(R.J. CVETANOVIC, Progress in Reaction Kinetics, 2, 62, (1964))



as the light intensity decrease. They concluded that the mechanism previously proposed by Cvetanovic for the photodecomposition of N_2O/n-butane mixtures is incomplete, and the value of δ_q^2 based on this mechanism may be in error. Further work is needed to determine a more complete mechanism and to find the specific conditions for the evaluation of reliable δ_q^2 values.

Comparison of the Two Cross Sections

Table 1.1 shows that the cross sections estimated by the two methods agree well in C_3H_8, C_2H_4 quenching and probably also in C_2H_6 quenching but not in $C(CH_3)_4$ or in $CH_3CD_2CH_3$ quenching which confirms previous work of Penzes et al.$^{(25)}$.

TABLE 1.1

Quenching Cross Sections Estimated by Physical and Chemical Methods

Quencher	δ^2_{phys} $(nm)^2$	δ^2_{chem} $(nm)^2$
$C(CH_3)_4$	0.019	0.008
$CH_2CD_2CH_3$	0.008	0.003
CH_3CH_3	0.004	0.003
$CH_3CH_2CH_3$	0.022	0.024
$CH_2 = CH_2$	0.482	0.482

From this work, Kang Yang(19) observed that the detectable metastable mercury atoms (Hg ^3P_o) are formed in those quenchings where $\delta^2_{phys} > \delta^2_{chem}$.

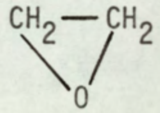
1.1.2 The Mechanism of Mercury Photosensitized Reactions and the Electrophilic Character of the Hg 6($^3P_1$)

A survey of quenching cross section data for Hg 6($^3P_1$) atoms and a comparison with the reactivity of other atomic species would suggest that the efficiency of energy transfer is related to the chemical nature of Hg 6($^3P_1$) atom. Rousseau, Strausz and Gunning(20) have pointed out that the triplet mercury atom exhibits electrophilic character. In general, atomic and radical reactants may be considered to exhibit in particular reactions either electrophilic, nucleophilic, or radical reagent character. Cvetanovic (21) has shown that ground state **oxygen** atoms [O($^3P_1$)] behave as distinctly electrophilic reagents in their reactions with olefins. In those studies, the reactivity of the olefins was found to increase as the electron-donating power of the olefins increased i.e. with increase in the number of alkyl groups attached to the doubly bonded carbon atoms.

If Hg ($^3P_1$) is electrophilic in character, the quenching cross-section values (δ^2_q) of the olefins should increase as the nucleophilic properties of the olefins increase. It can be seen from Table 1.2 that the olefins show a far larger cross-sectional area than the saturated hydrocarbons of comparable molecular size.

TABLE 1.2

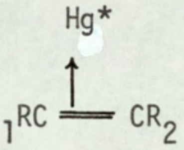
Relative Rate Constants for $O(^3P_1)$ Addition to Olefins compared with the Quenching Cross Sections (δ_q^2) of Olefins for $Hg(^3P_1)$ Atoms

Substrate	k_q	δ_q^2	$\frac{k\ \text{olefin}}{k\ C_2H_4}$ $O(^3P)$	Substrate	k_q	δ_q^2	$\frac{k\ \text{olefin}}{k\ C_2H_4}$ $O(^3P)$
C_2H_6	0.20	0.0022	-	$CH_2 = CH_2$	46.1	0.482	1.00
C_3H_8	2.0	0.026	-	$CH_2 = CHF$	36.3	0.461	0.38
$CH_3CD_2CH_3$	0.29	0.0039	-	$CH_2 = CF_2$	28.7	0.423	0.22
n-C_4H_{10}	5.5	0.079	-	$CF_2 = CHF$	18.9	0.306	0.57
i - C_4H_{10}	7.5	0.105	-	$CF_2 = CF_2$	9.5	0.165	1.60
C_2H_4	46.1	0.482	1.00	$(CH_3)_2\ CO$	58.5	0.795	-
$CH_3CH = CH_2$	53.0	0.653	5.30	CH_3CHO	48.0	0.611	-
2-C_4H_8	61.6	0.854	-		4.7	0.059	-

Notes: Units of k_q are $\ell.mol^{-1}sec^{-1}$ c 10^{-10} at 25^oC. Units of δ_q^2 are $(nm)^2$

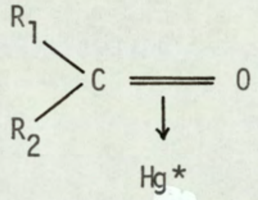
This is because of the high Π electron density of the olefinic double bond which makes the olefins nucleophilic in nature. It has been reported(20) that the substitution of a methyl group in ammonia causes a very marked increase in δ_q^2 as compared to the sum of the quenching cross sections of methyl and ammonia. Here δ_q^2 follows the increase in basicity of methyl substituted ammonia. The primary quenching interaction between Hg (^{3}Pi) atoms and substrate molecules leads to the following configurations for the quenching complex, based on the electrophilic nature of Hg(^{3}Pi).

Olefins

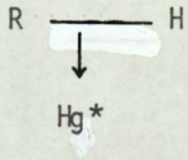


$$\underset{{}_1RC = CR_2}{\overset{Hg^*}{\uparrow}}$$

Carbonyl compounds:



Alkanes

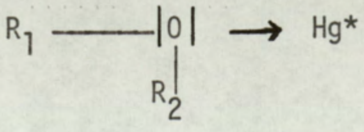


$$R \underset{\overset{\downarrow}{Hg^*}}{\text{———}} H$$

Alkyl halides (RX) with the exception of fluorides:

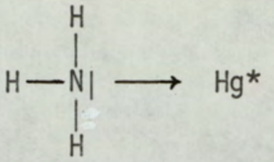
$$R - \overline{\underline{X}}| \longrightarrow Hg^*$$

H_2O, H_2S, alcohols and esters:



$$R_1 - \underset{R_2}{|\overline{\underline{O}}|} \longrightarrow Hg^*$$

NH_3, PH_3, AsH_3 and their alkyl derivatives:



$$H-\overset{H}{\underset{H}{N}}| \longrightarrow Hg^*$$

From the above mechanism, it can be seen that the triplet mercury atom quenches itself at the site of maximum electron density. Further evidence which support this mechanism is by studying kinetics isotope effects.

Rousseau and Gunning(22) have investigated the effect of deuterium substitution on the rate of the quenching interaction between hydrocarbon molecules and triplet mercury atoms. The quenching cross sections of various deuterated compounds are compared with the undeuterated parent in Table 1.3.

We would expect to see a considerable isotope effect for the quenching cross section if the quenching site of $Hg(^{3}Pi)$ atom is one of the C-D bonds. From Table 1.3 the results show that the initial interaction between $Hg(^{3}Pi)$ atoms and C_3H_8 occurs almost exclusively at the secondary C-H bonds. On the other hand, the secondary C-H bonds quench very much more effectively than the primary C-H bonds. Similarly a tertiary C-H bond quenches more effectively than a secondary C-H bond.

TABLE 1.3

Quenching Cross-Section Data of some Deuterated Compounds for Hg(^{3}P1) Atoms

Substrate	$\delta_q^2(\mathrm{nm})^2$	Substrate	$\delta_q^2(\mathrm{nm})^2$
$CH_3CH_2CH_2CH_3$	0.036		
$CH_3CH_2CH_3$	0.012	$CD_3CD_2CD_3$	0.0009
		$CH_3CD_2CH_3$	0.0017
		$CD_3CH_2CD_3$	0.01
cyclo- C_3H_6	0.011	cyclo- C_3D_6	0.0029
$(CH_3)_3$ CH	0.048	$(CH_3)_3$ CD	0.0044
CH_2 = CH CH_3	0.298	CD_2 = CD CD_3	0.287
H_2O	0.010	D_2O	0.0046
NH_3	0.029	ND_3	0.0109
PH_3	0.262	PD_3	0.295

Note: Taken from Rousseau, Y. Strausz,O.P. and Gunning,H.E. J.Chem.Phys.; 39, 965 (1963).

TABLE 1.4

Quenching Efficiency of some Deuterated Molecules with Hg($^3P_1$) Atoms

Compound	Minimum Quenching on the CH_2 or CH group (%)
$CH_3CH_2CH_3$	87
$CH_3CD_2CH_3$	64
$CD_3CH_2CD_3$	96
$CD_3CD_2CD_3$	87
$(CH_3)_3$ CH	91
$(CH_3)_3$ CD	71

From Table 1.3 the olefin shows a small isotope effect, the decrease in quenching cross-section of $CD_2 = CDCD_3$ is very small (relative to CH_3 CH = CH_2). This suggests that the quenching site of Hg($^3P_1$) is more likely to be on the electron rich CC double bond, but not on a C-H bond (deuteration does not affect the electron density of the bond significantly).

D_2O, ND_3 and PD_3 showed a small isotope effect. This also suggests that the quenching site is the lone pair of the electronegative atom and not the bonds to hydrogen.

The kinetic isotope effect studies confirm the mechanism proposed previously that the quenching site of triplet mercury atom,

$Hg(^3P_1)$, is on the C-H bond of saturated hydrocarbon molecules, on the CC double bond of unsaturated compounds and probably at the lone pair of the electronegative atom of H_2O, NH_3 and PH_3.

1.1.3 Some Typical Primary Processes in Mercury Photosensitization

These reactions are classified according to the primary compound decomposed by $Hg(^3P_1)$

a) Decomposition of Hydrogen

This reaction was first investigated by Cario and Franck(1) and more recent work has been carried out by a number of workers(7,8,19,26). In 1970, Callear and Hedges(9) investigated this reaction by using mercury flash-photosensitized decomposition of hydrogen, Hg H was detected, which suggests that the primary process is

$$Hg(^3P_1) + H_2 \longrightarrow Hg\,H + H$$

b) Decomposition of Hydrogen Chloride and Methyl Chloride

Both reactions have been studied by Strausz and co-workers(23,24) and by Callear and Hedges(8). The principal primary processes are

$$Hg(^3P_1) + HC\ell \longrightarrow Hg\,C\ell + H$$

$$Hg(^3P_1) + CH_3C\ell \longrightarrow Hg\,C\ell + CH_3$$

c) Decomposition of Carbonyl Sulphide

The mercury photosensitized decomposition of carbonyl sulphide has been used as a source of sulphur atoms (^3P). This reaction was investigated by Gunning and Strausz(29) who proposed the primary process as

$$Hg(^3P_1) + COS(^1\varepsilon) \longrightarrow Hg(^1S_0) + CO(^1\varepsilon) + S(^3P)$$

d) Decomposition of Dimethyl Ether

The mercury photosensitized decomposition of dimethyl ether has previously been examined by Marcus, Darwent and Steacie(27) and by Pottie, Harrison and Lossing(28). They studied the reaction over the range 25 - 292°C and at a pressure of 28 and 110 mm Hg. Takazaki, Mori and Kawasaki(30) have briefly investigated this reaction at room temperature. Recently Loucks and Laidler(31) have studied the decomposition of dimethyl ether at 200 - 300°C and over the pressure range 3 to 600 mm Hg. They concluded that the only primary process of this reaction is

$$Hg(^3P_1) + CH_3CO\ CH_3 \longrightarrow Hg(^1S_0) + CH_3CO\ CH_2 + H$$

e) Decomposition of Ethylfluoride

Scott and Jennings(32) studied the mercury photosensitized decomposition of ethylfluoride at room temperature and found that the major products are $CH_3\text{-}CHF\cdot CH\cdot CH_3$ and $CH_3\text{-}CHF\text{-}CH_2\text{-}CH_3$ together with smaller quantities of $n\text{-}C_4H_{10}$, C_2H_6, C_2H_4, $CH_2 = CHF$ and H_2. These suggest that the primary process is:

$$Hg(^3P_1) + CH_3CH_2F \longrightarrow Hg(^1S_0) + H + CH_3CHF$$

f) Decomposition of n-Butane

The mercury photosensitized decomposition of n-butane has been studied in detail by Cvetanovic, Falconer and Jennings(33) who showed that the experimental behaviour of the system could be explained without having to invoke the occurrence of metastable mercury atoms. It has been reported by Callear and Hedges(9) that Hg H is not produced in the reaction of Hg(^{3}P$_1$) with saturated hydrocarbons. They suggest the primary process is either

$$Hg(^3P_1) + RH \longrightarrow Hg + R. + H.$$

or $$Hg(^3P_1) + RH \longrightarrow HgR + H.$$

the reaction is much used as a source of hydrogen atoms for quantitative studies.

g) Decomposition of Nitrous Oxide

When nitrous oxide is used as the quenching gas no Hg(^{3}P$_0$) atoms are formed(7) (less than 1%) in this reaction. Two possible processes have been concluded by Manning and Noyes(34) as follows:

a) $N_2O + Hg(^3P_1) \longrightarrow NO(^2\pi) + N(^4S) + Hg(^1S_0)$

or

b) $N_2O + Hg(^3P_1) \longrightarrow Hg(^1S_0) + N_2(^1\varepsilon) + O(^3P_1)$

Cvetanovic(17,18) re-investigated this reaction in 1955, he showed that the primary process in the mercury photosentisized decomposition of nitrous oxide was the formation of oxygen atoms and nitrogen molecule (i.e. process b). More details of this reaction will be described in Section 1.2.3.

1.2 SOURCES OF GROUND STATE OXYGEN ATOMS

Many methods have been used to produce ground state oxygen atoms for investigation of their reactions. The important methods are described below:-

1.2.1. The Electrical Discharge Technique

Avramenko and Kolesnikova(35) used the electrical discharge technique to generate oxygen atoms by passing molecular oxygen through an electrical discharge at pressure of about 1 mm Hg. The main disadvantage of this process is that the excess molecular oxygen taking part in the process can influence the nature of the products. The products formed are not the same as are formed in the absence of oxygen molecules.

Another disadvantage of this technique is that at the low pressures used in the discharge, fragmentation of the "hot" primary addition product occurs readily, possibly obscuring the nature and yield of the primary products.

1.2.2 The Photolysis of Nitrogen Dioxide

Photolysis of nitrogen dioxide is of some importance as a source of oxygen atoms. It is believed(36) that dissociation into nitric oxide and ground state oxygen atoms occurs in the spectral region 370 - 245 nm.

$$N_2O + h\nu \longrightarrow NO(^2\Pi) + O(^3P)$$

The wavelength for the onset of the photodissociation has been discussed by several workers(37,40-43). Sato and Cvetanovic(38) studied the photo-oxidation of butene - 1 by nitrogen dioxide at wavelengths between 404.7 and 228.8 nm. They found that the same addition products, α-butene oxide and n-butanal were formed at all these wavelengths. Furthermore, they found that the ratio of their yields was the same at wavelengths between 404.7 nm and 326.1 nm while α-butene oxide was three times as much as n-butanal at the wavelengths between 253.7 nm and 228.8 nm. It was concluded(38, 39) that the photo-oxidation at the wavelengths between 404.7 nm to 326.1 nm led to $O(^3P)$ atoms and $O(^1D)$ at shorter wavelengths.

The disadvantages of using this method as a source of oxygen atoms are:

1. The parent molecule is very reactive, the nitrogen oxide has been found to react with olefin and its products to yield alkyl nitrates and nitroalkanes in the reaction of oxygen atoms with olefins.
2. NO_2 also reacts rapidly with oxygen atoms to give molecular oxygen

$$NO_2 + O \longrightarrow NO + O_2$$

1.2.3 The Mercury Photosensitized Decomposition of Nitrous Oxide

The mercury photosensitized decomposition of nitrous oxide has been studied by Manning and Noyes(34) in 1932 who found that when the reaction was allowed to go to completion the products were nitrogen and mercuric oxide.

$$N_2O + Hg^* \longrightarrow N_2 + HgO$$

They also studied the change of pressure during this reaction, but it was found that the overall reaction proceeded without a pressure change, although initially small pressure increase had been indicated. This indicated that the intermediate decomposition products may be other than nitrogen. Two possible primary processes may be represented by the equations

$$Hg(^3P_1) + N_2O \longrightarrow NO(^2\pi) + N(^4S) + Hg(^1So)$$

$$Hg(^3P_1) + N_2O \longrightarrow N_2(^1\varepsilon) + O(^3P) + Hg(^1So)$$

Cvetanovic(17) re-investigated this reaction in 1955 and found that at small conversion the products were nitrogen and oxygen in the ratio 2:1. A small deficiency of oxygen occurred owing to the formation of mercuric oxide. From this work, Cvetanovic concluded that the primary process in the mercury photosensitized decomposition of nitrous oxide was the formation of oxygen atom and nitrogen molecule. He has noted that the quantum yields of the reaction $Hg(^3P) + N_2O \longrightarrow N_2 + O(^3P) + Hg(^1So)$ proceeds with a quantum yield of unity. It has also been noted that in the presence of an oxygen consuming compound (olefin or alkane) no mercury depletion occurred and no mercuric oxide was formed. Cvetanovic found the rate of decomposition of nitrous oxide was identical to the rate of formation of nitrogen molecule. Spin conservation rules predict that the ground state oxygen atoms formed by this reaction should be in the triplet state.

The mercury photosensitized decomposition of nitrous oxide is widely used as the most convenient source of ground state oxygen atoms because there are several advantages of using this process

1. The system can be used over a wide pressure range.
2. The nitrogen formed in the primary decomposition process can be easily measured, allowing the number of oxygen atoms generated to be calculated.
3. The rate of atom production is easily controlled by changing the intensity of the incident radiation.
4. The absence of molecular oxygen can be ensured.
5. Nitrous oxide is inert to oxygen atom and free radical attack under the conditions used

The quenching efficiency of nitrous oxide is only about half as large as that for olefin. However, by using a large excess of nitrous oxide, the quenching of mercury atoms by olefin can be minimised.

1.3 THE REACTIONS OF GROUND STATE OXYGEN ATOMS

1.3.1 The Reaction of Oxygen Atoms with Olefins

The reaction of oxygen atoms with olefins has been first reported by Avramenko and Kolesnikova(35) and Cvetanovic(45) in 1955. Avramenko and Kolesnikova used the electrical discharge technique to generate oxygen atoms whereas Cvetanovic used the mercury photosensitized decomposition of nitrous oxide.

Avramenko and Kolesnikova studied the reaction of oxygen atoms with ethylene, propylene and butadiene and reached the following generalized conclusions:

1. An atom of oxygen is capable of disrupting the carbon-carbon double bond with formation of aldehyde.
2. During disruption of the double bond higher aldehydes are formed preferentially.
3. Insertion into CH bonds may occur both at saturated and unsaturated carbon atoms.
4. In the case of propylene the probabilities of attack on single bonds (CH_3 group) and double bond are about the same.

These results differed considerably from those of Cvetanovic. This is because the electrical discharge technique requires the pressure of only a few millimeters and that molecular oxygen is present. These two factors can influence the nature of the products (see Section 1.2.1.).

Cvetanovic(45) studied the reaction of oxygen atoms with ethylene and his results led to the conclusion that the primary process was a direct addition of an oxygen atom to the double bond to form an energy-rich intermediate ("hot" adduct molecule) which then underwent further reactions. The products formed were carbon monoxide, hydrogen, several paraffins (CH_4, C_2H_6, C_3H_8, C_4H_{10}), aldehydes (mainly CH_3CHO and some higher homologs) and a small amount of ethylene oxide. These reaction products were explained by a predominant primary split of the "hot" adduct into $.CH_3$ and $.CHO$.

$$.CHO \longrightarrow CO + H. \xrightarrow{C_2H_4} .C_2H_5 \xrightarrow{\text{radicals}} \text{paraffins}$$

$$.C_2H_5 + CHO + M \longrightarrow C_2H_5CHO + M$$

Acetaldehyde could result from combination of CH_3 and CHO or from direct stabilization of the initial adduct. Cvetanovic found that the yield of CO decreases while CH_3CHO and ethylene oxide increase with increasing pressure.

When Cvetanovic studied the reaction of oxygen atoms with the higher homologs of ethylene(46,47,48), much more definite information on the formation of "hot" adducts was obtained. In general, the major reaction products were addition products, e.g. epoxides and isomeric carbonyl compounds and fragmentation products were mainly carbon monoxide, acetaldehyde and ethane. They also noted that the amount of addition products increase and fragmentation products decrease with increasing pressure. This trend is shown in Fig. 1.3 and indicated "hot" precursors of very short lifetimes.

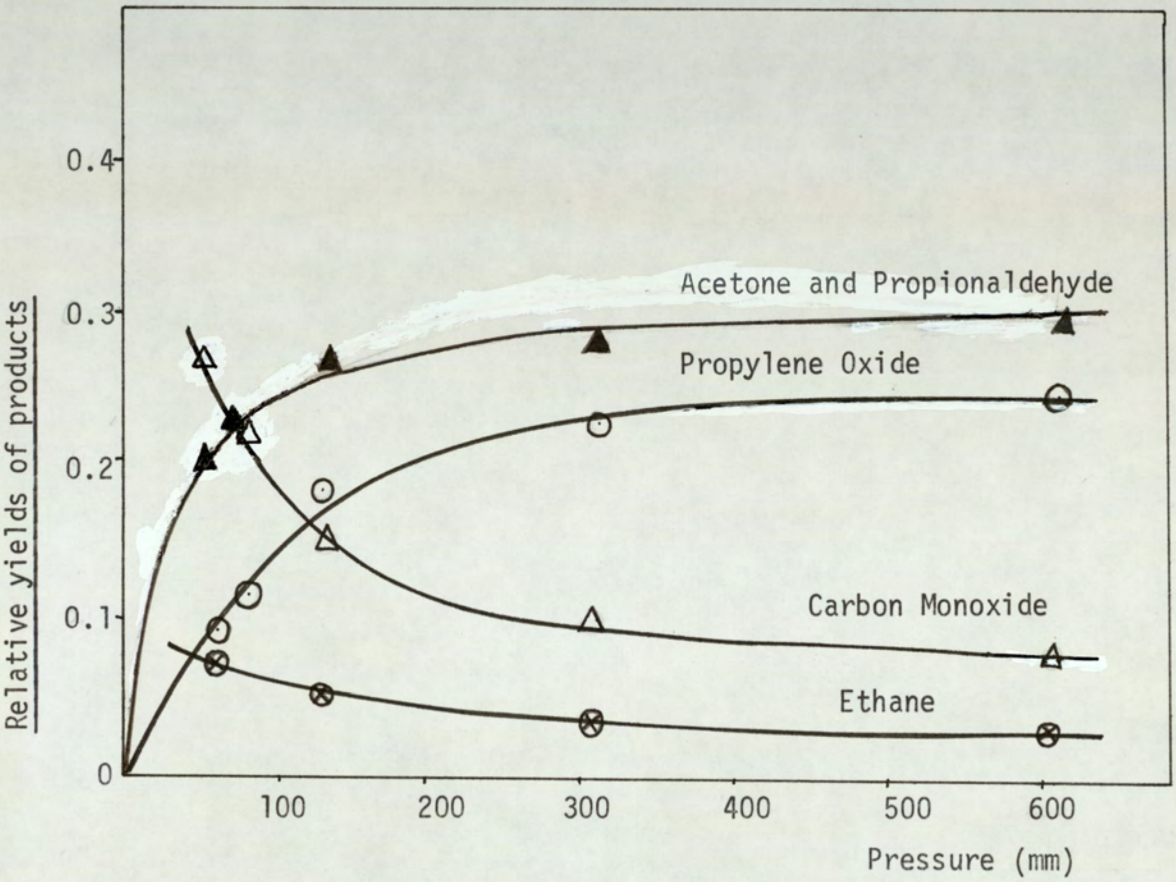


Fig. 1.3 Pressure effect on the yield of addition and fragmentation products in the reaction of $O(^3P)$ with propylene.

When the epoxide and carbonyl compounds formed by the addition of oxygen atoms to olefins, they possess excess energies of the order of 376.2 and 480.7 kJ mol^{-1} respectively, as a result of the high exothermicities of these reactions. The pressures at which efficient removal of this excess energy by collisional deactivations will occur depends on the lifetimes of the "hot" products with respect to their fregmentation. These lifetimes depend on the number of degrees of freedom and on the bond strengths of the weak bonds in the molecules formed. In the case of ethylene the number of degrees of freedom is relatively small, and predominant fragmentation occurs at all pressures below one atmosphere where the products from propylene and 1,3-butadiene are largely stabilized.

TABLE 1.5

Lifetimes of "Hot" Addition Products

Reacting Olefin	"Hot" Product.	Lifetime (sec)
Ethylene	Ethylene oxide	10^{-10}
Ethylene	Acetaldehyde	3×10^{-10}
Butadiene	3-Butenal	1.4×10^{-9}
Butadiene	Butadiene monoxide	2.7×10^{-9}
Propylene	Propylene Oxide	5.8×10^{-9}
Propylene	Propionaldehyde	8.0×10^{-9}
Isobutene	Isobutyraldehyde	1.5×10^{-7}
Butene - 1	n-Butyraldehyde	2×10^{-7}
Butene - 1	α-Butene oxide	3×10^{-7}

a) Mechanism of Addition of Ground State Oxygen Atoms to Olefins

The major products of these reactions for propylene and butene series are the epoxide and isomeric carbonyl compounds. The products of these reactions are shown in Table 1.6.

TABLE 1.6

Addition Products Formed from $O(^3P)$ + Olefins

Olefin	Addition products and their fractions	
Propylene	Propylene oxide (0.50)	Propionaldehyde (0.50)
Butene - 1	α-Butene oxide (0.53)	n-Butyraldehyde (0.43) Methylethyl ketone (0.04)
Isobutene	Isobutene oxide(0.54)	Isobutyraldehyde (0.43) Methylethyl ketone (0.03)
Cis-Butene-2	Cis-β-Butene oxide(0.25) trans-β-Butene oxide (0.26)	Isobutyraldehyde (0.23) Methylethyl ketone (0.26)
trans-Butene-2	cis-β-Butene oxide(0.15) trans-β-Butene oxide (0.33)	Isobutyraldehyde (0.21) Methylethyl ketone (0.31)
cis-pentene-2	cis-β-Pentene oxide(0.23) trans-β-Pentene oxide (0.31)	2-Methyl Butanal (0.21) Methyl-n-propyl ketone (0.25)

Reference: Cvetanovic, R.J.

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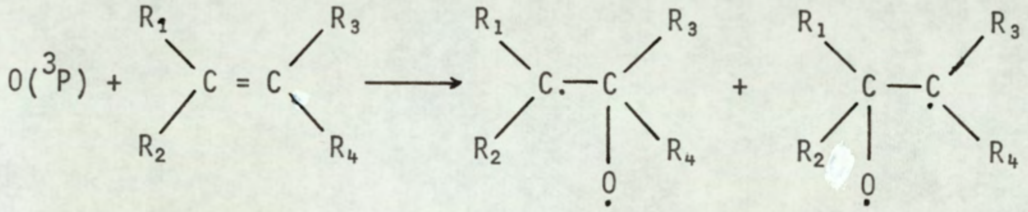
The formation of these products may be explained in the following manner.

1. Addition is non-stereospecific

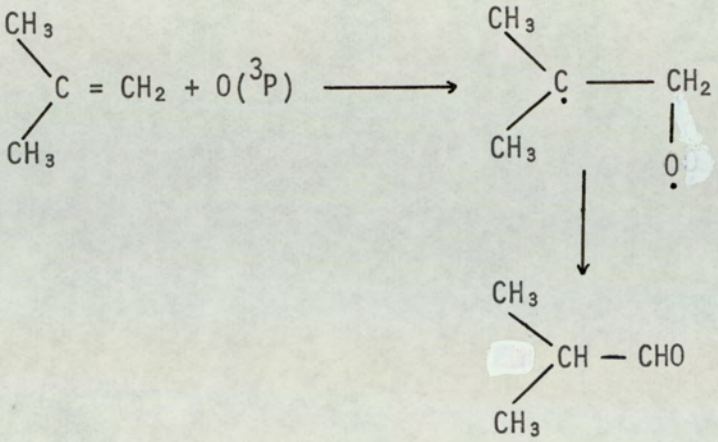
The addition products do not retain the stereospecific character of the olefin. This is evident from the fact that when oxygen atoms reacted with either cis- or trans-butene-2 both cis- and trans-β-butene oxide are formed. Therefore there must be some rotation around the original bond before ring closure to form the epoxide. The following step has been proposed:



Rotation around the original double bond of the biradical intermediate lead to loss of the stereospecific character of the original olefin. The difference in ratios of cis- and trans-β-butene oxide formed from cis- and trans-butene-2 suggest that these biradicals are probably very short-lived. A spin conservation rule agrees well with the formation of the biradical intermediate.

2. Oxygen atom adds preferentially to the less substituted carbon of the double bond

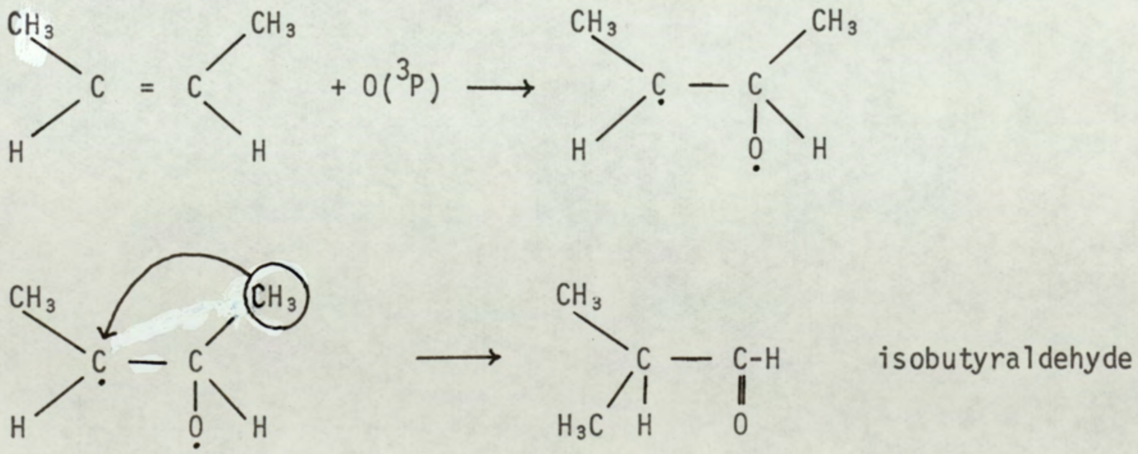
For example, with isobutene, the main carbonyl product is isobutyraldehyde and not methylethyl ketone.



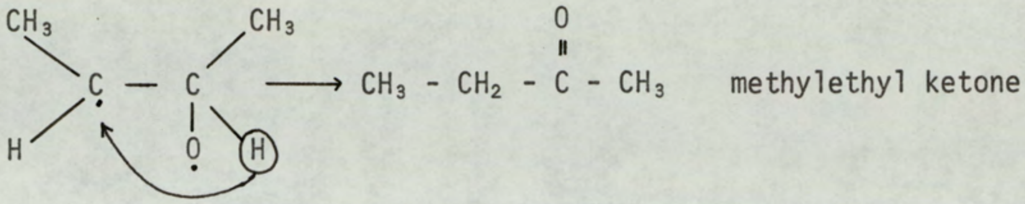
This behaviour is also observed with the other olefins.

3. Internal re-arrangements

This always occurs in the formation of carbonyl compounds with the migration of hydrogen atom or an alkyl group to the other carbon atom of the original double bond. The migration is always from the carbon to which the oxygen is attached. This phenomenon may be illustrated by the following example. Starting from cis-butene-2

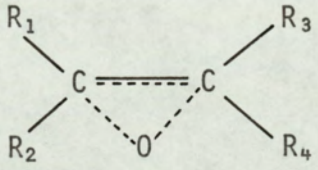


or

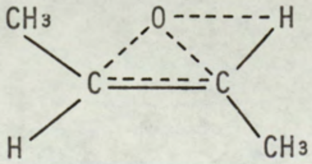


Cvetanovic(49) suggested that the migration of hydrogen atom process is entirely internal but migration of an alkyl group is only partly internal process, since these products could be substantially reduced by the presence of molecularoxygen.

The reactions of $O(^3P)$ with olefins have also been studied at the low temperature range (77 - 90 K) by Klein and co-workers(50,51,52). The products obtained from this method were the same as those at 300 K. They have proposed that the intermediate adduct is a loose three numbered ring which oxygen is bound in the plane of the olefinic structure.

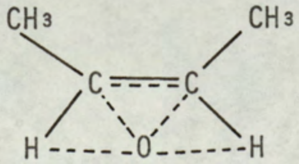


It was also proposed that oxygen can form weak bond with neighbouring hydrogens as shown below.



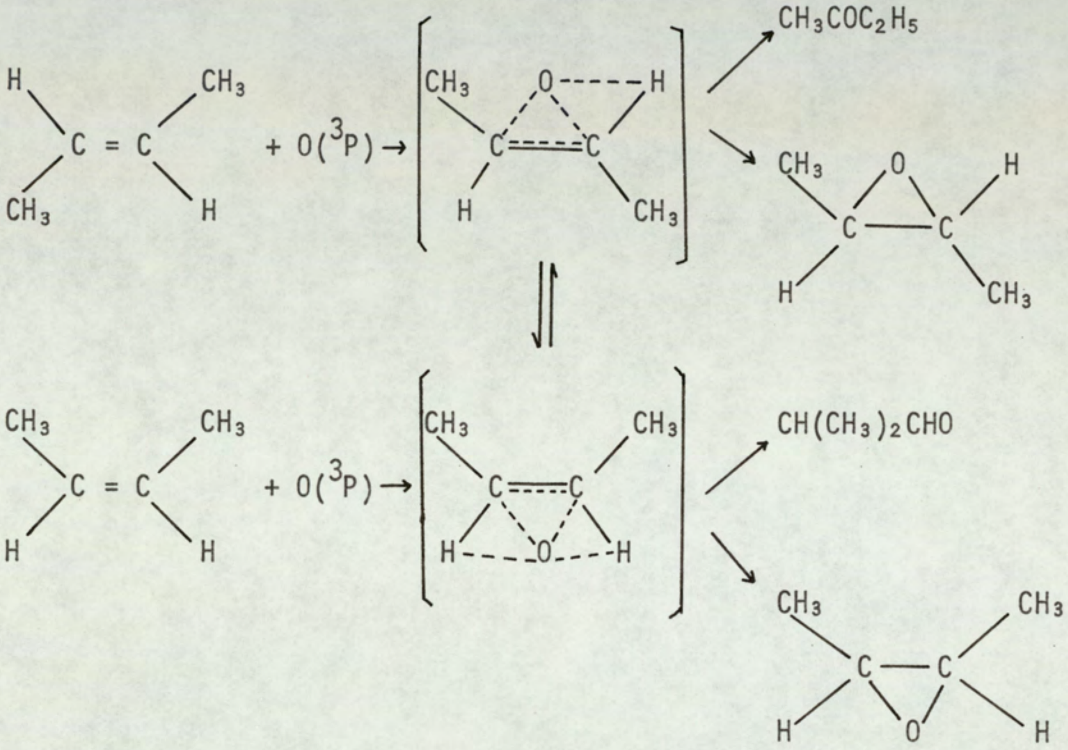
(A)

or

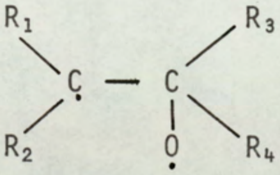


(B)

These rings allow a certain amount of rotation about the very much weakened original double bond, the reactions can be written as follows:



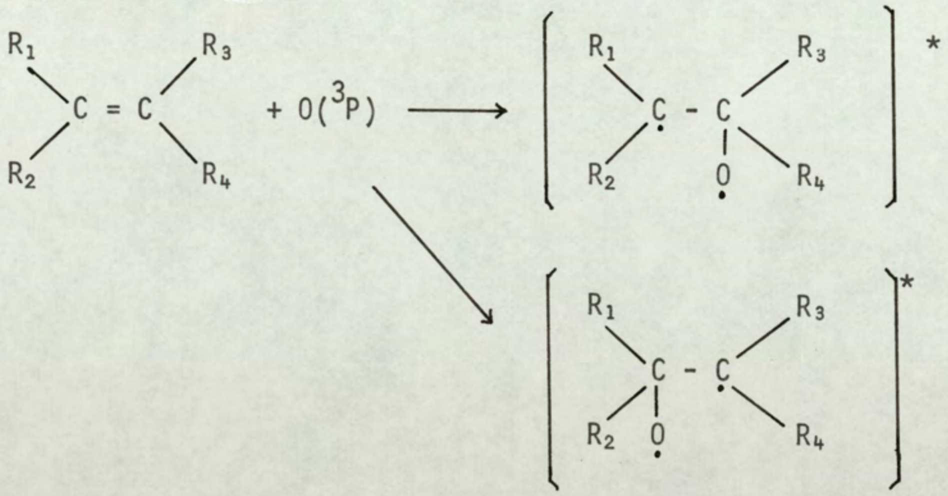
The proposition of this transition state do not conflict with those of Cvetanovic if we consider the initial biradical

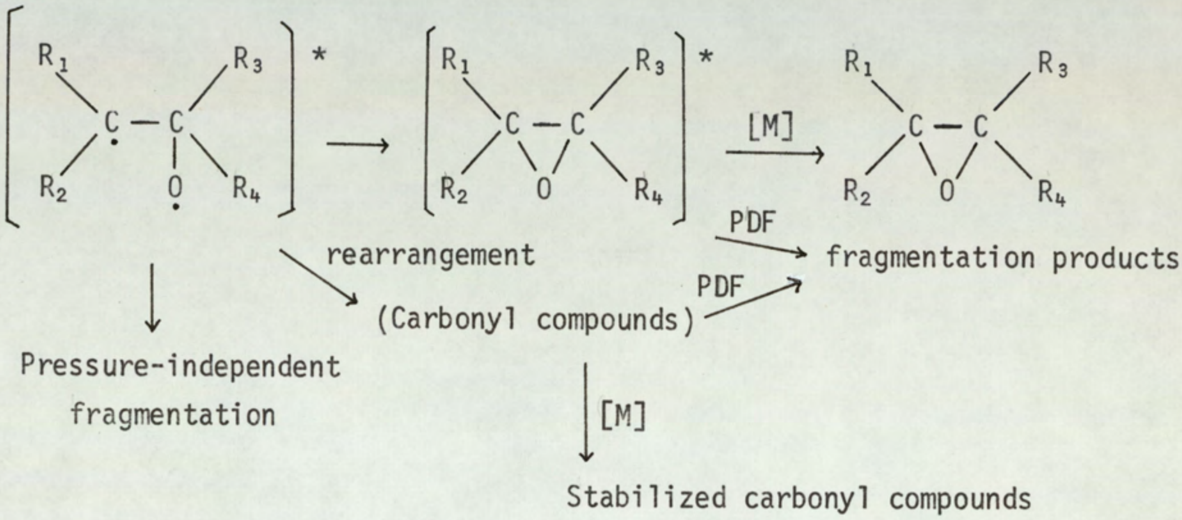


allowing rotation about the single bond and then formation of the two intermiediates (A and B) proposed by Klein.

b) Pressure Dependent and Pressure Independent Fragmentation

The results of Cvetanovic show that yields of addition products increased and those of fragmentation decreased with increasing pressure in the system. This type of fragmentation of the addition products is known as "Pressure dependent fragmentation". The initial biradicals possess appreciable quantities of vibrational energy and they are therefore capable of very rapid reactions along several paths. One of these paths is a "Pressure Independent Fragmentation" which occurs at high pressures where the fragmentation of the 'hot' products ("the pressure dependent fragmentation") is completely suppressed. The pressure independent fragmentation products are formed because the biradical is presumably very short lived and does not experience a collision before partially decomposing by the pressure independent route. The diagram of pressure dependent and pressure independent fragmentation of the reaction of $O(^3P)$ with olefins can be written as follows:





If the excess energy of the biradical is not removed by a collisional deactivation, it will be carried over to the "hot" addition products of the reaction. These "hot" products can be stabilized by collision and forms the observed addition products (epoxide and aldehyde) at high pressures. If the pressure is kept low, most of the energy remains with the adduct leading to a greater degree of fragmentation, some of the products decompose by the pressure dependent pathway.

c) Determination of Relative Rate Constants

The nitrous oxide technique has been developed to obtain accurate values of relative rate constants by carrying out competitive reactions of oxygen atoms with two olefins.

When mixture of two olefins are irradiated in the presence of nitrous oxide, the reaction scheme can be written as

$$\begin{aligned}
&\mathrm{Hg}({}^1S_o) + h\nu(253.7\ \mathrm{nm}) \longrightarrow \mathrm{Hg}^*\,({}^3P_1)\\
&\mathrm{Hg}^*\,({}^3P_1) + N_2O \longrightarrow \mathrm{Hg}({}^1S_o) + N_2 + O({}^3P)\\
&O({}^3P) + \text{Olefin (1)} \xrightarrow{k_1} \alpha_1 P_1 + \ldots\\
&O({}^3P) + \text{Olefin (2)} \xrightarrow{k_2} \alpha_2 P_2 + \ldots
\end{aligned}$$

where α is the fraction of the total number of oxygen atoms reacting with each olefin to produce product P.

$$\Delta P_1 = k_1\alpha_1[O]\,[Ol_1] \qquad (1)$$

and

$$\Delta P_2 = k_2\alpha_2[O]\,[Ol_2] \qquad (2)$$

(2) divided by (1)

$$\frac{k_2}{k_1} = \frac{\alpha_1}{\alpha_2}\,\frac{[Ol_1]}{[Ol_2]}\,\frac{\Delta P_2}{\Delta P_1} \qquad (3)$$

where ΔP indicates the rate of formation of product P.

Steady state considerations

$$\frac{d}{dt}[O] = R_{N_2} - k_1[O][Ol_1] - k_2[O][Ol_2] = 0 \qquad (4)$$

substituting (1) and (2) into (4)

$$R_{N_2} = \frac{\Delta P_1}{\alpha_1} + \frac{\Delta P_2}{\alpha_2} \qquad (5)$$

where R_{N_2} is rate of formation of nitrogen. Substituting (5) into

(3), the ratio of rate constants in terms of one product can be expressed as

$$\frac{k_2}{k_1} = \frac{[Ol_1]}{[Ol_2]} \cdot \left(\alpha_1 \frac{\Delta P_2}{\Delta P_1} - 1 \right) \tag{6}$$

If the detector response is linear, both the calibration factors (f) and the α values can be eliminated by performing experiments with olefin individually but otherwise under the same conditions as those used in the mixed runs.

Let ΔA_1 be the increase in peak area corresponding to the increase in product ΔP_1.

$$\Delta P_1 = f \, \Delta A_1$$

α values are determined in experiments with single olefin (denoted by *) by comparison with the product yield of nitrogen.

$$\alpha = \frac{\Delta P^*}{R_{N_2}} = f . \frac{\Delta A^*}{R_{N_2}} = f . Q^* \tag{7}$$

where $Q = \frac{\Delta P}{R_{N_2}}$

Substituting (7) into (3) and (6) respectively, the following equations are obtained:

$$\frac{[Ol_1]}{[Ol_2]} = \frac{k_2}{k_1} \cdot \frac{Q_2^*}{Q_1^*} \cdot \frac{A_1}{A_2} \tag{8}$$

and

$$\frac{[Ol_2]}{[Ol_1]} = \frac{k_1}{k_2} \left(\frac{Q_1^*}{Q} - 1 \right) \tag{9}$$

The above equations are derived on the assumption of zero change in olefin concentration. However, it is possible to correct the small consumption of reactants by calculating the final olefin concentration and using the mean value.

Cvetanovic has measured the relative rate constants of reaction of oxygen atoms with various olefins by using the competitive method, based on the theory discussed above. The experimental uncertainty of the values of the relative rate constants obtained by this technique is believed(21) not to be greater than a few per cent. The results obtained by Cvetanovic are summarised in Table 1.7.

TABLE 1.7

Relative Rates of Reactions of Oxygen Atoms at 25^{o}C

Compound	Relative Rate constant	Compound	Relative Rate constant
Ethylene	1.00	cis-2-Pentene	22.5
Propylene	5.75	cyclopentene	29.5
Butene-1	5.75	Tetramethylethylene	102.
Hexene -1	6.5	Trimethylethylene	79.
Isobutene	25.0	1,3-butadiene	24.3
cis-Butene-2	23.8		
trans-Butene-2	28.3		

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The above results are quoted with the rate of the ethylene reaction taken arbitrarily as unity.

It was found that the rates increase as the number of alkyl groups attached to the CC double bond increase.

The temperature dependence of the relative rate constants for several olefins has been studied by Cvetanovic(53). The ratios of the pre-exponential factors and differences in the activation energies have been calculated from the mean values of the relative rate constants at the two temperatures. The results obtained show that the differences in reactivities are primarily due to differences in the activation energies while the pre-exponential factors remain approximately constant.

TABLE 1.8

Activation Energies and "A" factors of the Reaction of Oxygen Atoms with olefins

Olefin	A/A_{CP}	$E-E_{TME}$ ($KJ.mol^{-1}$)
Ethylene	1.01	11.9
Butene-1	0.74	5.9
Isobutene	0.67	2.1
cyclopentene	1.00	2.5
cyclohexene	0.89	2.5
Trimethylethylene	1.18	0.4
Tetramethylethylene	1.25	0
1,3-Butadiene	1.14	3.4

A/A_{CP} represent ratio of the pre-exponential factors (CP=cyclopentene)
$E-E_{TME}$ represent activation energy differences (TME=tetramethylethylene)

It is of interest to know the absolute value of the rate constants and Arrhenius parameters for the reaction of oxygen atoms with olefins. These values have been derived indirectly from measurements of the rates of related reactions. Sato and Cvetanovic(38) found that oxygen atoms react with nitrogen dioxide 1.9 times faster than with butene-1. The rate constant for the reaction of oxygen atom with butene-1 should be 1.1×10^9 litre mole^{-1} sec^{-1} (at 25°C).

The absolute rate constant for the reaction of oxygen atom with ethylene has been measured directly by Elias and Schiff(54) using the fast flow technique. Their results lead indirectly to a value of $k_{butene-1} = 3.6 \times 10^9$ litre mole^{-1} sec^{-1}. Recently Elias(55), using the same technique, measured directly the rate constant for the reaction of butene-1, and $k_{butene-1} = 3.1 \times 10^9$ litre mole^{-1} sec^{-1} was obtained. By taking the value of $k_{butene-1} = 3.1 \times 10^9$ litre mole^{-1} sec^{-1}, the relative values in Table 1.8 can be placed on an absolute basis as shown in Table 1.9.

TABLE 1.9

Absolute Rate Constants and Arrhenius Parameters for O+ Olefins

Olefin	$10^{12}k$, 25°C (cc mole^{-1} sec^{-1})	Relative k		E_a (kJmole^{-1})	10^{12} A (cc mole^{-1} sec^{-1})
		Elias	Cvetanovic		
Ethylene	0.57	1	1	6.7	8.4
Butene-1	3.1	5.5	5.8	3.6	13
Isobutene	10	18	25	1.7	21
Cis-butene-2	12.6	22	24	1.5	23
Reference	55	55	53	55	55

Recently, Westenberg and de Hass(130) have measured the absolute rate constant of the reaction of oxygen atom with ethylene using a fast-flow system with ESR detection.

The absolute rate constant, $k_{C_2H_4} = 0.45 \times 10^{12}$ cc mole^{-1} sec^{-1}, and the activation energy, Ea = 6.2 kJ mole^{-1} obtained are close to the results reported by Elias as shown in Table 1.9.

1.3.2 The Reactions of Oxygen Atoms with Fluorinated Olefins

(a) Perfluoro-Olefins

Heicklen and co-workers$^{(56-60)}$ found that in the reaction of $O(^3P)$ from N_2O/Hg^* with $CF_2 = CF_2$, $CF_3CF = CF_2$ and $CF_2 = CF - CF = CF_2$ the major primary processes was cleavage of the double bond to form CF_2O and a biradical:

$$O(^3P) + R\,CF = CF_2 \longrightarrow CF_2O + R\ddot{C}F$$

where R = F, CF_3 and $CF_2 = CF$

Reactions of oxygen atoms with some perfluoro-olefins are described in detail below.

(a.1) Tetrafluoroethylene

The reaction of oxygen atom with tetrafluoroethylene has been studied at temperature of 23^o to 125^{o}Cm over a wide range of pressure and lamp intensities (i.e. oxygen atom concentration) by Saunders and Heicklen$^{(57)}$. They found that the quantum yield of carbonyl-fluoride (CF_2O) was 1.0 for all conditions.

The only products formed in the absence of molecular oxygen were CF_2O and perfluorocyclopropane ($C\text{-}C_3F_6$). No evidence for the formation of stabilized tetrafluoroethylene oxide (C_2F_4O) or CF_3CFO has been found.

Cohen and Heicklen(58) re-investigated this reaction at 22, 95 and 150^oC. Two possible mechanisms were proposed to explain the products.

Mechanism I

1. $O(^3P) + C_2F_4 \longrightarrow CF_2O + CF_2$
2. $CF_2 + CF_2 \longrightarrow C_2F_4$
3. $CF_2 + C_2F_4 \longrightarrow (C\text{-}C_3F_6)^*$

Mechanism II

4. $O(^3P) + C_2F_4 \longrightarrow (C_2F_4O)^*$
5. $(C_2F_4O)^* + C_2F_4 \longrightarrow CF_2O + C\text{-}C_3F_6$
6. $(C_2F_4O)^* \longrightarrow CF_2O + CF_2$

CF_2 formed in reaction (1) was probably in the triplet state(59-61) according to the spin conservation rule. The triplet CF_2 can be scavenged by molecular oxygen as found in the reaction of oxygen atom with C_2F_4.

$$^3CF_2 + O_2 \longrightarrow CF_2O_2$$

The molecular oxygen can also react with oxygen atoms and the $C_2F_4O^*$ intermediate.

$$O + O_2 + N_2O \longrightarrow O_3 + N_2O$$
$$C_2F_4O^* + O_2 \longrightarrow CF_2O + CF_2O_2$$

The result is to decrease the quantum yield of cyclo-C_3F_6, because in the absence of O_2, most of the cyclo-C_3F_6 comes from the reactions.

$$C_2F_4O^* + C_2F_4 \longrightarrow CF_2O + \text{cyclo-}C_3F_6$$
$$\text{or} \quad CF_2 + C_2F_4 \longrightarrow (C\text{-}C_3F_6)^* \longrightarrow C\text{-}C_3F_6$$

The singlet CF_2 was produced by the mercury photosensitized decomposition of C_2F_4(62).

$$Hg^* + C_2F_4 \longrightarrow Hg + {}^1CF_2 + {}^1CF_2$$

It is known that singlet CF_2 is not scavenged by molecular oxygen and the results(62) show that molecular oxygen has no influence on the cyclo-C_3F_6 yield.

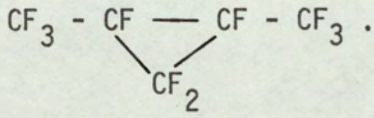
This evidence supports strongly that the CF_2 produced in the reaction (1) is in the triplet state. Furthermore Cohen and Heicklen(58) found that in the absence of molecular oxygen, the triplet CF_2 converts to the singlet state by the following reactions.

$$O(^3P) + C_2F_4 \longrightarrow {}^3CF_2 + {}^3CF_2$$

$${}^3CF_2 + {}^3CF_2 \longrightarrow C_2F_4^* \longrightarrow {}^1CF_2 + {}^1CF_2$$

(a.2) <u>Perfluoropropylene</u> (C_3F_6)

The products of this reaction were found(57,63,64) to be CF_2O, CF_3CFO and C_5F_{10} presumably as,



$CF_3-CF\overset{\displaystyle CF_2}{—}CF-CF_3$.

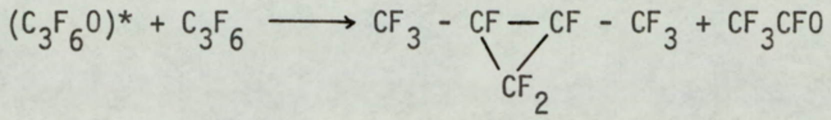
Again there was no evidence of the stabilized fluoroepoxide (C_3F_6O), C_2F_4 was probably formed but the analytical system could not detect its presence. Heicklen and co-workers have proposed three possible primary schemes

1. $O(^3P) + C_3F_6 \longrightarrow CF_2O + CF_3CF:$
2. $O(^3P) + C_3F_6 \longrightarrow CF_3CFO + {}^3CF_2:$
3. $O(^3P) + C_3F_6 \longrightarrow (C_3F_6O)^*$

and also secondary reactions were proposed as

4. $(C_3F_6O)^* + C_3F_6 \longrightarrow C_5F_{10} + CF_2O$

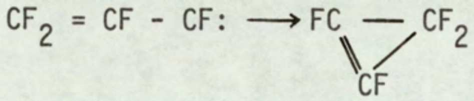
5.



6. $(C_3F_6O)^* \longrightarrow CF_2O + CF_3CF{:}$

(a.3) Perfluoro-1,3-Butadiene

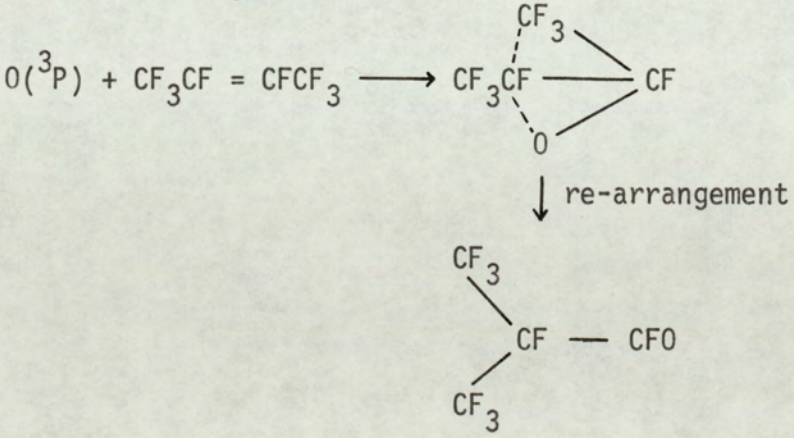
The reaction of oxygen atom with perfluoro-1,3-butadiene may be written as follows: $O(^3P) + CF_2{=}CF - CF{=}CF_2 \longrightarrow CF_2O + CF_2 = CF - CF{:}$



The products of this reaction were found to be CF_2O and cyclo-C_3F_4.

(a.4) Perfluorobutene-2

The products were CF_2O, i-C_3F_7CFO and CF_3CFO.
The main route of this reaction is not cleavage of the double bond in contrast to the previous reactions. It is probably addition followed by rearrangement.



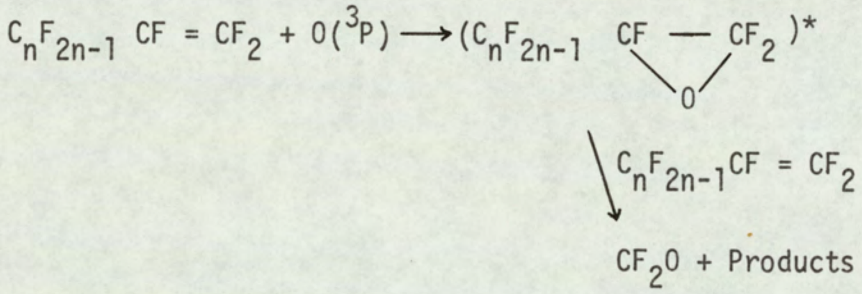
By studying the reaction of oxygen atoms with several perfluoro-olefins it is found that if the perfluoro-olefin has a terminal double bond, the product is always carbonyl fluoride (CF_2O) i.e.

$$C_nF_{2n-1}\,CF = CF_2 \xrightarrow{+O(^3P)} C_nF_{2n-1}CF: + CF_2O$$

The biradicals formed then can:

1. add to the original olefin,
2. cyclise or re-arrange,
3. dimerise with another biradical.

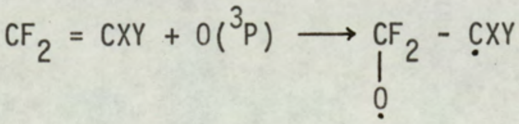
The reaction scheme can be written as follows:



b) Partially Fluorinated Olefins

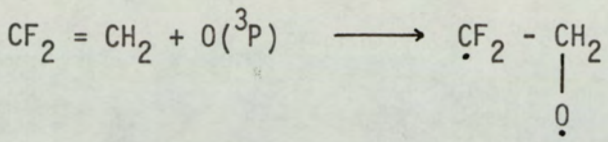
The reaction of $O(^3P)$ with halogenated 1,1-difluoroethylenes, $CF_2 = CXY$, has been studied by Mitchell and Simons(65) using flash photolysis technique. They found that the oxygen atom adds to fluorinated carbon when X and Y are halogens, but to the other carbon if X and Y are hydrogens.

If X, Y are halogens



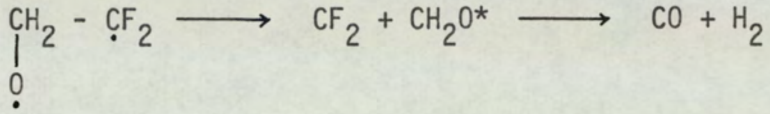
$$CF_2 = CXY + O(^3P) \longrightarrow \underset{\underset{\dot{O}}{|}}{CF_2} - \dot{C}XY$$

If X,Y are hydrogens



$$CF_2 = CH_2 + O(^3P) \longrightarrow \underset{\cdot}{C}F_2 - \underset{\underset{\underset{\cdot}{O}}{|}}{CH_2}$$

The main reaction products of 1,1-difluoroethylene were unexpectedly found to be carbon monoxide and hydrogen



$$\underset{\underset{\underset{\cdot}{O}}{|}}{CH_2} - \underset{\cdot}{C}F_2 \longrightarrow CF_2 + CH_2O^* \longrightarrow CO + H_2$$

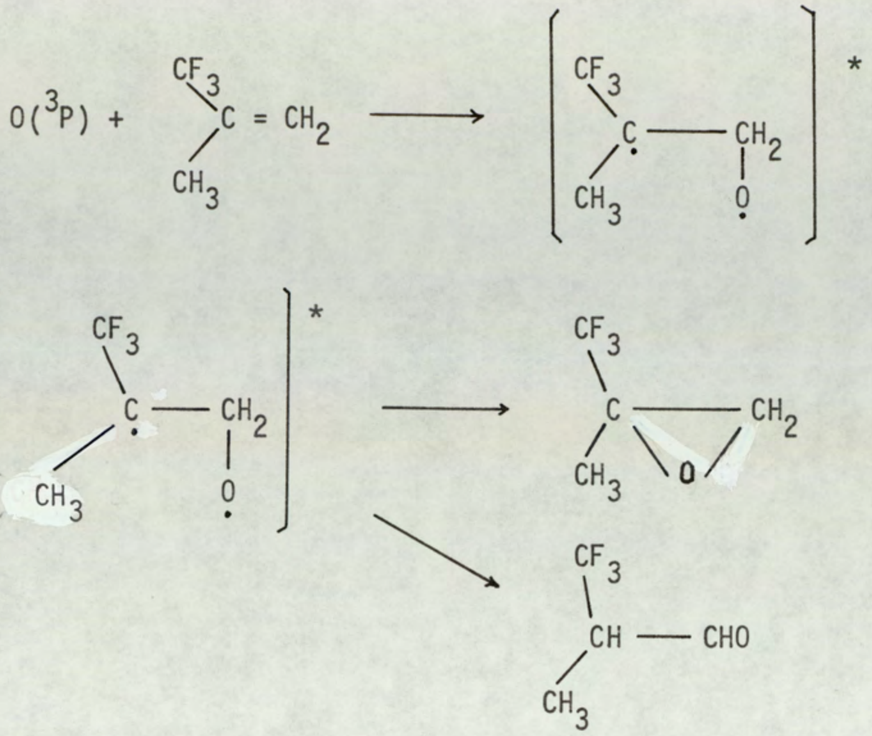
The reaction products of halogenated 1,1-difluoroethylene was carbonyl fluoride

$$CF_2 = CXY + O(^3P) \longrightarrow CF_2O + CXY$$

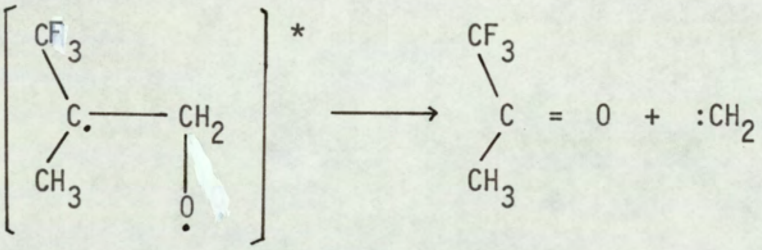
Some partially fluorinated olefins behaved much more like their corresponding unsubstituted olefin than the perfluoro-olefins. The reaction products of oxygen atom with 2-trifluoromethylpropene(66) were found to be the epoxides and isomeric carbonyl compound. This mechanism can probably be applied to most partially fluorinated olefins but excluding those with fluorine substitution at the double bond. The olefins with a fully fluorinated double bond behave similarly to the perfluoro-olefins.

(b.1) Reaction of $O(^3P)$ with 2-trifluoromethyl propene

Moss and Jennings(66) have studied this reaction in detail and found that the products were the expected 2-trifluoro methylpropylene oxide and 2-trifluoromethyl propionaldehyde together with a small amount of 1,1,1-trifluoroacetone (1%). The mechanism proposed for this addition reaction was analogous to the one proposed by Cvetanovic for the reaction of $O(^3P)$ with unsubstituted olefins.



1,1,1-trifluoroacetone was probably formed by the elimination of CH_2 biradical.

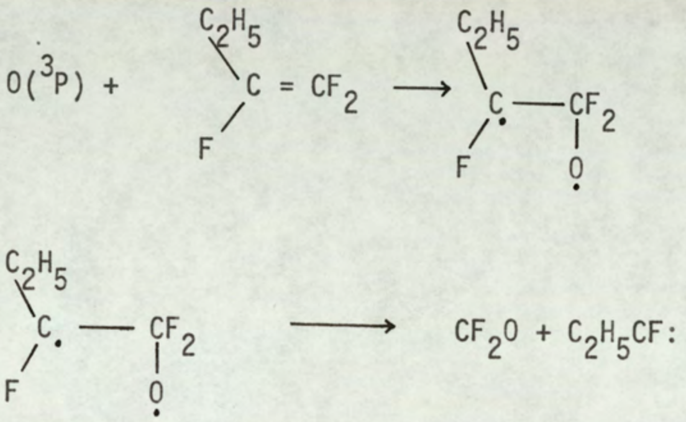


In a similar study with 2-fluoropropene, Morley(65) found that the major products 2-fluoropropene epoxide and 2-fluoropropionaldehyde accounted for 90% of the oxygen atoms at pressure higher than 500 mm.

From both reactions, 2-trifluoromethylpropene and 2-fluoropropene, the oxygen appears to add to the less substituted carbon atom to form a biradical which can then cyclise to form the epoxide or re-arrange to form the aldehyde.

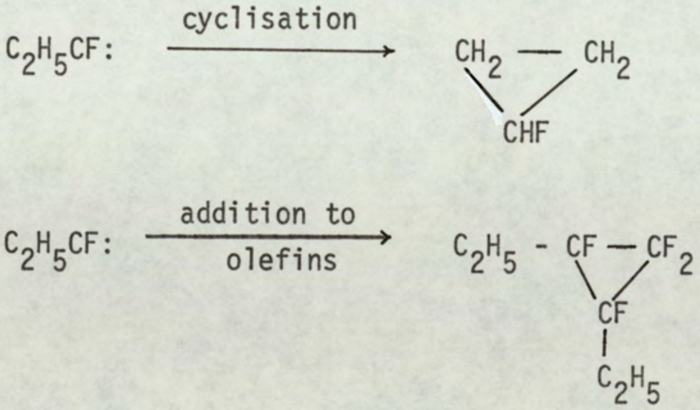
(b.2) Reaction of $O(^3P)$ with 1,1,2-trifluorobutene-1.

Jones(68) found that the major products of this reaction were cis-and trans-1-fluoropropene and carbonyl fluoride. Minor products were fluorocyclopropane, propionyl fluoride, ethane, ethylene and propane. No detectable amounts of epoxide were formed, the reaction scheme can be written as follows.



The quantum yield of carbonyl fluoride, ϕCF_2O, was 0.90 and Jones suggested that the carbene, $C_2H_5CF:$ formed from the above reaction was in the triplet state. The carbene can then undergo a variety of reactions. The three most important are

$$C_2H_5CF: \xrightarrow{\text{isomerization}} \text{cis-and trans-}CH_3CH = CHF$$



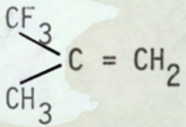
cis-and trans-$CH_3CH = CHF$ accounted for more than 95% of the products from the carbene.

c) Relative Rate Constants of the Reaction of $O(^3P)$ with Fluorinated Olefins

Moss and Jennings(69,70) have measured the relative rate constants of the reaction of oxygen atoms with the fluorinated ethylenes and partly fluorinated propylenes and butenes by using the nitrous oxide technique. Table 1.10 shows collected results for the relative rate constants.

TABLE 1.10

Relative Rate Constants for Reaction of $O(^3P)$ with Some Fluorinated Olefins at 25°C.(69,70)

Olefin	$k_{olefin}/k_{C_2H_4}$	$k_{olefin}/k_{hydrocarbon}$
$CH_2 = CH_2$	1.00	1.00
$CH_2 = CHF$	0.38	0.38
$CH_2 = CF_2$	0.22	0.22
cis-CHF=CHF	0.32	0.32
trans-CHF = CHF	0.54	0.54
$CF_2 = CHF$	0.57	0.57
$CF_2 = CF_2$	1.60	1.60
 $(CF_3)(CH_3)C = CH_2$	0.43	0.018
$CH_3CF = CH_2$	2.66	0.50
$CH_2F.CH = CH_2$	1.12	0.21
$CF_2CH = CH_2$	0.057	0.011
$CH_2F.CH_2CH = CH_2$	3.30	0.58
$CH_3CH_2CF = CF_3$	5.30	0.93
$CH_3CH = CF_2$	2.40	0.45

Note: k(hydrocarbon) refers to the rate constant for the compound obtained by replacing all the fluorine atoms by hydrogen.

The results in Table 1.10 show that the rate of addition of oxygen atom toward the fluoro-olefins is decreased progressively with increasing fluorine atom in any position of the molecule. The only exception is that for C_2F_4, the rate constant is greater than the ethylene itself. This has been discussed in detail by Moss and Jennings(69,70) as follows: When a fluorine atom is introduced into an unsaturated molecule, fluorine exerts a strong withdrawing inductive effect ($-I\sigma$) and it also exerts a strong electrondonating mesomeric effect (+M). The spectroscopic evidence(14) leads to the conclusion that fluorine atoms are strongly electron-repelling ($+I_{\Pi}$) and weakly electron donating (+M). Fluorine attracts σ-electrons ($-I\sigma$) because of its high electronegativity resulting in the formation of C-F dipole which can attract other electron in the molecule. On the other hand, when fluorine is situated at carbon atom of the double bond, the fully occupied 2p orbitals of the fluorine have Π symmetry and the electrons in these orbitals will repel the Π-electrons i.e. they will give rise to a ($+I_{\Pi}$) effect.

The combined effects of the $-I_{\sigma}$, $+I_{\Pi}$ and +M effects will lead to a <u>reduction</u> in the electron density at the fluorinated carbon atom but to an increase in electron density of the double bond. A possible explanation of the oxygen atom results is that the $-I_\sigma$ effect falls off with increasing fluorine substitution whereas the mesomeric and $+I_\Pi$ persist producing an overall enrichment of the Π-electron system of the fully fluorinated ethylene. This may explain why tetrafluoroethylene reacts with oxygen atoms faster than ethylene itself. The above explanation could be applied to the similar trend observed for the other fluoro-olefins.

1.4 THE ELECTROPHILIC CHARACTER OF OXYGEN ATOMS

Cvetanovic(21,49) has found that the oxygen atoms exhibit electrophilic character. The results for the series of unsaturated olefins and fluorinated olefins demonstrate the strong electrophilic nature of the oxygen atom. For the unsaturated olefins, the rate increases progressively as the number of alkyl groups attached to the carbon-carbon double bond increase, because alkyl groups are electron donating. The rates are in order:

$CH_2 = CH_2 < CH_3CH = CH_2 < CH_3CH = CH\ CH_3 < (CH_3)_2C = CH\ CH_3 <$

$(CH_3)_2\ C = (CH_3)_2$

On the other hand, fluorine atoms exert a strong electron withdrawing effect and the result is to decrease the electron density in the double bond. The rates are decreased progressively with increasing fluorine atoms in the molecule. The rates also depend on the position of fluorine substitution.

$CH_2 = CHCF_3 < CH_2 = C(CH_3)CF_3 < CH_2 = CHCH_2F < CH_2 = CFCH_3 < CH_3CH=CH_2$

This is found for all the fluorinated olefins except those with three or four atoms of fluorine substituted on the CC double bond, i.e. C_2F_4 and $CF_2 = CFCH_2CH_3$. This has been discussed in section 1.3.2.c.

Cvetanovic(71) compared the reaction of oxygen atom with olefins and the reaction of electrophilic reagent with the same olefins. He found that the reaction of oxygen atoms with olefins is closely related to the reaction of peracetic acid, bromine, dichlorocarbene and dibromocarbene with the corresponding olefins. It can be illustrated by a free energy plot of the logarithms of the rate constant of oxygen atoms with olefins against the logarithms of the rate constants of each of the above reagents with the same olefins. This plot is shown in Fig. 1.4, and based on the following theory.

The specific rate constant for any reaction is defined by transition state theory.

$$k = \frac{k^1 T}{h} \exp.(-\Delta G^{\dagger}/RT)$$

where k = specific rate constant

k^1 = Boltzmann's constant

h = Planck's constant

T = absolute temperature

$\Delta G^{\dagger}$ = the free energy of activation

$$\ln k = \ln (k^1 T/h) - G^{\dagger}/RT$$

If a series of reactions carry out at constant temperature the equation can be written as

$$\ln k_i = a_i + b_i G_i^{\dagger} \qquad (1)$$

where $a = \ln(k^1 T/h)$ = constant

$b = 1/RT$ = constant

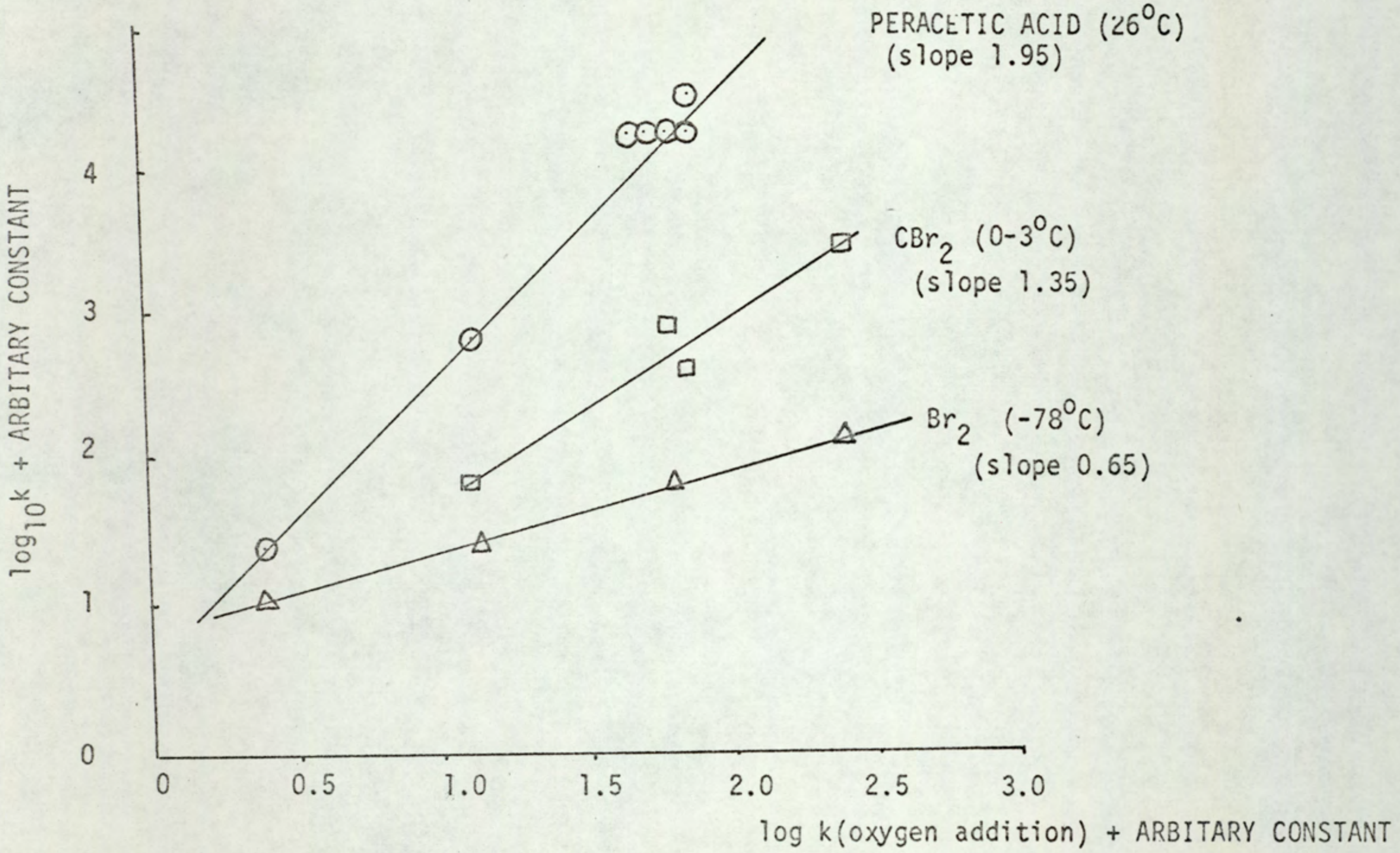


FIG. 1.4 FREE ENERGY PLOTS FOR BROMINE, PERACETIC ACID and OXYGEN ATOM REACTIONS WITH OLEFINS

(R.J. CVETANOVIC, J.Chem.Phys., <u>30</u>, (1959)) the subscripts i represent the reaction of the number of the series with a particular reagent (e.g. O^3P).

The equation of the reactions of the same series with a different reagent may be written the same as equation (1) at constant temperature.

$$\ln k_j = a_j + b_j \, \Delta G_j^{\dagger} \qquad (2)$$

From equations (1) and (2), if we plot ln(k) for peracetic acid, bromine, dibromocarbene reactions with olefins against ln k for oxygen atoms, and a linear relationship is observed then the free energy of activation must be related by

$$\Delta G_j = d + n \, \Delta G_i^{\dagger} \qquad (3)$$

(n and d are constants)

Equation (3) showed that there must be a linear free energy relationship between the reaction of oxygen atoms with olefins and the other three reactants. This suggests that the two series of reactions are related. Since peracetic acid, bromine and dibromocarbene are electrophilic reagents, Cvetanovic concludes that oxygen atoms must have an electrophilic character.

Another argument pointing to the electrophilic character of oxygen atoms is the approximate correlation between the ionization potential of an olefin and the rate of oxygen atom reaction with that olefin. Cvetanovic(71) has observed that the reactivity of oxygen atom to olefin increases with decreasing the ionization potential. He also showed that the other physical properties correlate well with the logarithm of the rate constant of oxygen atom with olefin. This relationship is similar to that observed with the free energy plot.

$$E_o^n - E_o^a = RTS_{ex}\ (E_{ex}^n - E_{ex}^a)$$

for spectroscopic excitation energies.

$$E_o^n - E_o^a = RTS_I\ (I^n - I^a)$$

for ionization potentials

$$E_o^n - E_o^a = RTS_h\ (\Delta H_h^n - \Delta H_h^a)$$

for heat of hydrogenation

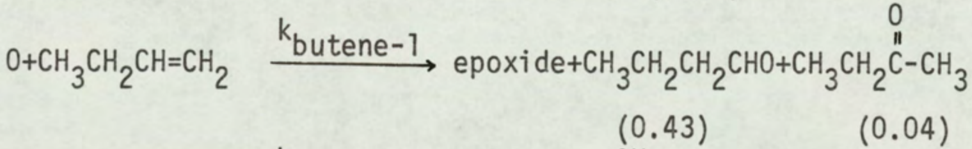
where S represents the slope of the plots of log k against value of the measured physical property. E_o^n and E_o^a represent the activation energy of oxygen atom react with n^{th} and a^{th} olefin respectively. These linear relationships were observed due to a constant "A" factor for the series of olefin reactions.

1.5 THE NATURE OF THE TRANSITION STATE

The nature of the transition state has been discussed by Cvetanovic(49) who suggests that the rate of addition of oxygen atom to olefins and the position of addition are not controlled by the same factors. If we consider the rate of the following addition reactions:

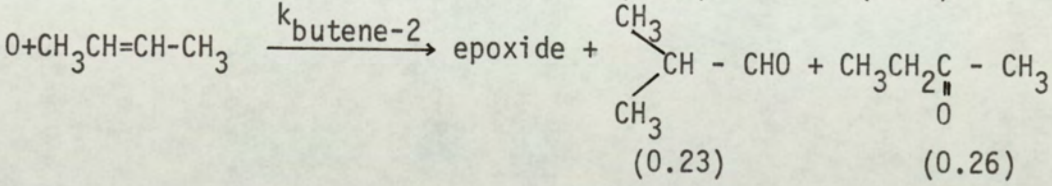
1. $$O + CH_3\ CH = CH_2 \xrightarrow{k_{propylene}} \text{epoxide} + \underset{(0.50)}{CH_3CH_2CHO}$$

2.



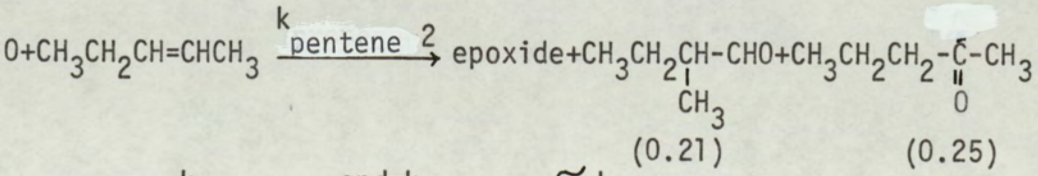
$$O+CH_3CH_2CH=CH_2 \xrightarrow{k_{butene-1}} \text{epoxide}+\underset{(0.43)}{CH_3CH_2CH_2CHO}+\underset{(0.04)}{CH_3CH_2\overset{O}{\overset{\|}{C}}-CH_3}$$

3.



$$O+CH_3CH=CH-CH_3 \xrightarrow{k_{butene-2}} \text{epoxide} + \underset{(0.23)}{\begin{array}{l}CH_3\\ \quad\ CH-CHO\\ CH_3\end{array}} + \underset{(0.26)}{CH_3CH_2\underset{O}{\underset{\|}{C}} - CH_3}$$

4.



$$O+CH_3CH_2CH=CHCH_3 \xrightarrow{k_{pentene\ 2}} \text{epoxide}+\underset{(0.21)}{CH_3CH_2\underset{CH_3}{\underset{|}{C}}H-CHO}+\underset{(0.25)}{CH_3CH_2CH_2-\underset{O}{\underset{\|}{C}}-CH_3}$$

$k_{propylene} = k_{butene-1}$ and $k_{butene-2} \simeq k_{pentene-2}$

It would suggest that the reactivities of olefins toward oxygen atoms are the same with either methyl or alkyl group attached to the carbon-carbon double bond. (see the above reactions).

Considering the case of pentene-2, if the rate of addition and position of addition are determined by the same factors then approximately equal addition would be expected at both carbons of the double bond (as the methyl and ethyl groups contribute equally to the reactivity). This does not occur because Cvetanovic found that the position of addition is almost exclusively at the doubly bonded carbon atom attached to the methyl group, (as can be seen from the products formed from pentene-2.)

From the above evidence Cvetanovic has suggested that the initial interaction of the oxygen atom is with the double bond as a whole and the oxygen atom localises itself on one of the two carbon atoms of the double bond at a later stage. Furthermore he has suggested that the rate constants depend on the polarisibility of the double bond rather than the stability of the intermediates. Because of the electrophilic trend in the rates, he proposed that a Π-complex may actually occur with a partial charge transfer from the olefin to the attacking oxygen atoms.

1.6 THE REACTIONS OF METHYLENE AND FLUOROMETHYLENES

The existence of methylene was first observed by Norrish et al.(72) They investigated the photochemical decomposition of ketene(72) which the initial step was proposed as the rupture of the carbon-carbon double bond to yield methylene and carbon monoxide, followed by the attack of the methylene on ketene to yield ethylene and another molecule of carbon monoxide.

$$CH_2CO + h\nu \longrightarrow CH_2 + CO$$
$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO$$

Previously the thermal decomposition of methane between 700 and 800^oC had been studied by Kassel(73) who suggested methylene as an intermediate, formed by the reaction $CH_4 \longrightarrow CH_2 + H_2$. Furthermore he concluded that methylene was a comparatively inert substance. This conclusion conflicts with that of Doering et al.(74) that methylene is the most indiscriminate reagent in organic chemistry. Indeed reliable information about the reactivity, stability or the electronic ground state of methylene were not available until about 1950. More reliable results on the study of the reaction of methylene are obtained by the use of gas chromatography, which has made it possible to analyse and detect trace amount of compounds formed accurately.

1.6.1 Ground State of Methylene and Fluoromethylenes

Herzberg(75)(76) first showed that free methylene does exist in the gas phase in both singlet and triplet states, depending on the conditions of the experiment. He flashphotolyzed diazomethane in the presence of nitrogen(76)(500:1), the spectrum observed indicates the triplet state species. If the inert gas ratio is lower(75)(50-100:1), then the spectrum observed shows the singlet species. Using deuterated diazomethane and also C-13 substituted diazomethane proved that these spectra were due to a species containing two hydrogen atoms and one carbon, CH_2.

A number of chemical arguments have been advanced concerning the reactive electronic state of methylene. Earlier arguments made by Skell and Woodworth(77,78) suggested that the product formed from the reaction of methylene with cis-or trans-butene-2 in the gaseous or liquid phase is almost entirely cis-or trans-dimethyl cyclopropane respectively. These workers$^{(77-80)}$ claimed that this stereospecificity implied a singlet state for methylene under these conditions. Anet, et al.$^{(81)}$ have repeated the work of Skell and found that the reaction of methylene with butene-2 becomes less stereospecific as the amount of nitrogen present during the decomposition is increased. About the same time Frey$^{(82)}$ has reported that at high ratios of argon to cis-butene-2 the addition products formed are cis-and trans-1,2-dimethyl cyclopropane. It is also observed that the formation of trans-1,2-dimethyl cyclopropane is inhibited almost completely in the presence of small amount of molecular oxygen. Anet,et al.$^{(81)}$ and Frey$^{(82)}$ interpreted their results in the following manner. Methylene initially produced in the singlet state and thus gives rise to reactions which are almost entirely stereospecific as the two new bonds may be formed simultaneously$^{(78)}$. When a large excess of inert gas is present, methylene undergoes deactivation to a triplet state after many collisions with an inert gas. From this evidence, it has been concluded that the triplet state is the ground state. Recent electron-spin resonance work of Bernheim et al.$^{(83)}$ and Wasserman et al.$^{(84)}$ confirms that the ground state of CH_2 is indeed triplet.

Powell and Lide$^{(87)}$ have detected the microwave spectrum of CF_2 by using the fast-flow microwave spectrometer. Their results lead to the conclusion that the singlet state is the ground state. Recently Tyerman$^{(85,86)}$ has studied the flash photolysis of $C_2F_4 + NO_2 + N_2$ mixtures. It has been found by kinetic spectroscopy that ground state of CF_2 is the singlet state.

A spectrum of the CHF free radical has been found by Merer and Travis(88) in the flash photolysis of $HCFBr_2$. The observed spectrum is a singlet spectrum. Jacon and Milligan(89) studied the infra-red spectrum of CHF free radical and concluded that the singlet is the ground state of CHF. The chemical study by Tang and Rowland(118) suggests that the ground state of CHF is indeed singlet.

1.6.2 Structures of Methylene and Fluoromethylenes

There has been a great deal of discussion on the question of whether methylene is linear or bent. When Herzberg and co-workers(75,76) first identified methylene by flash photolysis they interpreted their spectrum as a linear triplet state. Recent epectron-spin resonance work on CH_2 by Berheim, Bernard, Wang, Wood and Skell(83) and Wasserman, Yager and Kuck(84), as well as theoretical calculations by Harrison and Allen(90) and Bender and Schaefer(91) suggest strongly that CH_2 is bent in its triplet ground state.

Recently, Harrison(92) made a theoretical study of the electronic structures of CH_2, CHF and CF_2. The results of this study may be represented by the following diagrams.

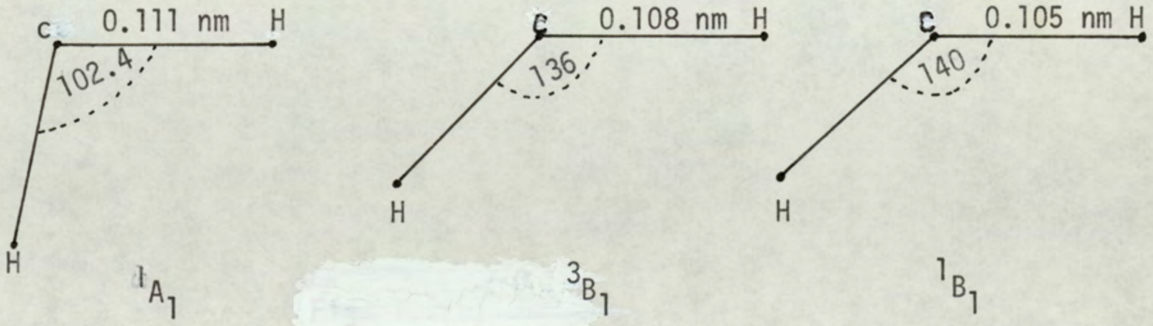
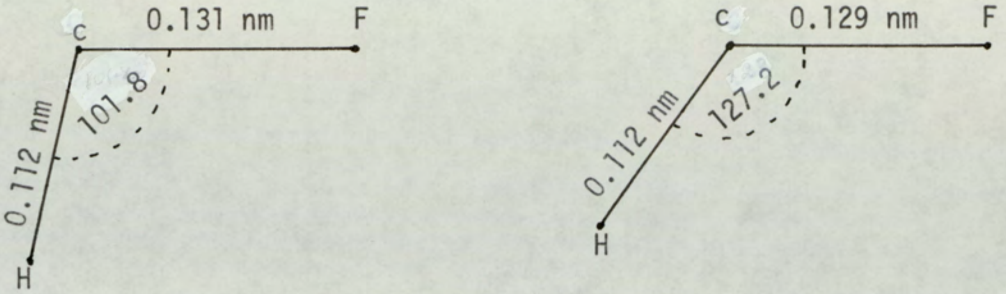
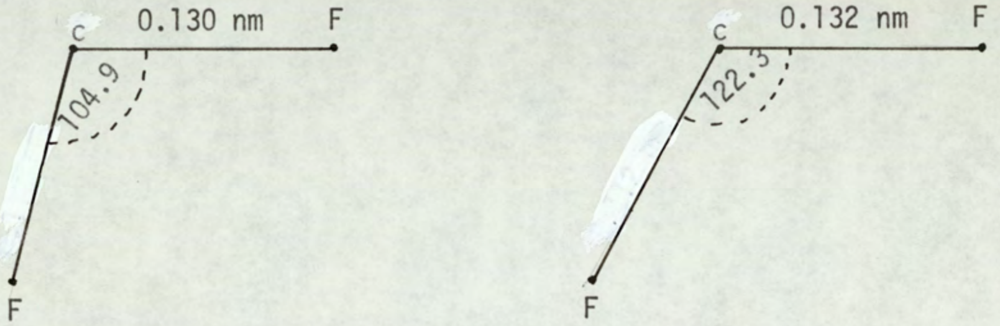


Fig. 1.5a. CH_2



'A'　'A"'

Fig. 1.5(b) CHF



$^1A_1$　$^1B_1$

Fig. 1.5(c) CF_2

Furthermore, Harrison predicted that in CF_2 the $^3B_1$ is 163.0 kJ mole^{-1} above the $^1A_1$ state, while in CHF the $^1A^1$ and $^3A^1$ are separated by a very small energy ($\sim$ 5 kJ mole^{-1}). Harrison's data indicated that in CH_2 the $^3B_1$ separate from the $^1A_1$ state by 100 kJ mole^{-1}. However, the result of CH_2 disagrees with recent experimental results of Carr et al.(120) which indicate a separation of 4.2 - 8.4 kJ mole^{-1}. Further work on CH_2 is needed to clarify this problem.

1.6.3 Methods of Production of Methylene and Fluoromethylenes

a) Photolysis of Ketene

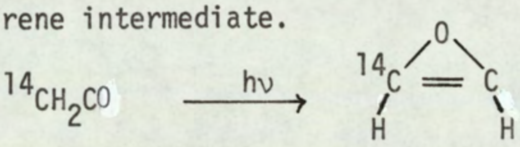
In 1933, Norrish and co-workers(72) found that the photolysis of ketene yielded methylene. Since then, this reaction has received much attention(93-97). In 1964, Simons and Rabinovitch(98) showed that both singlet and triplet methylenes are produced when ketene is excited by radiation of 313.0 nm. It has been shown by several authors(99-101) that the ratio of singlet to triplet CH_2 produced in the photolysis of ketene is wavelength dependent. The ratio of triplet methylene increase with increasing wavelength. The primary process of this reaction is

$$CH_2CO + h\nu \longrightarrow CH_2 + CO$$

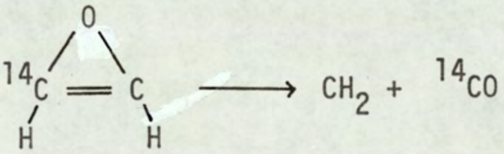
then

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO$$

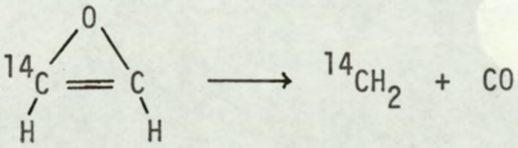
Ressell and Rowland(97) found that the photolysis of $^{14}CH_2CO$ showed a pressure-dependent yield of ^{14}CO. This indicates that the reaction involves the oxirene intermediate.



This intermediate can then undergo the decomposition either



or



after rearrangement.

Rowland et al.(112) re-investigated the photolysis of $^{14}CH_2CO$ and found that $^{14}CH_2CO$ rearranged to $CH_2{}^{14}CO$ during direct photolysis, this evidence supports strongly that the reaction involves the oxirene intermediate.

b) Photolysis of Diazomethane

The photolysis of diazomethane was first examined by Norrish and Kirkbride(102), who found that methylene was formed in the primary step.

$$CH_2N_2 + h\nu \longrightarrow CH_2 + N_2$$

followed by $$CH_2N_2 + CH_2 \longrightarrow C_2H_4 + N_2$$

Since then, the photolysis of diazomethane has been used as a source of methylene by a number of workers(101,103). Both singlet and triplet methylene were produced by this reaction. Voisey(101) has concluded that triplet methylene is formed from singlet methylene by collisional process. Recently, Taylor and Simons(104) studied the photolysis of diazomethane/cis-butene-2/ethylene mixture at 366.0 and 435.8 nm. They found that the proportion of ground triplet state methylene produced in the primary process is wavelength independent. Photolysis of difluorodiazirine (CF_2N_2) is used as a source of difluoromethylene(CF_2).

c) Mercury Photosensitized Decomposition of Ketene

The mercury photosensitized decomposition of ketene was believed(105) to be only a source of triplet methylene. Avery and Cvetanovic(94) and Frey and Walsh(106) reinvestigated this reaction and their results led to the conclusion that methylene resulting from this reaction appears to be entirely triplet methylene. The primary process is

$$Hg(^3P_1) + CH_2CO \longrightarrow {}^3CH_2 + CO + Hg(^1So)$$

However, a few per cent of singlet methylene is also formed by this reaction. They suggested two alternative mechanisms.

$$CH_2CO + Hg(^3P_1) \longrightarrow {}^1CH_2 + CO + Hg(^1So)$$

$${}^3CH_2{}^* + M \longrightarrow {}^1CH_2 + M$$

d) Tang and Rowland(118) generated CTF by using the method of recoil tritium reaction. The species CTF was formed by the unimolecular decomposition of excited $CHTF_2{}^*$, which was itself formed by energetic tritium atom reactions with CH_2F_2.

The basic sequence of reactions with CH_2F_2 is

$$T^* + CH_2F_2 \longrightarrow CHTF_2^* + H$$

$$CHTF_2^* \longrightarrow CTF + HF$$

1.6.4 Reactions of Methylene and Fluoromethylenes

The conversion of singlet methylene to triplet methylene is now well established.

$$CH_2(\uparrow\downarrow) + M \longrightarrow CH_2(\uparrow\uparrow) + M$$

It was pointed out(100,101) that the conversion of $^1CH_2$ to $^3CH_2$ depends upon the chemical source of methylene, the wavelength of the irradiating light, the total pressure of the reaction mixture and the presence and nature of any other gases. The flash photolysis of ketene(103) indicates that the only primary process is

$$CH_2CO + h\nu \longrightarrow {}^1CH_2 + CO$$

followed by

$$^1CH_2 + M \longrightarrow {}^3CH_2 + M$$

Oxygen scavenger was used to remove triplet methylene in small enough proportions to minimize any scavenging of singlet methylene. The two oxidation reactions for $^3CH_2$ with O_2 may be proposed as follows:

$$^3CH_2 + O_2 \longrightarrow CO_2 + H_2 \text{ (or 2H)}$$

$$^3CH_2 + O_2 \longrightarrow CO + H_2O \text{ (or H + OH)}$$

Rowland et al.(112) have recently suggested that the oxidation of singlet methylene by O_2 leads to the same reaction products in essentially the same ratios as with the triplet experiments, but with a less relative efficiency of reaction by factor of 10^{-1}. It has been suggested that the $^1CH_2$ is collisionally converted to $^3CH_2$ by collision with molecular oxygen, and the oxidation products are then formed by subsequent reaction of $^3CH_2$ with another molecule of oxygen.

The absolute and relative rate constants for the reaction of $^{1}CH_2 + M \longrightarrow {}^{3}CH_2 + M$, with various M are listed in the Table 1.11.

TABLE 1.11

Absolute and Relative Rate constants for the reaction $^{1}CH_2 + M \rightarrow {}^{3}CH_2 + M$

Absolute k_1 $\quad ^{1}CH_2 + M \longrightarrow {}^{3}CH_2 + M \qquad (1)$

M	CH_4	He	Ar	N_2	
k_1	9.6×10^{11}	1.8×10^{11}	4.0×10^{11}	5.4×10^{11}	all at 25°C

Relative k_1

(a) relative to $^{1}CH_2 + CH_2CO \longrightarrow CH_4 + CO$

M	He	Ar	Kr	Xe	N_2	CF_4
k_1/k_a	0.018	0.014	0.033	0.074	0.052	0.047

(b) relative to $^{1}CH_2 + C_3H_8 \rightarrow n\text{-}C_4H_{10} + i\text{-}C_4H_{10}$

M	He	Ar	Xe	N_2	CF_4
k_1/k_b	0.009	0.025	0.05	0.037	0.047

(c) relative to $^{1}CH_2 + CH_2N_2 \rightarrow C_2H_4 + N_2$

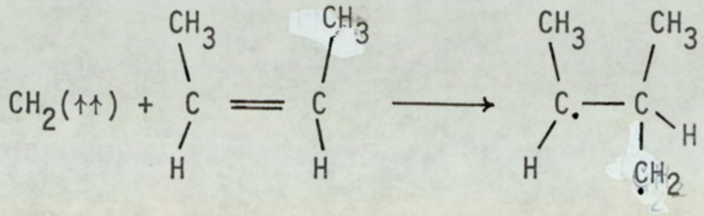
Temp.(°C)	240	260	383
k_1/k_c	0.0021	0.0024	0.0023

Note: Units of k_1 are $cm^3\ mol^{-1}\ sec^{-1}$

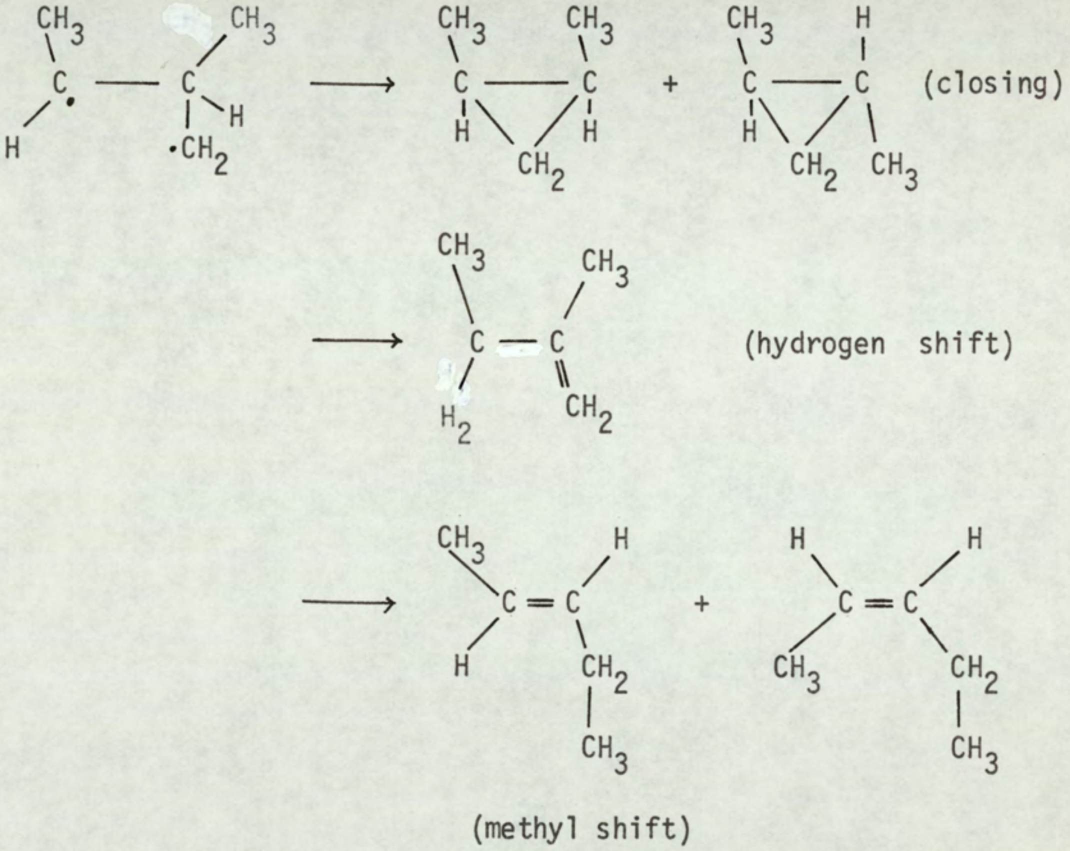
Taken from Whittle, E. MTP International Review of Science Chemical Kinetics, 9, 98 (1972)

The above results show that the reactivity of $^{1}CH_2$ toward various M is relatively slow compared with the other reactions of $^{1}CH_2$. These results agree reasonably well with the few values which have previously been determined(107,108) and with values which estimated from data in the literature(82,109).

It is generally known that triplet methylene adds to the olefins nonstereospecifically. Starting with cis-butene-2, a mixture of cis- and trans-1,2-dimethyl-cyclopropane are obtained as addition products.



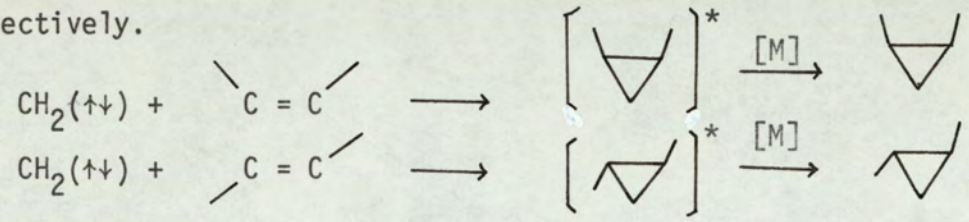
This biradical intermediate then undergoes



The same pattern is observed in the case of trans-butene-2.

The difference in ratio of the addition products from cis- and trans-butene-2 suggest strongly that this biradical must be formed as an intermediate. Rotation around original double bond of this biradical intermediate lead to loss of the stereospecific character of the original olefin.

It is usually assumed that triplet methylene abstract hydrogen atom from the substrate molecule (RH). The occurrence of this type of abstraction reactions has been postulated to explain the production of ethane and n-butane in systems involving the reaction of methylene with ethylene(110). Recent work of Frey and Walsh(113) confirms that $^3CH_2$ reacts only by abstraction in the reaction of $^3CH_2$ with neopentane. Unlike $^3CH_2$, the addition reaction of $^1CH_2$ to olefin appears to retain the stereospecific character of the olefin. Starting with cis- or trans-butene-2, the addition product is almost entirely cis- or trans-1,2-dimethylcyclopropane respectively.



It is known that singlet methylene insert into a C-H bond. The simplet system involving the insertion reaction is that of methylene with methane.

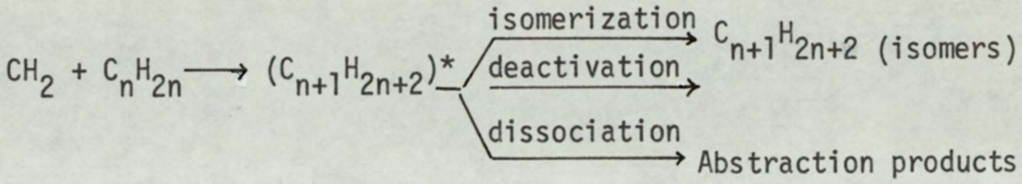
$$CH_2 + CH_4 \longrightarrow C_2H_6$$

This result was confirmed by investigation of the system CH_2N_2/CD_4.

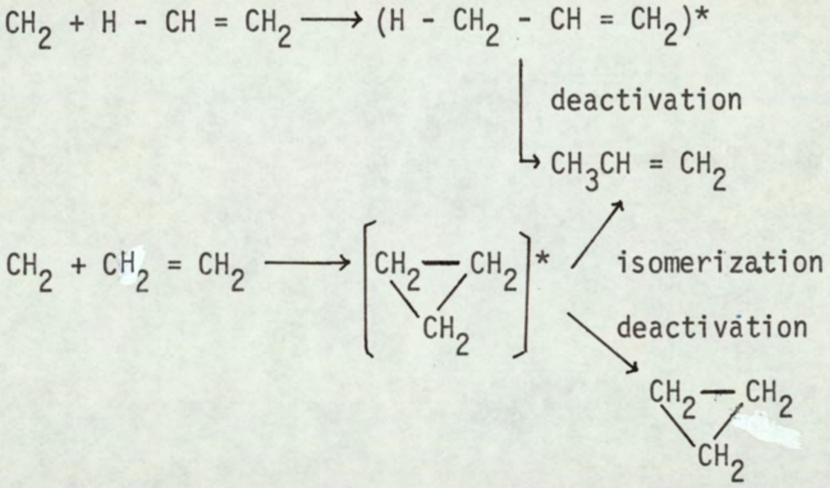
$$CH_2 + CD_4 \longrightarrow (CH_2D.CD_3)^* \xrightarrow{[M]} CH_2D.CD_3$$

Now it becomes clear that CH_2 exists in both singlet and triplet states which have entirely different reactivities. Singlet methylene has been shown to add stereospecifically to olefins and to insert into carbon-hydrogen bonds. Triplet methylene, on the other hand, adds to olefins nonstereospecifically and is believed to abstract hydrogen atoms. These distinctions have been used as diagnostic tests for the two spin states.

The reactions of methylene are highly exothermic and lead to vibrationally "hot" adducts which may undergo isomerization, collisional deactivation, or dissociation. The reaction of methylene with olefins may be written by a general diagramatic scheme as follows:



For example, the major products of the reaction of methylene and ethylene are propylene and cyclopropane. It is known that propylene is formed by direct insertion of CH_2 to C-H bond as well as by the structural isomerization of excited cyclopropane. This may be explained by the following diagrams.

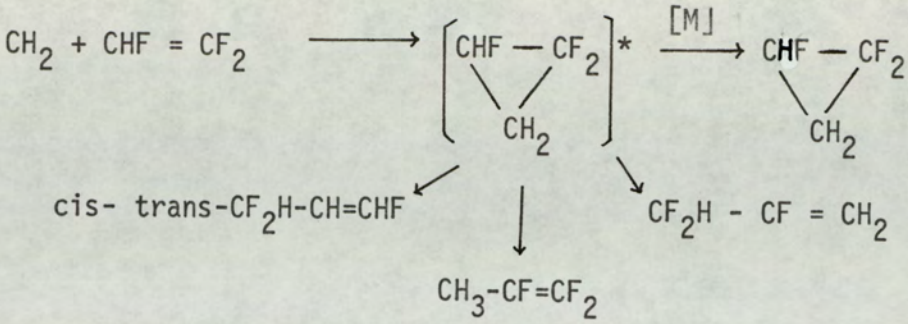


The reactions of methylene with mono-, 1,1-di- and tri-fluoroethylene have been studied by Casas, Kerr and Trotman-Dickenson(114). They also interpreted their results in terms of initial insertion of methylene to C-H bonds and addition to the double bond.

$$CH_2CO + h\nu \longrightarrow CH_2 + CO$$

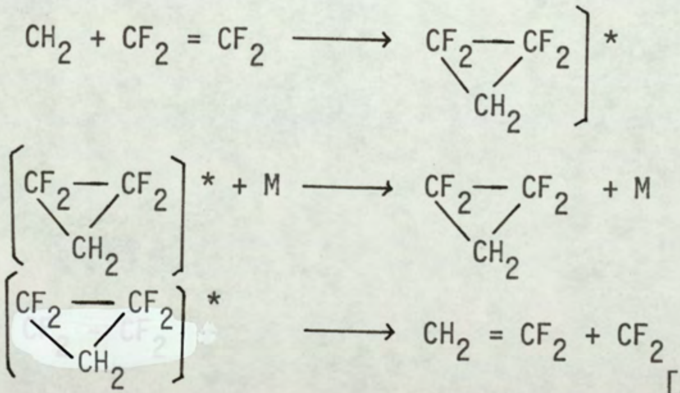
The reaction of methylene with trifluoroethylene is shown to follow the path:

$$CH_2 + H - CF = CF_2 \longrightarrow CH_3 - CF = CF_2$$



The product composition depends on the pressure, temperature and methylene energy (therefore, the methylene source).

The reaction of methylene with tetrafluoroethylene was first studied by Crzybowska et al.(115). In 1968, Craig et al.(116) reinvestigated this reaction and found that perfluorocyclopropane, 1,1-difluoroethylene and 1,1,2,2-tetrafluorocyclopropane were formed as the major products. No significant quantity of fluoropropene was found. This suggests that only elimination of difluoromethylene occurred rather than the isomerization to fluoropropene by hydrogen atom migration. The probable mechanism is



$$CF_2 + CF_2 = CF_2 \longrightarrow (\text{cyclo-}C_3F_6)^* \xrightarrow{[M]} \text{cyclo-}C_3F_6 + M$$

1.6.5 Relative Rate Constants for Reaction of Methylene and Fluoromethylenes with Olefins and Fluorinated Olefins

a) Relative Rate Constants for Reactions of CH_2 with Olefins and Fluorinated Olefins

A collection of relative rates constants of singlet and triplet methylenes with a series of olefins compared with atoms and radical species with olefins are shown in Table 1.14. The relative reactivities of fluoroethylene with atoms and radicals are shown below.

TABLE 1.12

Relative Reactivities of Fluoroethylene with Atoms and Radicals

Olefin	CH_2	$O(^3P)$	H		$Hg(^3P)$	CF_3	I.P.
	(25°C)	(25°C)	(25°C)	(25°C)		(164°C)	(ev)
$CH_2 = CH_2$	1.00	1.00	1.00	1.00	1.00	1.00	10.66
$CH_2 = CHF$	0.60	0.38	0.51	0.79	0.79	0.79	10.45
$CH_2 = CF_2$	0.33	0.22	0.42	1.45	0.62	0.62	10.45
cis-CHF=CHF	-	0.32	0.07	0.70	-	-	-
trans-CHF=CHF	-	0.54	0.10	1.15	-	-	-
$CF_2 = CHF$	0.16	0.57	0.07	1.65	0.41	0.41	10.33
$CF_2 = CF_2$	0.10	1.60	0.09	1.70	0.21	0.21	10.12
Reference	114	70	121	122	123	124	125

b) Relative Rate Constants for the Reactions of CF_2 + Olefins

Mitsch and Rodgers(117) have determined the relative rates of addition of difluoromethylene (CF_2) to a series of methyl-substituted olefins. The photolysis of difluorodiazirine has been used as a source of difluoromethylene. Their results are shown in Table 1.13.

It is shown that the relative rates of difluoromethylene with olefins is markedly influenced by structural variation in the olefin. The rate of CF_2 addition to olefins increased progressively with increasing methyl group in the double bond of olefins. The results show that tetramethylethylene reacts 724 times faster than propylene at 36°C. This may indicate that difluoromethylene acts as electrophilic reagents.

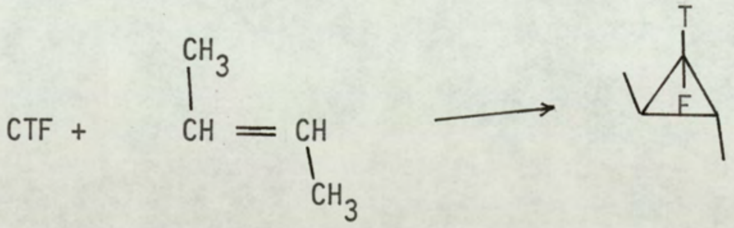
TABLE 1.13

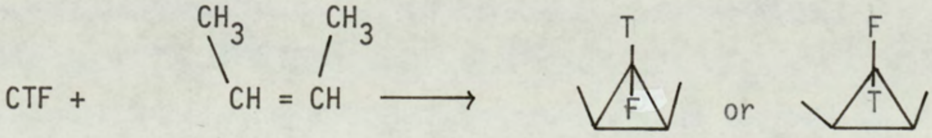
Relative rate constants of the reactions of CF_2 + olefins

Olefin	Relative Rates		E - E_{TME}	A/A_{TME} Pre-exponential factor
	36°	91°	kJ mole^{-1}	
$Me_2C = CMe_2$	13.1	6.46	0.00 ± 0.2	1.00 ± 0.3
$Me_2C = CHMe$	3.53	2.16	3.64 ± 0.3	1.11 ± 0.3
$Me_2C = CH_2$	1.00	1.00	12.02 ± 0.2	8.41 ± 2.0
$CH_2=CH-CH=CH_2$	0.294	0.404	18.75 ± 0.2	15.1 ± 4
MeCH=CHMe(trans)	0.071	0.097	16.58 ± 0.3	3.6 ± 1.0
MeCH=CHMe(cis)	0.065	0.082	15.92 ± 0.3	2.47 ± 0.8
$MeCH = CH_2$	0.0181	0.0325	21.18 ± 0.2	7.64 ± 1.7
$EtCH = CH_2$	0.0105	0.0096	10.58 ± 0.2	0.047 ± 0.011

c) Reactions and Relative Rate Constants for CTF + Olefins

Tang and Rowland$^{(118)}$ found that the reaction of monofluoromethylene with eight hydrocarbon olefins yielded fluorocyclopropane, using the tritium lebelled methylene, CTF. It is observed that the addition of CTF to the double bond of either cis- or trans-butene-2 is more than 99% stereospecific.





It is also found that the product formed from this reaction is not affected by small amounts of molecular oxygen. This evidence suggests that the electronic state of CTF is singlet. Furthermore, Rowland et al (118) have concluded that the singlet CTF is the ground electronic state. (The singlet state of dihalocarbenes has already been established as the ground state(119)). It has also been observed that CTF does not insert into C-H bonds of olefins and no isomerization of excited fluorocyclopropane to the fluoropropenes has been found. It has been concluded that the addition of CTF to ethylene did not release sufficient energy to the product molecule to permit isomerization to the fluoropropenes.

Estimation of the relative reactivities of CTF toward a series of olefins in direct competition with ethylene have been made by Tang and Rowland(118). These results can be compared with the relative rate constants of singlet and triplet methylene and other atoms or radical species with olefins, as shown in Table 1.14.

TABLE 1.14

Comparison of the Relative Rates of Addition of Atoms and Radicals with a series of Olefins

Olefin	CTF	$^3CH_2$	$^1CH_2$	$O(^3P)$	H	CH_3	
	(22°C)	(25°C)	(25°C)	(25°C)	(25°C)	65°	180°
$CH_2 = CH_2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$CH_3CH = CH_2$	2.06	1.00	1.30	5.80	1.80	0.6	0.7
$C_2H_5CH = CH_2$	2.03	1.60	1.60	5.80	1.90	0.8	0.6
$(CH_3)_2C = CH_2$	3.73	2.90	2.00	25	4.40	1.1	1.1
cis-$CH_3CH=CHCH_3$	3.02	0.94	1.40	24	0.80	0.10	0.23
trans-$CH_3CH=CHCH_3$	3.90	0.89	1.40	28	1.10	0.20	0.33
$(CH_3)_2C = CHCH_3$	4.13	1.80	2.10	79	-	0.16	0.32
$(CH_3)_2C =C(CH_3)_2$	5.87	2.70	2.20	102	1.50	-	0.20
$CH_2= CHCH = CH_2$	-	19.0	3.90	24	8.7	59	12
Reference	118	126	126	53	127	128	129

It can be seen that both CTF and CH_2 are very much less electrophilic than oxygen atoms. On the other hand, CTF is more electrophilic in character than CH_2. Harrison$^{(92)}$ predicted that the electrophilicity should decrease along the series $CH_2 > CHF > CF_2$. The experimental results seem to disagree with his prediction. There is therefore a good reason for developing another new CHF source in order to see if there are any noticeable differences in reactivities and electrophilicity compared with CH_2.

CHAPTER TWO

EXPERIMENTAL SECTION

2.1 APPARATUS

The apparatus consisted of the following components described more fully later:

1. pumping system
2. main line and storage bulbs
3. greaseless manifold connecting (4),(5) and (6)
4. gas burette
5. reaction system with quartz reaction cell
6. analysis line for non-condensibles with Toepler pump gas burette
7. gas sampling valve connecting (5) to
8. gas chromatograph.

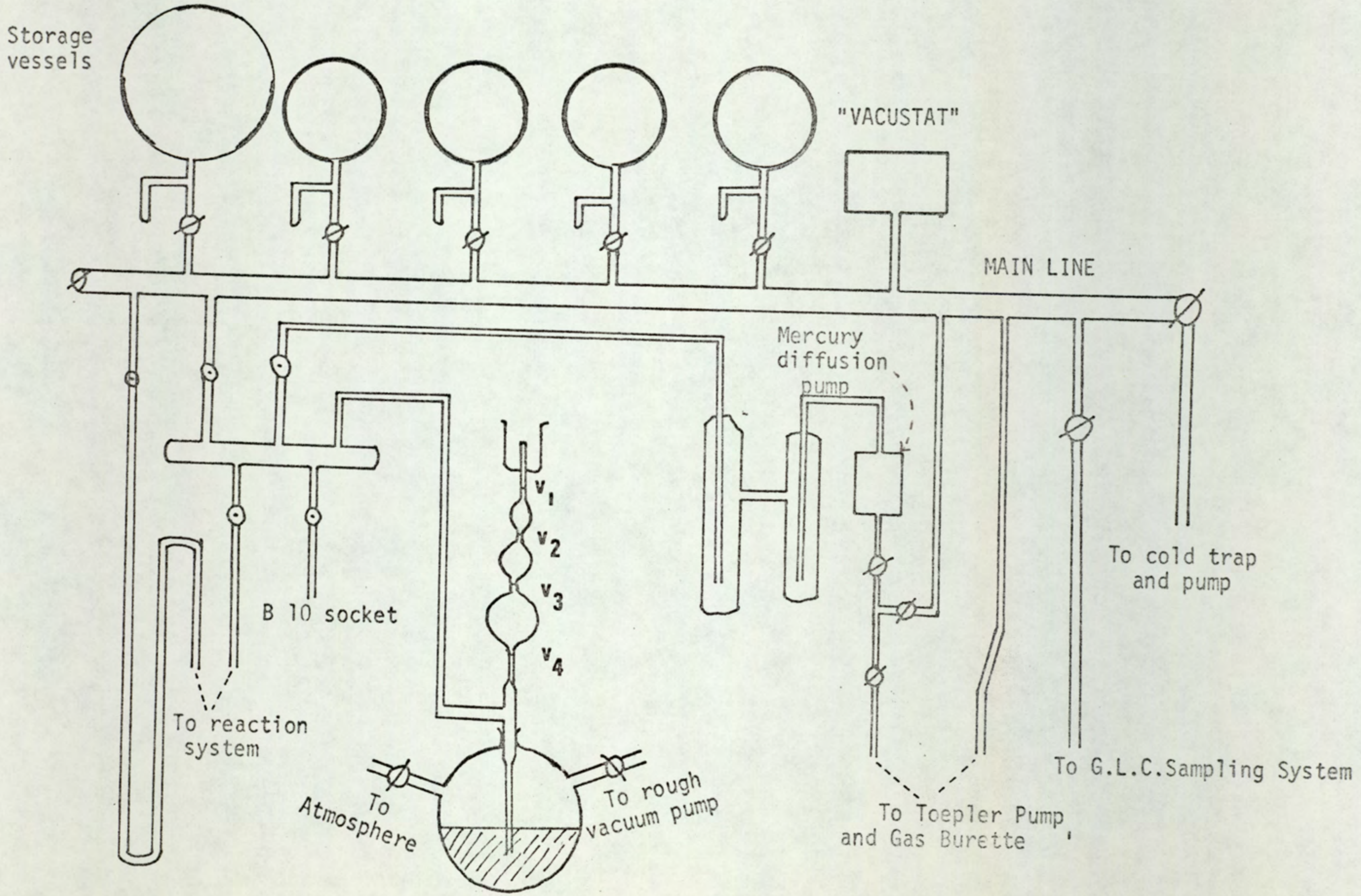
1. Pumping System

The pumping system consisted of a mercury diffusion pump (water cooled), backed by a rotary pump. Both of them were capable of evacuating the apparatus to less than 10^{-4} - 10^{-5} mm of Hg which was indicated by a "vacustat". A by-pass was connected to the diffusion pump so that large amounts of gas could be pumped out through the rotary pump without passing through the diffusion pump. The cold trap was surrounded by liquid nitrogen (-196°C) when the line was in use, in order to remove condensible gases before they entered the pump.

2. Main Line and Storage Bulbs

The main vacuum line was isolated from a cold trap and the pumping system by a greased tap. The storage bulbs were attached directly to the

Fig. 2.1 The Main Vacuum Line and Gas Burette



main line and isolated from it by greased taps. (see figure 2.1). These consisted of spherical glass bulbs, with cold fingers attached so that gas could be condensed into them. Four of the five storage bulbs were of 2 litres capacity and the other one was of 5 litres. One side of a mercury manometer was connected directly to the main line and isolated from it by a greased tap, the other side was connected to the reaction system. (figure 2.2). A mirror scale, graduated in millimetres was placed behind the mercury manometer so that the difference in mercury levels could be read accurately. The main line was calibrated using a standard fixed volume. The volume of the main line was 600 ml.

3. Greaseless Manifold

A greaseless manifold was attached to the main line by a greaseless tap (G. Springham & Co.) with viton A diaphram. All the other sections of the apparatus were connected to the main line via the manifold, and were isolated from the manifold by greaseless taps. This enabled gas to be transferred from one part of the apparatus to another, particularly from the main line to the gas burette and from the gas burette to the reaction system, without coming into contact with grease. (figure 2.1)

An inlet-outlet point, which terminated in a B10 socket, was connected to the greaseless manifold and isolated from it by a greaseless tap.

4. Gas Burette

The fixed-volume gas burette was attached to the greaseless manifold as shown in figure 2.1. Graduation marks were provided under each of the bulbs. The four bulbs were of different volume, and gas could be frozen into the finger at the top of the burette (the smallest bulb) by filling the reservoir with liquid nitrogen. A mirror scale, graduated in millimetres, was placed behind the straight limb (left hand limb in figure) of the burette. The pressure of gas in any of the bulbs could be determined accurately by measuring the height of the measuring level in the left-hand limb when the mercury level in the right hand limb was brought to the appropriate graduation mark, after the gas reached thermal equilibrium and the temperature measured. The zero was determined when the burette was evacuated. The mercury level was adjusted by means of the two side taps of the mercury reservoir. The tap on the left hand side could be opened to the atmosphere and the other tap was connected to the rough vacuum pump. All the bulbs of the gas burette were accurately calibrated by using the standard fixed volume of 5.09 ml, 33.3 ml and Boyle's Law. The calibrating gas used in this case was nitrous oxide. The gas burette volumes were 3.95, 18.26, 70.54 and 241.99 ml.

5. Reaction System with Quartz Reaction Cell

The all-glass system incorporated a cold trap, a circulating pump, a cylindrical quartz reaction cell, which was 10 cm long and 5 cm in diameter and a shallow pool of "clean mercury" in the U-bend at the base of the system as shown in figure 2.2. Outlets were provided to the greaseless manifold and main line, to a manometer and to the G.L.C. sampling system. All exits were closed by greaseless taps, excepting that to the manometer. The volume of the reaction system was calibrated, by using the standard fixed volume. The volume of the reaction system was 760 ml.

The circulating pump is shown in figure 2.2. It was constructed such that all surfaces exposed to the reactant gas were pyrex glass, except for the springs which were coated with polythene. The coil was

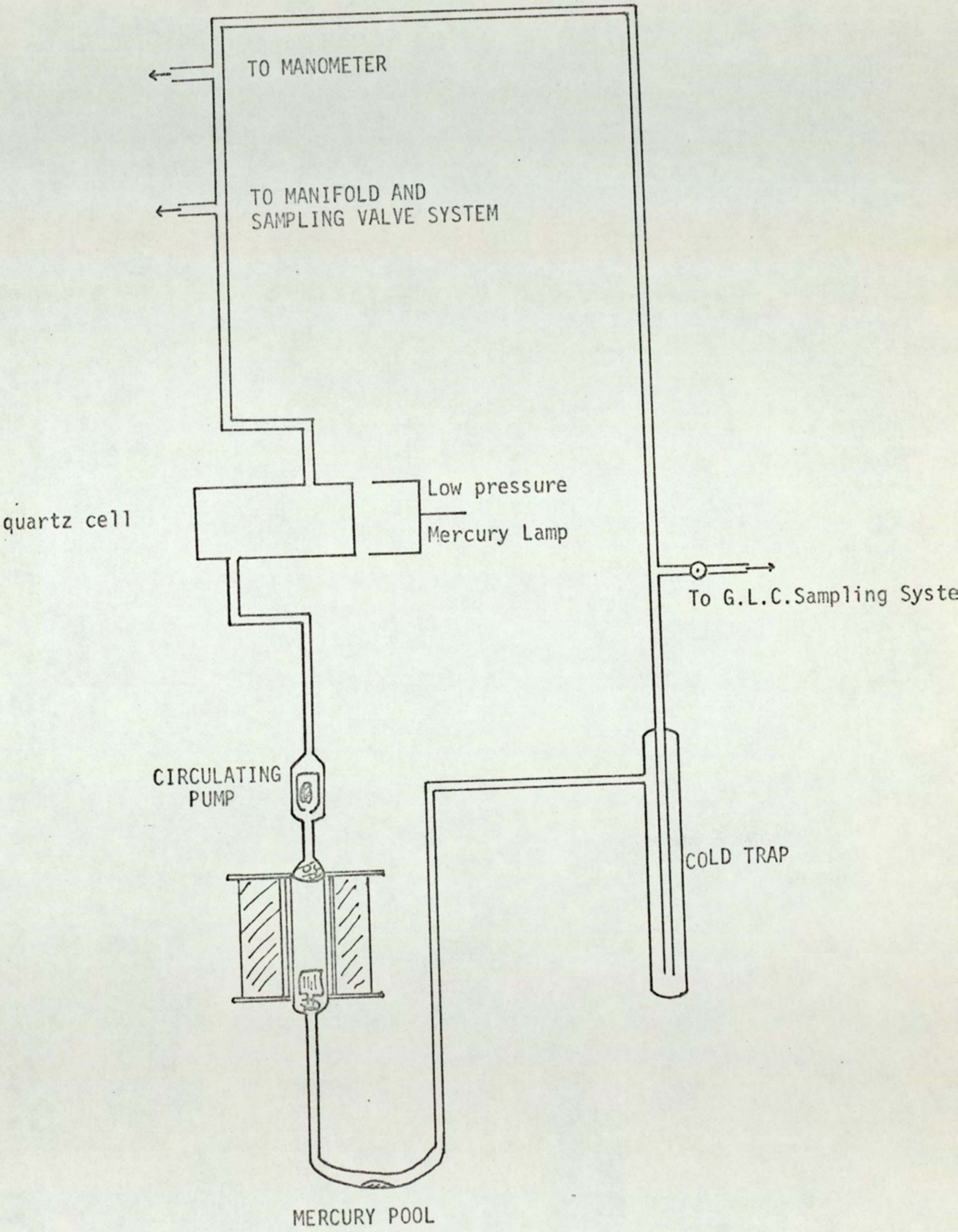


Fig. 2.2. Reaction System

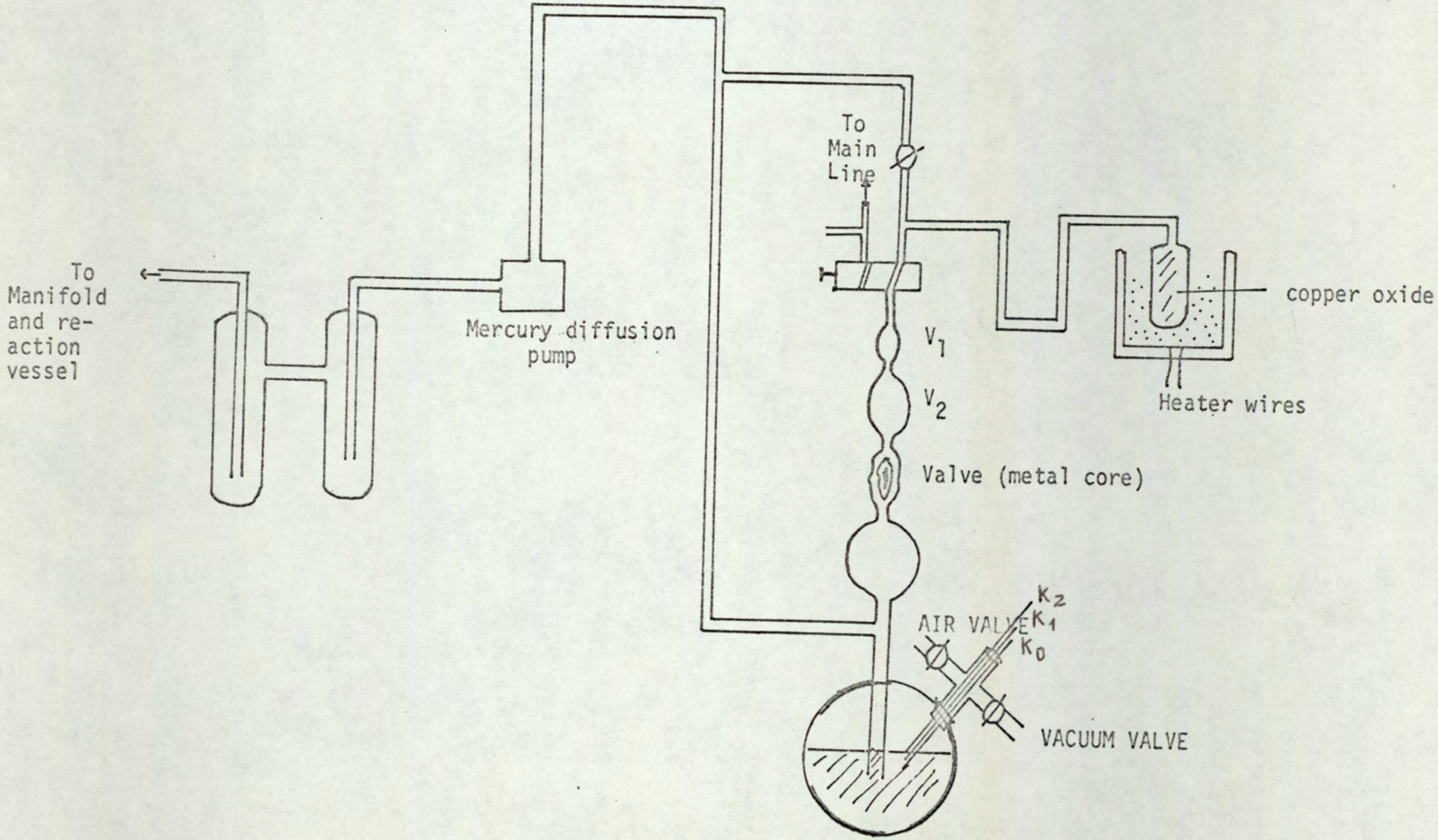
mounted on a brass former and consisted of approximately 5,000 turns of lacquered 22 gauge wire of total resistance 40 ohms. Pulsing of the mains voltage was achieved by means of a small electric motor, driving a cam, which was shaped in such a way that it made contact with a 10 amp microswitch in the mains supply line once every second. The pulsed magnetic field lifted the metal-cored piston up the glass cylinder, the piston falling back when the current to the coil was switched off. The glass cylinder and piston were protected by the springs as shown in figure 2.2. The metal-core valve at the top of the cylinder ensured one-way pumping and could be held open with a permanent magnet in order to pump out the reaction system.

The 253.7 nm radiation required for the mercury photosentisized decomposition of nitrous oxide to produce the ground state oxygen atoms, was provided by a Hanovia (type 752/68) low-pressure mercury spiral lamp. The power to the lamp was provided by the mains via a constant voltage transformer. Two lamps were placed about 9 cm from the opposite ends of the quartz reaction cell (but normally only one lamp was used). The lamp was housed in a cylindrical can, which acted as a support for the lamp and a callimator of the light.

6. The Gas Analysis System

The analysis system consisted of a combined automatic Toepler-pump and gas burette, contacted via two cold traps, to the greaseless manifold and again isolated from it by a greaseless tap. The system is shown in figure 2.3. A mercury diffusion pump greatly assisted transfer of gas from the reaction vessel to the gas burette. When the system was in use, the two cold traps were surrounded by liquid nitrogen, to prevent any condensible gases being purified over into the gas burette.

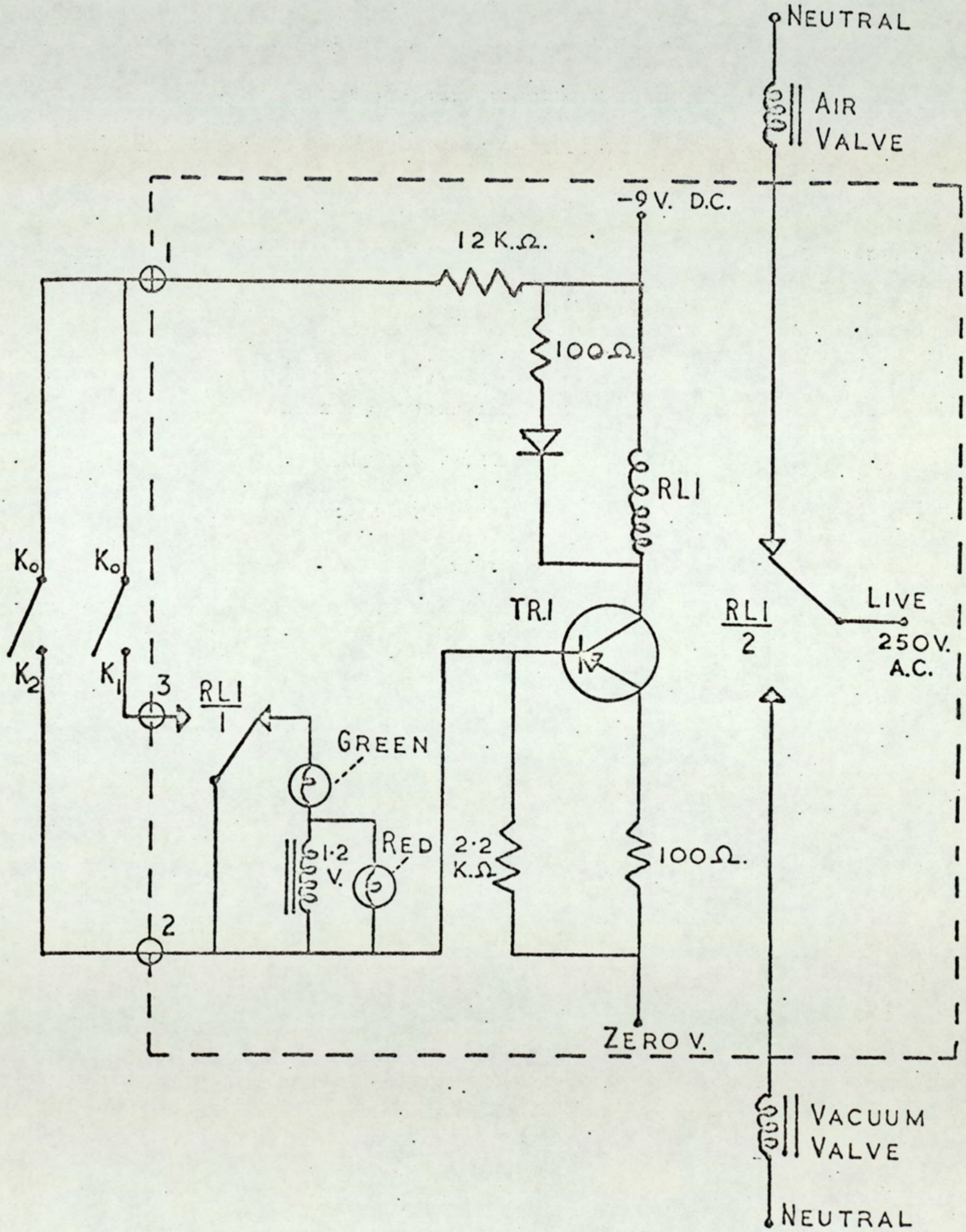
Fig.2.3 The Analysis System



The operation of raising and lowering the mercury, to trap the gas above the Toepler pump valve, (non-condensible gases) was automated. Contacts K_0, K_1 and K_2 were placed in the mercury reservoir as shown in figure 2.3 and the air inlet and rough vacuum were controlled by electro-magnetic valves. When the Toepler-pump power was switched off, the valves were normally open and the mercury level in the Toepler-pump gas burette could be controlled manually. The electro-magnet valves were operated in conjunction with a relay as shown in figure 2.4 and the sequence of events in one cycle of operation of the pump were as follows. With the mercury at its highest level in the reservoir, K_0 was in electrical contact with K_1 and K_2. When the power was switched on the air valve opened and the vacuum valve closed, allowing the mercury in the gas burette to rise. The mercury level in the reservoir dropped, and K_0/K_2 opened but had no effect since K_0/K_1 was closed. When the mercury has risen past the Toepler-pump valve on the high vacuum side, the mercury level in the reservoir dropped such that K_0/K_1 opened. At this stage the air valve was energised and it closed. The vacuum valve opened, allowing the mercury level in the reservoir to rise, making K_0/K_1 again. This again had no effect, because the relay switch on the low voltage side was in the open position. The mercury level in the high vacuum side dropped, leaving a mercury pool around the Toepler-pump valve, thus sealing off any gas above it. When K_0/K_2 made contact,the air valve opened, the vacuum valve closed and the cycle was repeated. The rate of rise and fall of the mercury was controlled by screw clips on the rubber connections to the electro-magnetic valves. The Toepler-pump valve had a metal-core, so that it could be raised by a permanent magnet for the purpose of pumping out the gas burette.

FIG. 2-4

AUTOMATIC TOEPLER PUMP CIRCUIT



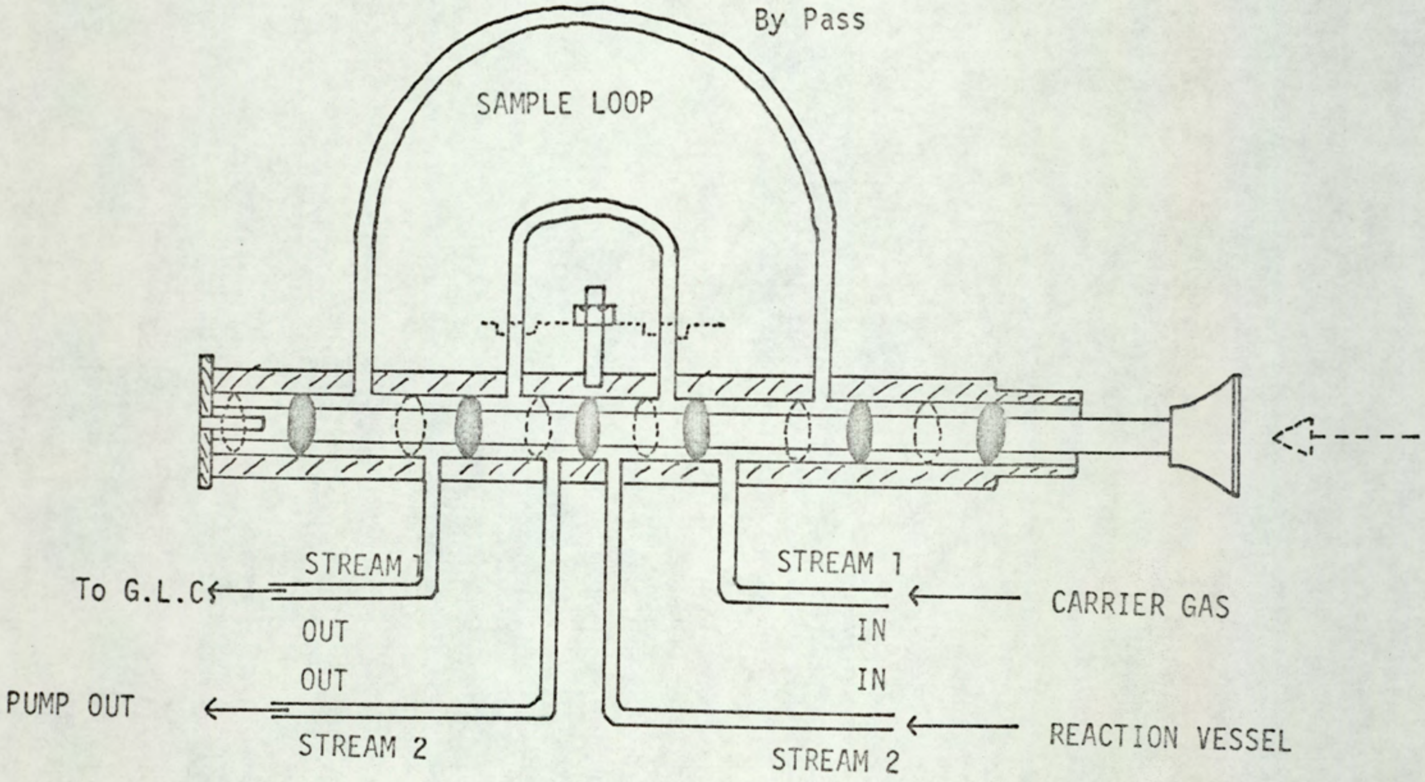
The copper oxide furnace was connected directly to the top of the Toepler-pump gas burette via a three-way tap. The non-condensible gas trapped above the Toepler-pump valve could be connected either to the outlet point which terminated in a B10 cone or it could be connected to the copper oxide furnace, as shown in figure 2.3. This consisted of a pyrex tube, packed with copper oxide wire, and preceded by a U-tube cold trap. The temperature of the furnace was controlled by a "variac" inserted into the voltage supply, and was maintained at about 240°C. The temperature was measured by an ordinary mercury thermometer placed between the furnace element and the pyrex tube containing the copper oxide.

The volume V_1 and V_2 of the Toepler-pump gas burette calibrated by using the standard fixed volume, were 3.53 and 10.26 ml. In this work, only the smallest volume was used. A mirror scale, graduated in millimeters placed behind the straight limb of the Toepler-pump gas burette allowed the pressure of gas in the fixed volume to be measured.

7. Gas Sampling Valve

A greaseless sampling (type GSV-106-S of H.C.Engineers Ltd.) system for injecting the sample onto the column of the Gas-liquid chromatography was used during this work. The advantage of this technique is that the sample could be injected directly from the reaction system into the column of the Gas-liquid chromatography. The sampling valve was evacuated by opening the greased tap which connected it to the main line. The sample was transferred to the 10 ml sample loop of the valve after the evacuation while the valve was isolated from the main line and then injected into the G.L.C. as shown in figure 2.5. Large

Fig. 2.5 The Gas Sampling Valve



samples (up to two to three atmospheric pressure) were successfully condensed into the sampling valve, for the purpose of separation and collection of the reaction products.

When a sample was taken from the reaction system, the pressure was reduced and the corresponding peak areas on the chromatogram for the following sample were reduced. A sampling correction factor was calculated, in terms of the reaction system volume and the sample volume. The sampling correction factor for the first sample was given by the ratio

$$:\frac{\text{Reaction System Volume + Sample Volume}}{\text{Reaction System Volume}}:$$

All the peak areas of the chromatograms obtained were corrected for sampling error by multiplying the actual area measured by the corresponding sampling correction factor. The correction factors for successive samples are given in Table 2.1. After correction, peak areas on the chromatograms were generally in agreement to better than ± 2%.

TABLE 2.1

Sample n	Correction Factor	Sample n	Correction Factor
1	1.032	4	1.127
2	1.064	5	1.160
3	1.096	6	1.192

8. Gas-liquid Chromatography Instruments

The instrument used was a Perkin-Elmer F11 gas chromatograph equipped with a flame ionization detector (FID). The carrier gas used was nitrogen, except when the instrument was being used for collection and purification purposes, when helium was used. The flow rate of nitrogen was controlled by the Flow Control Unit, but the hydrogen (17½ lb/sq.in.) and air (25 lb/sq.in.) supplied to the flame were controlled by the Pressure Control Unit. It was important to ensure that the hydrogen air supplied for the flame remained constant throughout the experiments. A Linear Temperature Programmer was used for all this work. The Kent Recorder was equipped with a disc chart integrator for the measurement of peak areas (142 counts 1 sq.cm.).

Two columns were used in this work. The normal quantitative runs were done by using a column of 4 metres, PORAPAK Q and the temperature programme were operated generally 10 minutes at initial temperature (about 30^o) then heated to 200^{o}C at 6^{o}C per minute. The separation and collection of products from the reaction of O(^{3}P) + 1,2-difluoroethylene were done on 1.5 metres, 30% di-n-butylphthalate column at 0^{o}C. The normal quantitative runs of this reaction were also successful by using this column at room temperature.

The principle of the flame ionization detector is basically as follows. When the sample was injected into the column of G.L.C. the carrier gas would bring it into a flame of high purity hydrogen burning in air. Any organic components present were burnt in the flame. Stepwise decomposition of the substance to highly unsaturated intermediates occurs, which are then broken down to carbon. This is ionised and the charged particles, with the electrons from the decomposition process, are collected by electrodes in an electric field applied to the flame. An ionic current is thus formed which is electronically amplified, converted into a voltage and fed into a recorder. A flame ionization detector (FID) is more sensitive for compounds of the kind used in this work than most other detectors by several orders of magnitude. This allows accurate product analyses at low conversion.

Calibration of the Flame Detector

When the absolute value of the amount of a particular reaction product formed is required, as in pressure dependence experiments, then the detector and amplifier system must be calibrated. The calibration was done by taking known amounts of a pure sample which was separated by the method described in Section 2.3c, measured in one of the gas burette volumes. The sample was transferred to the reaction system, nitrous oxide, approximately 100 mm of Hg was added. After thirty minutes of circulation, the G.L.C. samples were taken in the usual quantitative way and injected into the column until at least three reproducibility chromatograms were obtained. The calibration factor of the flame detector could be calculated from the equation

$$P = f.A$$

where P is the pressure of sample

A is the peak area of chromatogram

f is the calibration factor of the flame ionization.

2.2 THE AUXILIARY EQUIPMENT

a) The Infra-red Equipment

The Perkin-Elmer 457 Infra-red spectrometer was used for identification of products and checking the impurities which might have been presented in the starting olefins. Spectra were run from 4000 cm^{-1} to 600 cm^{-1} using a reference beam attenuator and a gas microcell. The total volume was approximately 7.7 ml; and had sodium chloride windows which were held by threaded caps with silicone rubber '0' rings. Pressure of between 30 and 100 mm Hg were necessary in the cell to obtain good infra-red spectra.

b) The M.S.9 Mass Spectrometer

An A.E.I., M.S.9 mass spectrometer was used to assist in the identification of the products. Samples could be transferred directly to the sample tubes from the apparatus via the greaseless manifold (figure 2.1). A sample was put through a Varian leak valve in place of the normal solid-sample probe on the M.S.9. The spectra are presented as bar graphs, plotting relative abundance (R.A.) V.S. M/l.

2.3 EXPERIMENTAL PROCEDURE

a) Preparation and Irradiation of Reaction Mixture

a.1) Single Olefin

The whole of the vacuum system was first pumped out to better than 10^{-4} mm Hg. The required amount of olefin was measured approximately in the main line and then condensed into the reaction system via the greaseless manifold, using liquid nitrogen as the coolant. Nitrous oxide, at the required pressure, was condensed into the reaction system. The system was pumped on in order to degas the olefin and nitrous oxide. The main valve at the top of the circulating pump cylinder was held open using a permanent magnet during the degassing process. After degassing, the reaction system was closed and the reaction mixture allowed to warm up. The degassing process was then repeated. After the final degassing the reaction system was again closed and the reaction mixture allowed to warm up. The mixture was then circulated for forty minutes so that the complete equilibrium to room temperature could take place, and then the total pressure was measured. Room temperature was also noted. Fifteen minutes before irradiation the lamp was switched on, although the shutter was not removed in order to allow the lamp to stabilize. After fifteen minutes, the shutter was removed and the reaction mixture was irradiated for the measured time. When the irradiation was completed, the lamp and circulating pump were switched off and the main circulating pump valve held open with a permanent magnet. The room temperature was also noted at the end of the irradiation.

a.2) Two Olefins in Competitive Run

For each olefin studied in the competitive run, a series of runs were carried out at constant irradiation time, but using various olefin ratios. The general method was the same as used in the "single olefin" run but the exact ratio od the olefin concentration was required. These two quantities were carefully measured in the gas burette, before the olefins were mixed in the reaction system. The experimental method was as follows.

The required amount of the first olefin was transferred from the appropriate storage bulb to the main line and then condensed into the finger at the top of the gas burette by filling the reservoir with liquid nitrogen. It was degassed twice as described in section (a.1). After the degassing, the olefin was trapped in the gas burette by raising the mercury level, vaporised using the hot air blower, and allowed to equilibrate to room temperature for fifteen minutes. The temperature and height of the mercury in the straight limb were then recorded. The olefin was transferred via manifold to the reaction system and condensed into the cold trap, using liquid nitrogen as coolant. The gas burette zero was then recorded. The second olefin to be studied was also accurately measured, using the same method as the first olefin. The second olefin was transferred to the reaction system, where it condensed into the cold trap containing the solid first olefin. And again the gas burette zero was then recorded. Nitrous oxide, about 700 mm Hg, was then added into the reaction system and the reaction mixture was thoroughly degassed. The mixture was then circulated for one hour in order to be sure that the three components were thoroughly mixed. The pressure and temperature were also recorded before the irradiation. The method of irradiation was the same as described in section (a.1).

b) Measurement of Non-condensible Gases

The irradiation mixture was frozen down in the reaction system cold trap for about ten minutes, with the circulating pump valve held open by means of the permanent magnet. The two cold traps in the analysis system were surrounded by liquid nitrogen. Following this, the reaction system was connected to the analysis system while it was isolated from the main line. Non-condensible gases at liquid nitrogen were then transferred by the mercury diffusion pump through the cold traps into the Toepler-pump gas burette. The magnet holding up the Toepler-pump valve was removed and the automatic Toepler-pump was operated for fifteen minutes. The reaction system was then isolated, the irradiated mixture was allowed to vaporize and then was refrozen again for at least ten minutes. The collection of non-condensible gases was repeated as above. The pressure and temperature of the gases (nitrogen, carbon monoxide etc.) trapped above the Toepler-pump valve were measured in the volume V_1, shown in figure 2.3, the zero having been determined previously.

The non-condensible gases in the Toepler-pump gas burette were transferred to the copper oxide furnace, which had already been brought to about 250^{o}C. The U-tube was immersed in liquid nitrogen so that the carbon dioxide and water formed in the combustion process could be trapped.

The gases were left in the furnace for at least one hour with occasional circulation, until the mercury level in the Toepler-pump gas burette tube reached a constant value. The copper oxide furnace tap was opened and the residual nitrogen in the furnace was transferred to the volume above the Toepler-pump valve by fifteen minutes operation of the Toepler-pump. The operation of the automatic Toepler-pump was repeated until there was no further change of pressure in the gas burette. Then the pressure of nitrogen was read in the volume V_1 and the temperature was also noted. The Toepler-pump was used to test for leaks in analysis line and copper oxide furnace during the last fifteen minutes of the irradiation.

While the non-condensible gases were in the furnace, the remaining irradiated mixture was allowed to warm up and was circulated for at least 45 minutes. The evacuation of the sampling valve system was going on. Samples were injected directly from the greaseless sampling valve to the gas-chromatograph until at least three reproducible chromatograms were obtained.

c) Collection and Identification of Products

The reactions were allowed to go to quite high conversions since large quantities of products were needed for collection purposes. The reaction mixtures were irradiated for 5 hours. The large excess of nitrous oxide was mostly removed after the irradiation time was finished. The products that needed to be collected were left in the reaction system. This process will be described as follows.

The reaction mixture was irradiated (for five hours) until a sufficient quantity of the products had been produced for collection.

A gas chromatogram was then obtained for the reaction mixture in order to show the positions of the product peaks. The reaction mixture was then condensed in the reaction system cold trap using liquid nitrogen. The liquid nitrogen dewar was immediately replaced by a dry-ice acetone mixture. Nitrous oxide boiled off at this temperature but the products were still condensed down. The concentration of products in the nitrous oxide boiled off were detected by using the Gas chromatograph. The nitrous oxide was carefully pumped away until a pressure of about 100 mm Hg ~~was~~ remained in the reaction system. The mixture was then allowed to warm up and circulated.

The products were collected using a trap system connected directly to the Gas-liquid chromatography as shown in figure 2.6. Helium was used as a carrier gas because the collection tubes, which have liquid nitrogen as coolant, would soon have blocked with condensed nitrogen if it has been used as the carrier gas. Helium was allowed in the U-tube by opening taps A, B and C, taps A and C were closed in five minutes so that air in the U-tube was replaced by helium gas. As liquid nitrogen was used as coolant to collect the products, the protective tube was connected to tap C in order to prevent back diffusion of air. The separated products which were required were frozen down in their own collecting tube as they eluted from the column. Two outlets on the manifold allowed two products to be collected in quick succession.

A large sample was needed in the case of collection (about 2-3 atmospheric pressure) and obtained by condensing a suitable amount of the reaction mixture into the 10 ml sample loop. Then it was vaporised by using hot air blower and was injected into the Gas-liquid chromatograph.

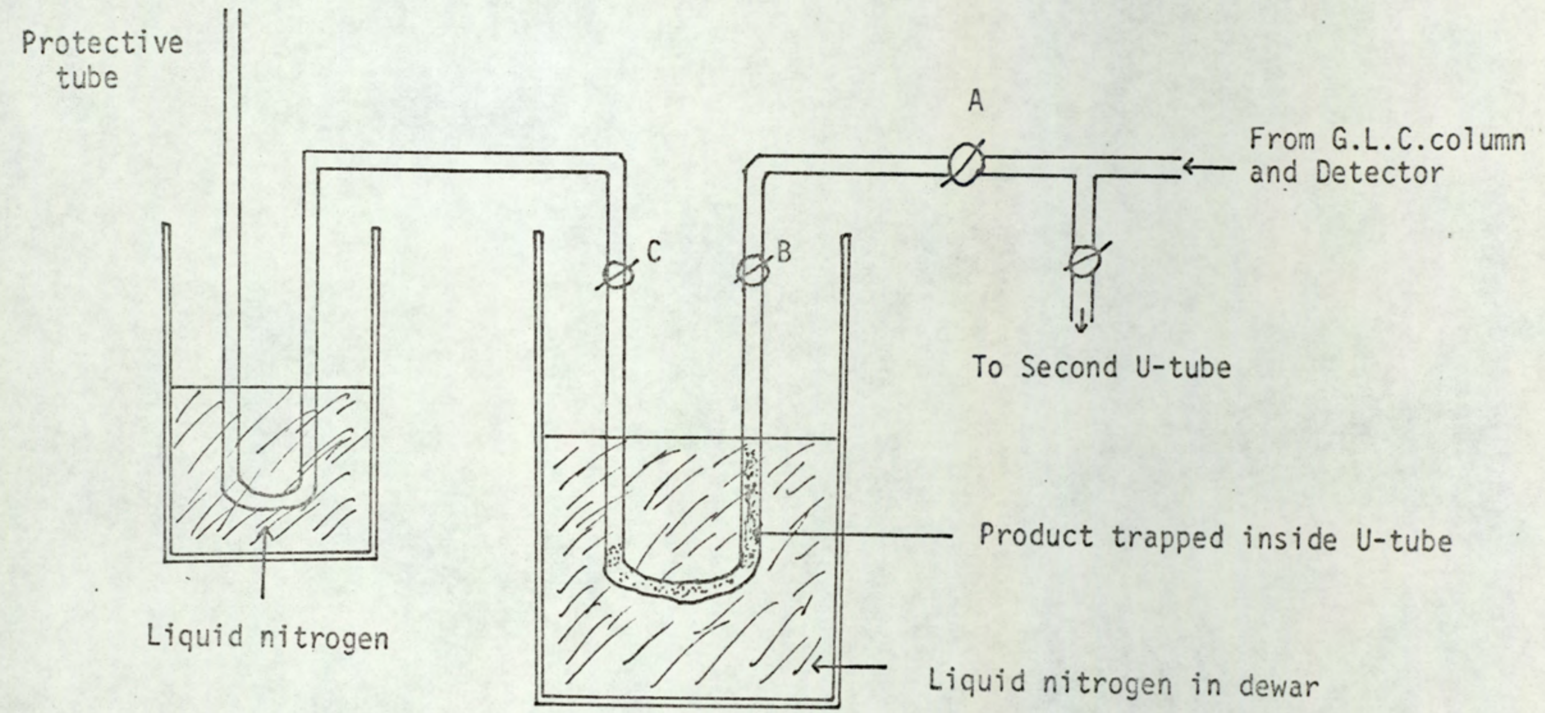


Fig. 2.6 Traps System for Collection of Products.

When the products to be collected started to appear on the chromatogram, the gas stream was diverted by opening the microtaps (tap A) to the respective tubes. The retention times of the required products under the conditions used were determined by passing a small sample through the column before the separation was started. The detector flame of the G.L.C. must be on during the collection of products.

After collection, the tube was transferred, still immersed in liquid nitrogen, to a vacuum line and was degassed. The product was measured in the gas burette and was transferred to the infra-red cell and finally to the mass spectrometer for analysis.

2.4 MATERIALS AND PURIFICATION

All the materials used in this work were obtained commercially, and these were purified, where necessary, as described below.

a) Nitrous Oxide

This was obtained from British Oxygen Company, and was purified on activated charcoal. The method will be described later.

b) Oxygen

This was obtained from British Oxygen - Medical grade and was transferred directly from the cylinder to the reaction system. It was used without further purification.

c) Cis- and Trans- 1,2-Diffluoroethylene

Obtained from Pierce Chemical Company and separated by Gas-liquid chromatography using 4 metres of Dimethoxyethyl adipate (13½%) and diethylhexyl sebacate (6½%) at 0°C with helium as the carrier gas. The trans-isomer is first to elute. After separation and analysis by G.L.C. the cis-isomer showed 1.3% of the trans-isomer as main contaminant.

while the trans-isomer contained about 0.3% of the cis-isomer (other impurities are less than 0.1%). The isomers were distinguished and identified by means of their infra-red spectra(131).

d) Trifluoroethylene

This was obtained from Cambrian Chemicals and was purified by fractionation from activated charcoal to better than 99%. The method is as follows.

A small cold trap which contained a small portion of activated charcoal was attached directly to the main vacuum line via the inlet-outlet point. The trap was gently heated under vacuum to activate the charcoal until the pressure in the main line was less than 10^{-3} mm Hg. The gas to be purified was allowed to the main line from the storage bulb and condensed onto the activated charcoal, left for five minutes and thoroughly pumped. The main tap to the pump was closed and the gas allowed to expand back into the main line. When only three-fourths of gas collected, the cold trap was isolated from the main line and the remainder in the cold trap being rejected. The purified gas collected in the main line was transferred into the storage bulb and was ready to use, after analysis by G.L.C. to check removal of impurities to suitably low levels.

e) Vinyl Fluoride

This was obtained from Cambrian Chemical and was purified by fractionation from activated charcoal to better tham 99.8%.

f) 1,1-Difluoroethylene

This was also obtained from Cambrian Chemical and was purified by fractiination to better than 99.7%.

g) Ethylene

This was also obtained from Cambrian Chemical and was purified by fractionation from activated charcoal. Residual impurities were less than 0.2% by G.L.C.

h) Tetrafluoroethylene

This compound was obtained from I.C.I., checking by G.L.C. analysis was better than 99.8% pure. Mass spectra showed negligible impurities (approximately 2% of unremovable C_3F_6). Compounds C_3F_6 are possibly perfluorocyclopropane or perfluoropropene which are known to be less reactive than C_2F_4(57).

i) Propylene

This was obtained from B.D.H. with 99% pure.

CHAPTER THREE

REACTION OF OXYGEN ATOMS WITH 1,2-DIFLUOROETHYLENE

RESULTS AND DISCUSSION

The results obtained in this chapter were carried out at room temperature and using the same irradiation time. Before the kinetics runs were carried out, many experiments were done in order to determine a convenient irradiation time. The products were successfully collected on porapak Q column under the normal conditions used. Infra-red spectroscopy and mass spectrometry were used for identification of the collected products.

Actually the reactions of oxygen atoms with both cis- and trans- 1,2-difluoroethylene gave similar products except in the reaction of cis- 1,2-difluoroethylene, the addition products derived from CHF radicals were formed in both cis- and trans- isomers. The mechanism of addition reaction of cis- 1,2-difluoroethylene is therefore a little more complicated than the trans- isomer. The reaction of trans- 1,2-difluoroethylene will be considered first because of its simpler mechanism.

SECTION A

REACTION OF OXYGEN ATOMS WITH TRANS- 1,2-DIFLUOROETHYLENE

A3.1 NATURE OF PRODUCTS

The chromatograms of the reaction of oxygen atoms with trans-1,2-difluoroethylene are presented in Figure A3.1. The following symbols are used in Figure A3.1 and will be used throughout the remainder of this chapter.

"M_t" represents "trans- 1,2,3-trifluorocyclopropane"
"M_c" represents "cis- 1,2,3-trifluorocyclopropane"
"$P_{t,c}$" represents "1,2,3-trifluoropropylene" (cis- or trans-)
"$P_{c,t}$" represents "1,2,3-trifluoropropylene" (cis- or trans-)
"P_{t+c}" represents "both cis- and trans- 1,2,3-trifluoropropylene"
"P_1-P_6" represents "unidentified products"

The main products were separated and identified as described in Section 2.3c. They were found to be formyl fluoride, trans- 1,2,3-trifluorocyclopropane, cis- and trans- trifluoropropylene. The infra-red and mass spectra of these products are shown in Figures A3.2 and A3.3 respectively. The remaining products, P_1 - P_5, not identified, correspond to less than 7% of the main products at pressure about 750 mm Hg. At low pressure about 65 mm Hg, these products were found to be about 13% of the main identified products. These products were probably monofluoroacetylene, fluoroethane, fluoromethane and fluoropropane.

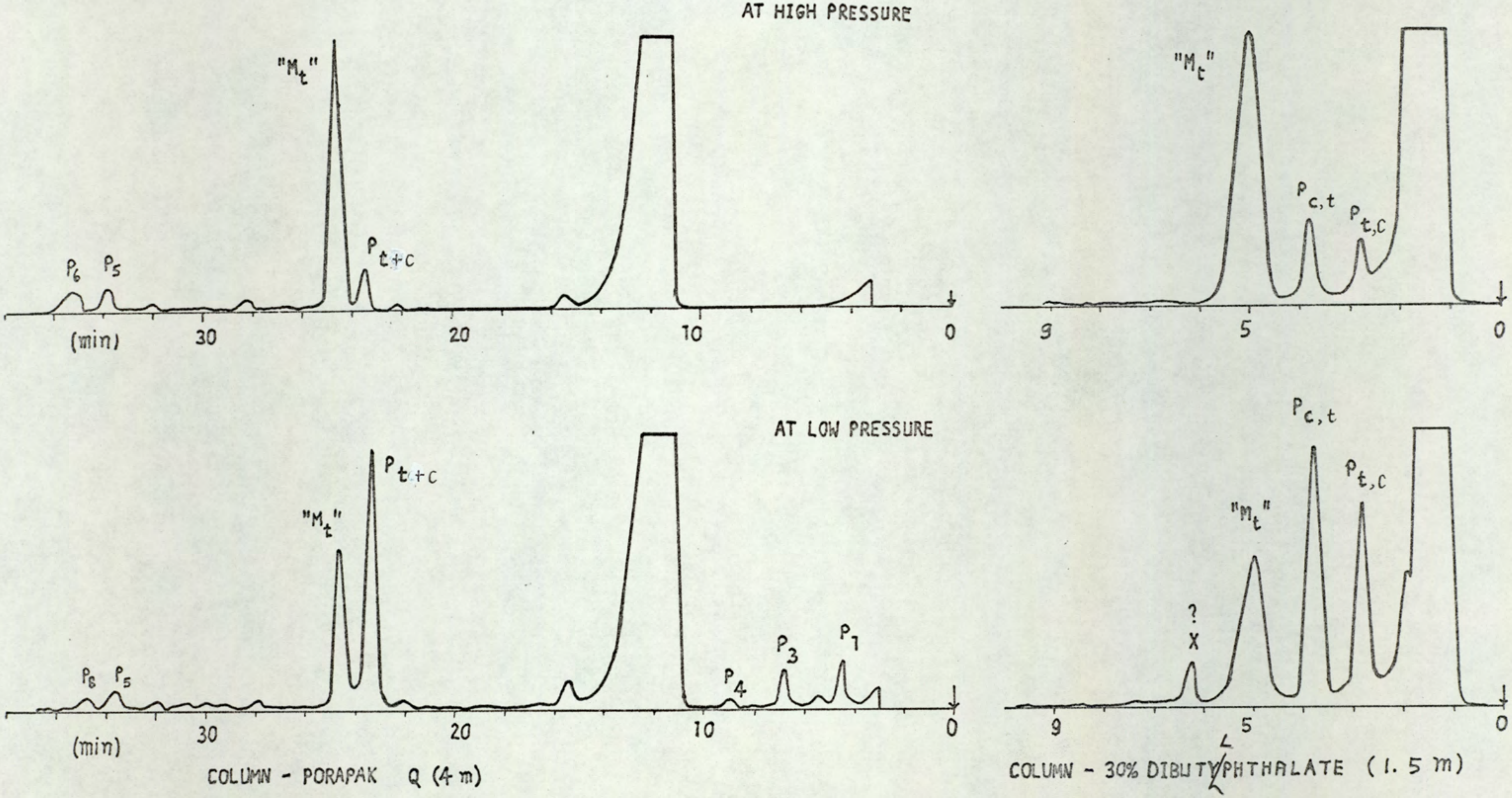
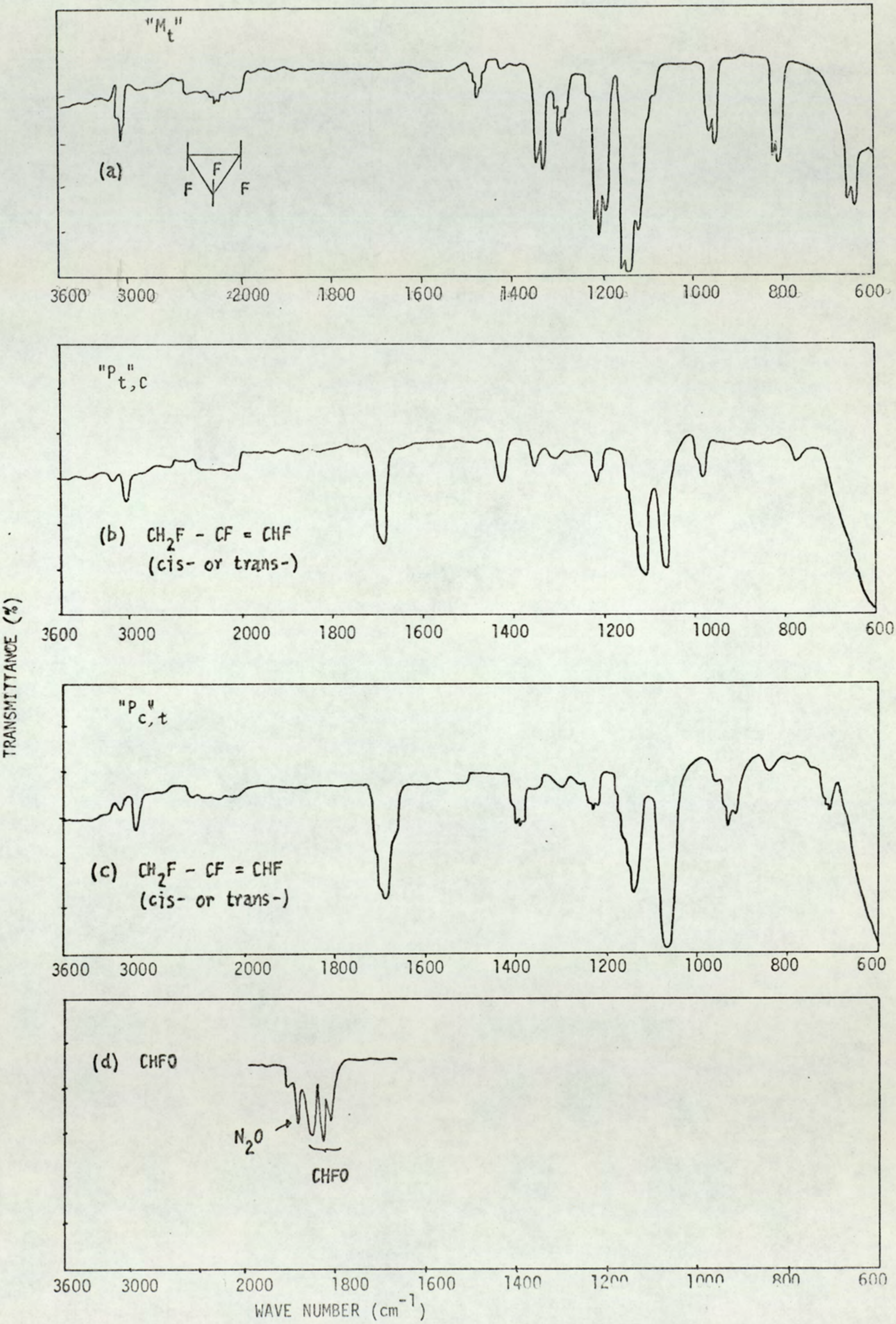


Fig. A3.1 GAS CHROMATOGRAMS FOR THE REACTION OF $O(^3P)$ + TRANS - CHF = CHF

Fig. A3.2 INFRA-RED SPECTRA OF PRODUCTS FROM O(^{3}P) + TRANS-CHF=CHF



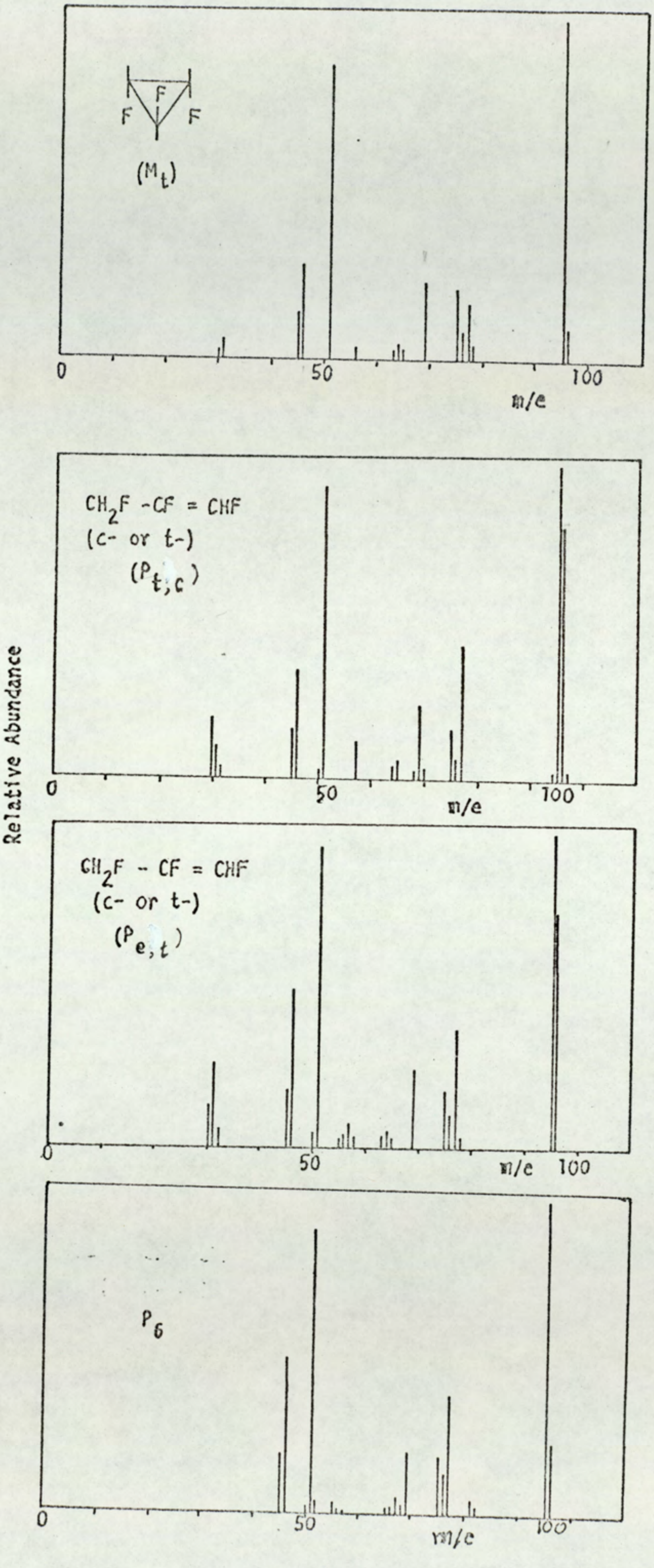


Fig. A3.3 MASS SPECTRA OF THE PRODUCTS FROM $O(^3P)$ + TRANS-CHF=CHF

Details of the identification of the identified products are given below:-

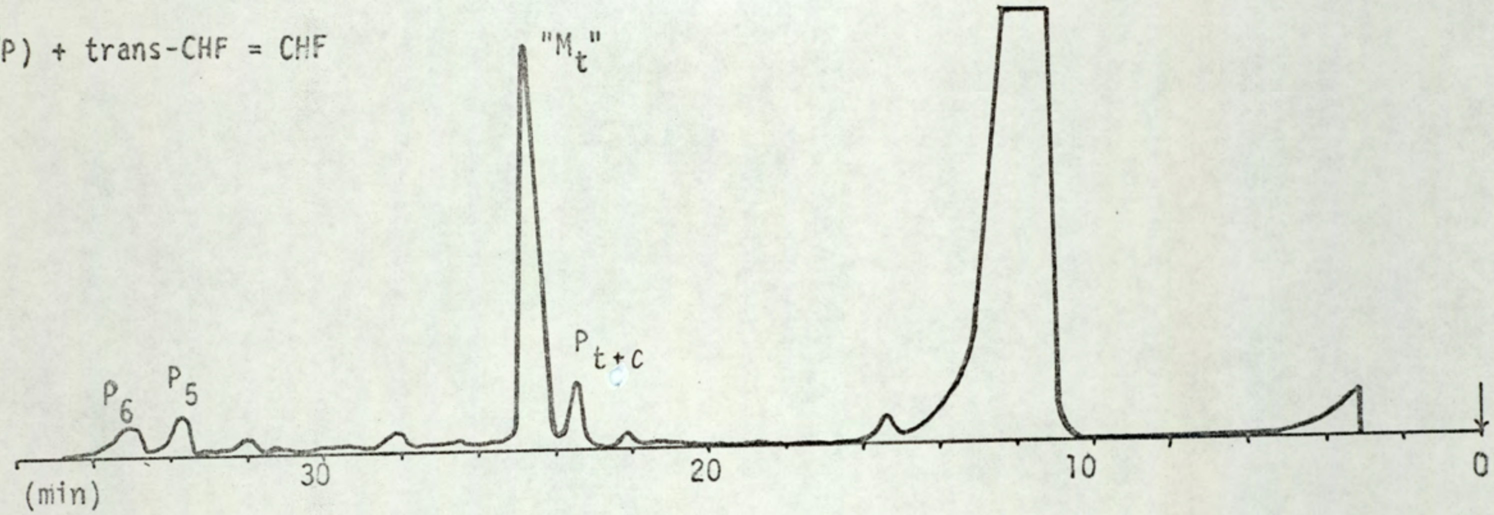
trans- 1,2,3-trifluorocyclopropane

The compound, M_t, was found by mass spectrometry to have the empirical formula $C_3H_3F_3$. A parent peak of molecular weight, M = 96, was obtained from the mass spectrum of this compound with a large $(P-1)^+$ peak at M = 95. This suggested that the structure of this compound is a trifluorocyclopropane type rather than trifluoropropylene. The trifluorocyclopropane ion, P^+, should readily lose hydrogen to form the more stable trifluorocyclopropyl ion, $(P-1)^+$. The absence of a peak at 1690 cm^{-1} in IR spectrum suggested that this compound is not trifluoropropylene. The medium peak at 3060 cm^{-1} could be assigned as ν(C-H) stretching vibration of a cyclopropane(133). The above evidence strongly suggested that this compound is trifluorocyclopropane. The chemical studies indicate that the compound is trans- 1,2,3-trifluorocyclopropane.

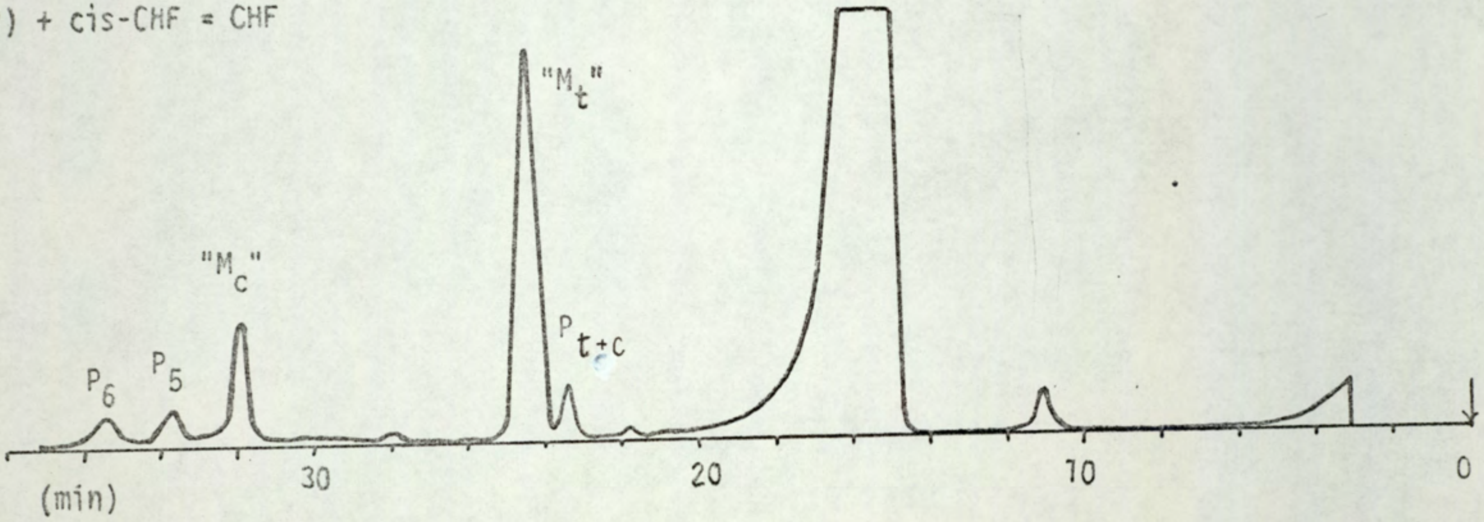
The cis- 1,2,3-trifluorocyclopropane is not formed in this reaction. This has been proved by comparing the retention times of the chromatogtams of the reactions of oxygen atoms with trans- CHF = CHF and cis- CHF = CHF, as shown in Figure A3.4. The product "M_t" which was present on the chromatogram of O + cis- CHF = CHF was collected and identified as the same trifluorocyclopropane by means of infra-red and mass spectrometry presumably the trans- isomer. Product "M_c" which was formed only in the reaction of O + cis- CHF = CHF system was also found by infra-red and mass spectrometry

Fig. A3.4 COMPARISON OF THE PRODUCTS FORMED FROM

a) $O(^3P)$ + trans-CHF = CHF



b) $O(^3P)$ + cis-CHF = CHF



to be a trifluorocyclopropane and had a different infra-red spectrum and retention time from the trans- 1,2,3-trifluorocyclopropane. The only alternative was that the product "M_c" was an isomer of "M_t" compound, namely cis- 1,2,3-trifluorocyclopropane. The absence of product peak "M_c" on the chromatogram of the reaction of O + trans-CHF = CHF system strongly suggested that only trans- 1,2,3-trifluorocyclopropane was formed in this reaction. This interpretation of the infra-red spectra of the two isomeric 1,2,3-trifluorocyclopropane has been accepted and strengthened by Professor N.C.Craig(134).

cis- and trans- 1,2,3-trifluoropropylene

These two compounds, $P_{t,c}$ and $P_{c,t}$, were collected separately on a di-n-butylphthalate column. Their retention times on the porapak Q column were then found to be identical (Peak P_{t+c} in Figure A3.1). These compounds were identified unambiguously by mass spectrometry and infra-red spectroscopy as trifluoropropylene (see Figure A3.2 and A3.3). The infra-red spectra of compounds $P_{t,c}$ and $P_{c,t}$ had a strong absorption band at 1690 cm^{-1} which indicated the presence of carbon-carbon double bond(133). A medium absorption band at 3060 cm^{-1} and a very weak one at 2980 cm^{-1} could be assigned as ν(C-H) stretching vibration of vinyl and alkyl groups(133) respectively (see Figure A3.2). Infra-red and mass spectrometry as well as the chemical studies strongly suggested that these compounds, P_t and P_c, were the isomeric cis- and trans- 1,2,3-trifluoropropylene. We cannot distinguish the possible isomers from the spectra available.

Product P_6 appeared by mass spectrometry to have the molecular formula $C_3H_3F_3$, but its structural formula was not determined unambiguously because the sample obtained for the infra-red spectroscopy was too small to give satisfactory absorption bands. The identity of P_6 is not known.

By using CuO furnace and Toepler pump, the CO yield was found to be less than 2% in the formation of nitrogen by this reaction throughout the pressure range studied (760 - 65 mm Hg).

Formyl fluoride

Formyl fluoride is not detected on the GLC because it does not give a response on a flame ionization detector. However, it is shown to be present from infra-red analysis. Identification was by the characteristic carbonyl frequency at 1834 cm^{-1} (Q branch), 1849 cm^{-1} (R branch) and 1819 cm^{-1} (P branch)(135). The method of analysis is as follows:

The infra-red spectrum of a reaction mixture of trans- 1,2-difluoroethylene and nitrous oxide was run using the large gas cell. The reaction mixture was then irradiated for five hours to ensure that the formation of CHFO was large enough to give a good infra-red spectrum (approximately 50% conversion). The infra-red spectrum showed fairly strong new peaks at 1819 cm^{-1}, 1834 cm^{-1}, and 1845 cm^{-1}. These corresponded to the carbonyl stretching of CHFO obtained from an infra-red spectrum of an authentic sample of CHFO(135).

A3.2 CALIBRATION OF THE FLAME IONIZATION DETECTOR

It is important to know the detector calibration factor for the products in order to determine the absolute concentration of products in the pressure dependence studies. Unfortunately the compounds trifluorocyclopropane and trifluoropropylene were not available commercially and undescribed in literature. An attempt has been made to separate and purify the compounds which formed in this system. Two columns, dibutylphthalate and porapak Q, were used to separate these compounds. The difficulty in this experiment was that the compounds liquified at room temperature even though the purification was done on charcoal. This made it difficult to measure the amount of these compounds accurately. The measurements were carried out at various low concentrations and the values of the detector calibration factor (f) were calculated at each measured pressure from the equation $P = f.A$. The results of this calibration are summarized in Table A3.1.

TABLE A3.1

Detector Calibration Factor

Run No.	Pressure at 23 ± 2°C (mm)		Mean area of Peak at S=1×10^2 (arbitrary units)	Calibration factor
	in V_1(3.95 ml)	in RV(760 ml)		
a) 1,2,3-trifluorocyclopropane				
1	56.1	0.292	2962	9.85×10^{-5}
2	43.5	0.226	2209	10.25×10^{-5}
			mean	10.05×10^{-5}
Calibration factor of trifluoroclyclopropane = $10.05 \pm 0.2 \times 10^{-5}$				
b) 1,2,3-trifluoropropylene				
3	60.0	0.312	3190	9.78×10^{-5}
4	49.7	0.259	2722	9.49×10^{-5}
5	62.5	0.325	3208	10.12×10^{-5}
			mean	9.80×10^{-5}
Calibration factor of trifluoropropylene = $9.80 \pm 0.31 \times 10^{-5}$				

The experimental uncertainty of the values of the calibration factor were probably not greater than ± 10%.

A3.3 EFFECT OF PRESSURE VARIATION

The pressure dependence of the major and minor products formed in the reaction of oxygen atoms with trans- 1,2-difluoroethylene are shown in Figure A3.5. Pressures were varied between 60 mm and 760 mm Hg. Ratios of nitrous oxide to olefin were always in excess of 20:1 in order to keep the reactions involving mercury photosensitized decomposition of the olefins to a minimum. All reactions were run at room temperature (23 ± $2^{o}C$) and carried to about 4 - 5% conversion. The yields of the compounds were expressed as a yield per oxygen atom generated in the reaction. The values for the yields of the minor products, P_1 - P_6, were probably not very reliable because of the inaccuracy in measuring the very small peaks.

The quantum yields of all the products at various pressures are shown in Table A3.2.

The total quantum yield of all the products derived from CHF radicals was probably 1.00 ±0.20 due to the uncertainty in the calibration factor. The yields of all these products were not affected by the pressure of about 5 mm of molecular oxygen in a high pressure run.

The quantum yield for formation of CHFO could not be reliably measured but was thought to be near unity.

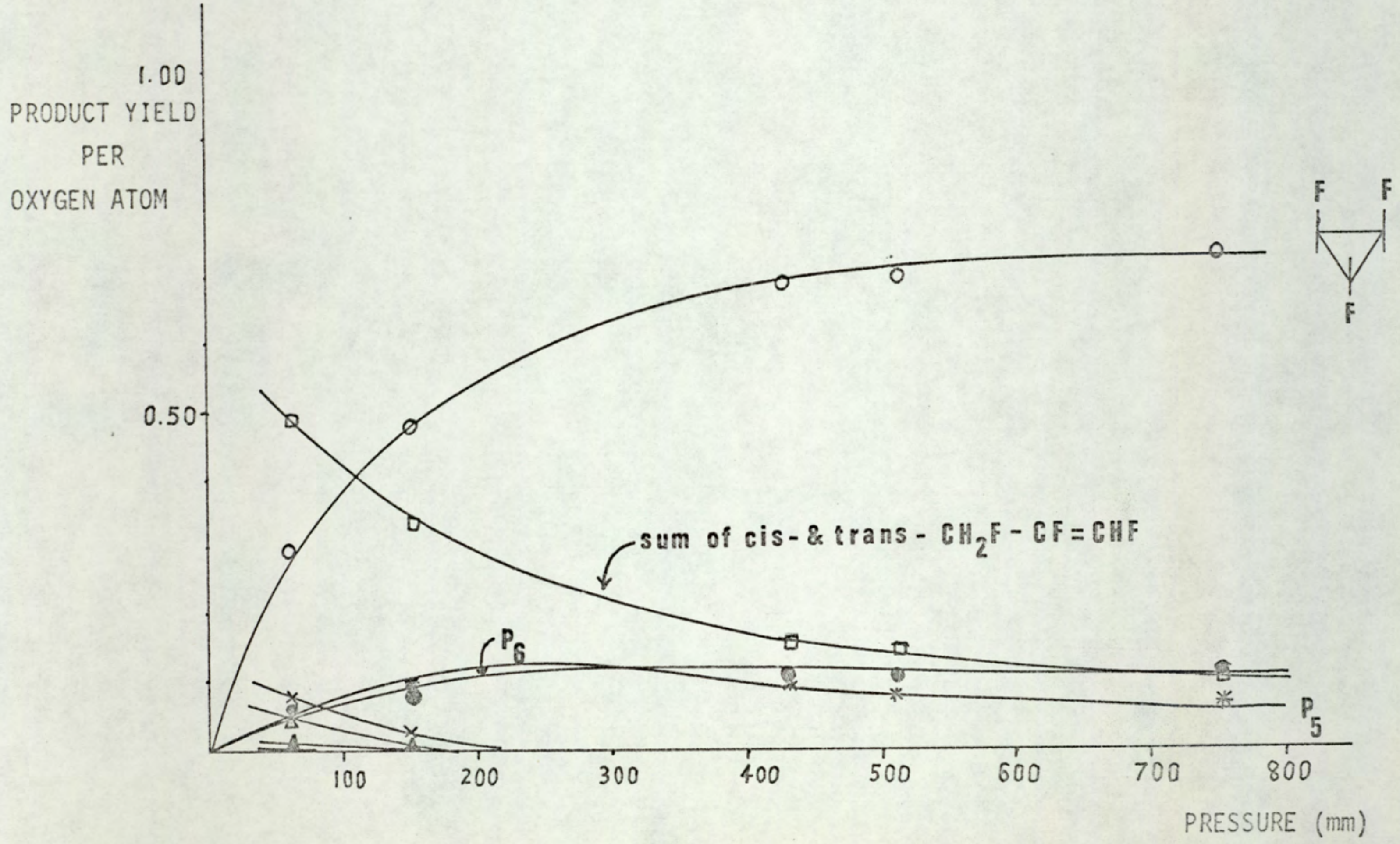
TABLE A3.2

The Effect of Pressure on Product Yields

(Quantum Yields Expressed as Yields of Products per yields of Nitrogen)

Pressure (mm)	P_1	P_2	P_3	P_4	 (a)	$CH_2F-CF=CHF$ cis- and trans- (b)	(a) + (b)	P_5	P_6	Total ϕ
753.5	-	-	-	-	0.725	0.104	0.829	0.066	0.112	1.01
152.0			0.028	0.007	0.478	0.335	0.813	0.099	0.083	1.03
432.0	-	-	-	-	0.686	0.155	0.841	0.096	0.112	1.05
61.5			0.071	0.015	0.296	0.485	0.781	0.075	0.061	1.00
514.0	-	-	-	-	0.696	0.145	0.841	0.082	0.109	1.03

Fig. A3.5 PRESSURE DEPENDENCE OF THE PRODUCTS FORMATION



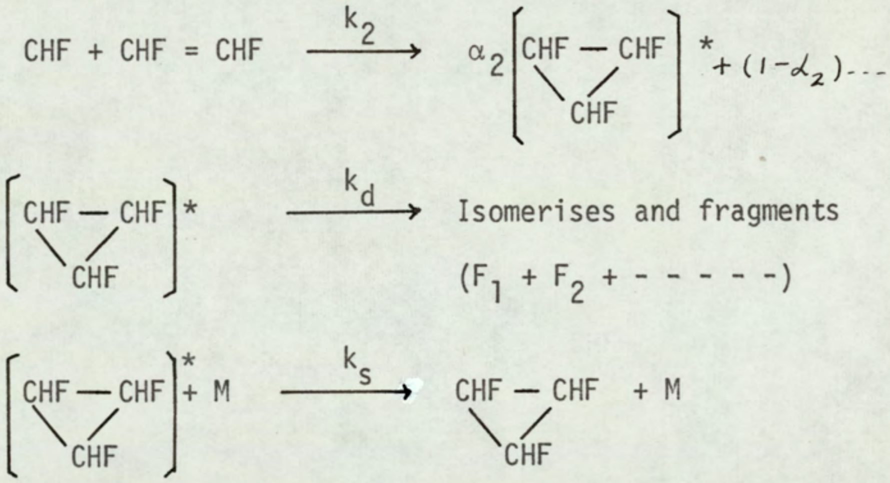
A3.4 MECHANISM OF THE REACTION OF OXYGEN ATOMS WITH TRANS- CHF = CHF

The results described in the preceding pages can be satisfactorily represented in terms of the formation of CHF radicals from the olefin. The CHF radicals then add to the olefin to form a "hot" cyclopropane which may be stabilised by collision (or isomerise or fragment).

$$Hg(^1So) + h\nu(253.7\ mm) \longrightarrow Hg^*\ (^3P_1) \qquad (1)$$

$$Hg^*(^3P_1) + N_2O \longrightarrow Hg(^1So) + N_2 + O(^3P) \qquad (2)$$

$$O(^3P) + CHF = CHF \xrightarrow{k_1} \alpha_1 CHFO + \alpha_1\ CHF \qquad (3)$$



$$CHF + CHF = CHF \xrightarrow{k_2} \alpha_2 \left[\text{CHF—CHF—CHF ring} \right]^* + (1-\alpha_2)\ldots \qquad (4)$$

$$\left[\text{CHF—CHF—CHF ring} \right]^* \xrightarrow{k_d} \text{Isomerises and fragments } (F_1 + F_2 + - - - - -) \qquad (5)$$

$$\left[\text{CHF—CHF—CHF ring} \right]^* + M \xrightarrow{k_s} \text{CHF—CHF—CHF ring} + M \qquad (6)$$

Steady state treatment leads to the following stationary concentrations of the intermediates

$$[O] = R_{N_2}/k_1\ [CHF = CHF]$$

$$[CHF] = \alpha_1 R_{N_2}/k_2\ [CHF = CHF]$$

$$[\Delta^*] = \alpha_1\alpha_2\ R_{N_2}/(k_s[M] + k_d)$$

Writing the rate of formation of the stabilized cyclopropane as R_Δ, and defining Q_Δ by R_Δ/R_{N_2},

$$R_\Delta = k_s[M]\,[\Delta^*]$$

$$\underline{Q_\Delta = \alpha_1\alpha_2 k_s[M]/(k_d + k_s[M])}$$

$$\underline{\frac{1}{Q_\Delta} = \frac{1}{\alpha_1\alpha_2} \cdot \frac{k_d}{k_s} \cdot \frac{1}{[M]} + \frac{1}{\alpha_1\alpha_2}}$$

Since [M] proportional to total pressure P, plot of $1/Q_\Delta$ VS. 1/P should be linear with ratio of slope to intercept equal to k_d/k_s. As Figure A3.6 shows, a good linear relation is obtained.

Consider now the formation of an isomer or other product (F_1) from the "hot" cyclopropane before stabilization by collision can occur. Again writing R_F as the rate of formation of F, and defining Q_F by R_F/R_{N_2}.

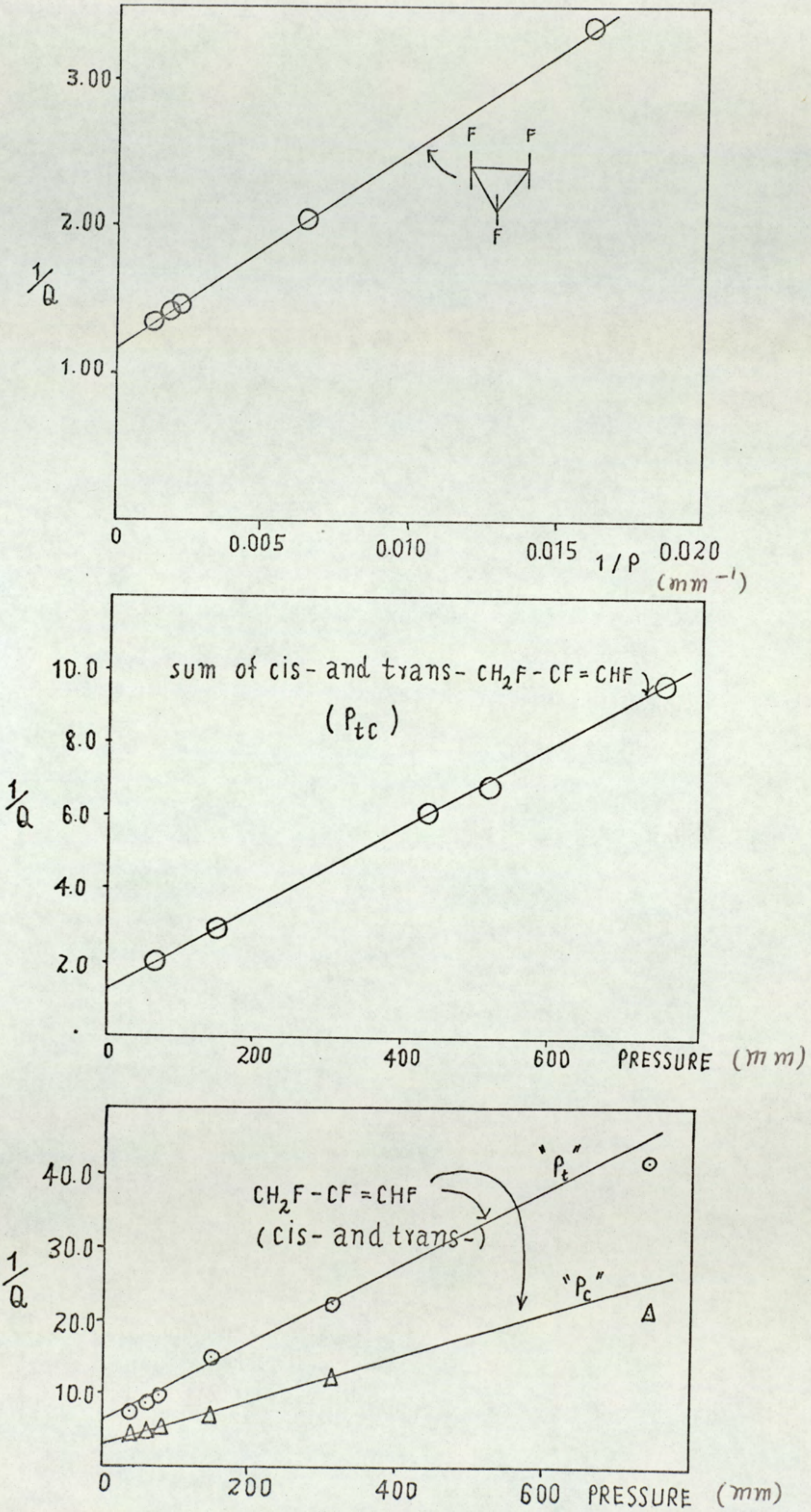
$$R_F = k_{d_1}\,[\Delta^*] \qquad (kd = k_{d_1} + k_{d_2} + - - -)$$

$$\underline{Q_F = \alpha_1\alpha_2 k_{d_1}/(k_s[M] + kd)}$$

$$\underline{\frac{1}{Q_F} = \frac{k_s}{\alpha_1\alpha_2 k_{d_1}} \cdot [M] + \frac{k_d}{\alpha_1\alpha_2 k_{d_1}}}$$

FIG. A3.6 PLOTS OF 1/Q AGAINST 1/P

AND 1/Q AGAINST P



Thus, a plot of $1/Q_F$ VS. P should be linear with ratio of slope to intercept equal to k_s/k_d. This behaviour is observed for the sum of the trifluoropropylenes (on porapak Q) and the individual isomers (on di-n-butylphthalate) as shown in Figure A3.6.

The lifetime of the "hot" molecule is equal to the reciprocal of k_d and will depend on the amount of excess energy and on the size of the molecule. For the same quantity of available excess energy, the lifetime increases with increasing size of the molecule. For a given size of molecule, the lifetime will decrease with increasing amounts of excess energy.

The estimation of the lifetime of the "hot" product are shown in Table A3.3.

TABLE A3.3

Lifetime of "Hot" Addition Product

Experimental method	"Hot" product	$\frac{k_d}{k_s}$	Lifetime (sec)	Remarks
Porapak Q column	trans- 1,2,3-trifluorocyclopropane	115.8	5.4×10^{-10}	calculated from t - Δ
			5.8×10^{-10}	calculated from c-& t-CH_2F-CF=CHF
Dibutylphthalate column	trans- 1,2,3-trifluorocyclopropane	127.9	4.9×10^{-10}	calculated from t - Δ
			5.5×10^{-10}	calculated from c-& t-CH_2F-CF=CHF

Units of k_d/k_s are mm^{-1}

N.B. a) using $k_s = 1.6 \times 10^7\ \text{mm}^{-1}\ \text{sec}^{-1}$

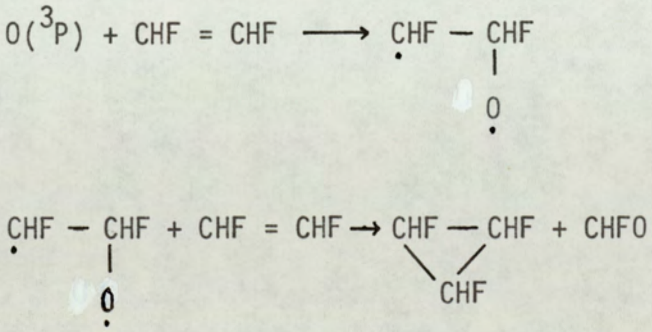
b) peak areas from dibutylphthalate column were measured by planimeter

c) disc integrator was used to measure the peak areas from porapak Q column.

It can be seen that the results obtained from the different methods of analysis differ by only ± 10% which is regarded as within the experimental uncertainty.

The good linearity of the plots based on previous equations (as shown in Figure A3.6) and the agreements in the measured lifetimes substantially confirm the correctness of the mechanism suggested. The major reaction product, trans- 1,2,3-trifluorocyclopropane, accounted for more than 90% of the total addition products at pressures greater than 550 mm.

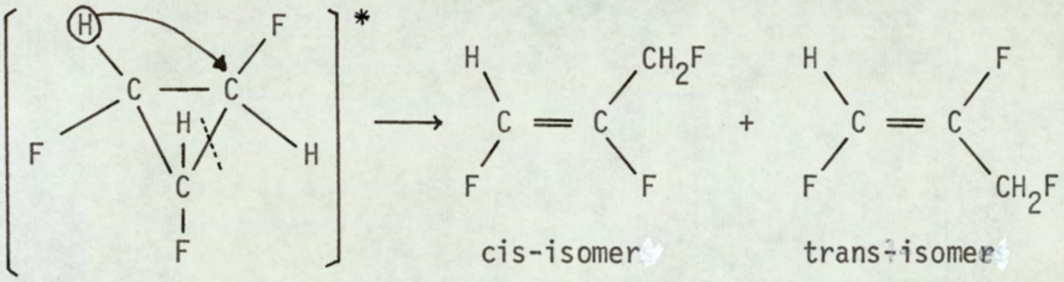
As the major addition product shows a very strong dependence on pressure, there is a good reason to believe that the following reaction pathway would not occur in this system.



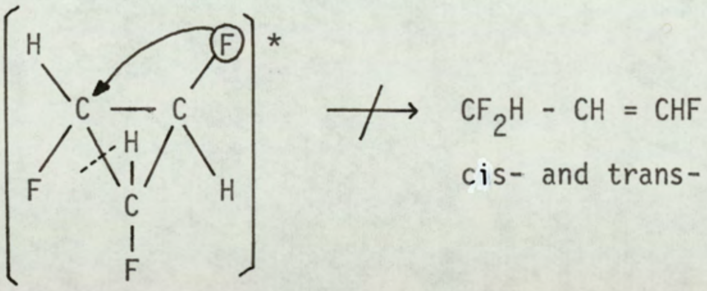
$$O(^3P) + CHF = CHF \longrightarrow \dot{C}HF - CHF(\dot{O})$$

If the reaction occurred according to this mechanism it would not show such marked pressure dependence, because the available excess energy can be converted into kinetics energy (with conservation of momentum).

Although it has not been possible to confirm the structures of the trifluoropropylenes conclusively, we believe these products to be cis- and trans- 1,2,3-trifluoropropylene. The formation of these isomers from the "hot" cyclopropane involves ring opening and a hydrogen atom transfer, e.g.

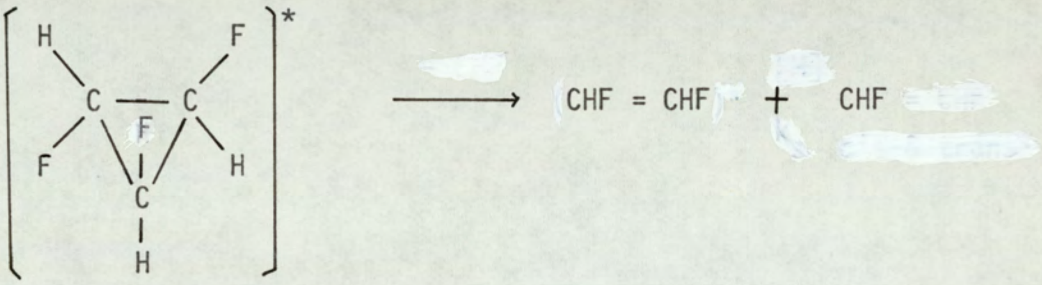


Fluorine atom transfer may occur but this is thought unlikely because of the high C-F bond strength:-



Small quantities of the 1,3,3-trifluoropropylenes may be present in the unidentified minor products.

There is also the possibility that CHF elimination can occur in this reaction. Craig et al.(116) studied the reaction of CH_2 with tetrafluoroethylene, the following products were found:- tetrafluorocyclopropane, perfluorocyclopropane (cyclo - C_3F_6) and 1,1-difluoroethylene. The product 1,1-difluoroethylene must be formed by the CF_2 elimination of the "hot" tetrafluorocyclopropane. CHF elimination from "hot" trifluorocyclopropane should give cis- and trans- 1,2-difluoroethylene and CHF radical similarly.



The presence of a small quantity of cis- 1,2-difluoroethylene in the reactant prevented experimental observation of this reaction.

CHF radicals may also recombine to form "hot" 1,2-difluoroethylene. The "hot" difluoroethylene will have a short lifetime and is likely to undergo intensive fragmentation even at atmospheric pressure, probably forming mainly monofluoroacetylene:

$$2CHF \longrightarrow (CHF = CHF)^*$$

$$(CHF = CHF)^* \longrightarrow HC \equiv CF + HF$$

Monofluoroacetylene is likely to be one of the small products eluted before the difluoroethylene on the GLC.

SECTION B

REACTION OF OXYGEN ATOMS WITH CIS-1,2-DIFLUOROETHYLENE

The reactions of oxygen atom with cis-1,2-difluoroethylene were carried out under the same conditions used for the trans-1,2-difluoroethylene reactions. The symbols used on the chromatogram of 0 + trans- - CHF = CHF will be used for the chromatogram of 0 + cis - CHF = CHF as shown in Figure B3.1.

B3.1 NATURE OF PRODUCTS

Using the same procedure of analysis in Section A3, the following products were identified:- formyl fluoride, cis- and trans- 1,2,3-trifluorocyclopropane, cis- and trans- 1,2,3-trifluoropropylene. The identities of both cis- and trans- 1,2,3-trifluorocyclopropane as well as cis- and trans- 1,2,3-trifluoropropylene have been established in Section A3.1. The infra-red and mass spectra of these products are presented in Figures B3.2 and B3.3 respectively. The remaining products were not identified because only small amount of products were formed. Their retention times were identical to those formed in the reaction of 0 + trans- CHF = CHF.

B3.2 EFFECT OF IRRADIATION TIME

The results of the time dependence studies of products formation in this reaction are shown in Figure B3.4. The reaction was carried out at high pressure (750 mm Hg) with the irradiation times up to 2 hours (approximately 20% conversion). All products show a linear variation with time.

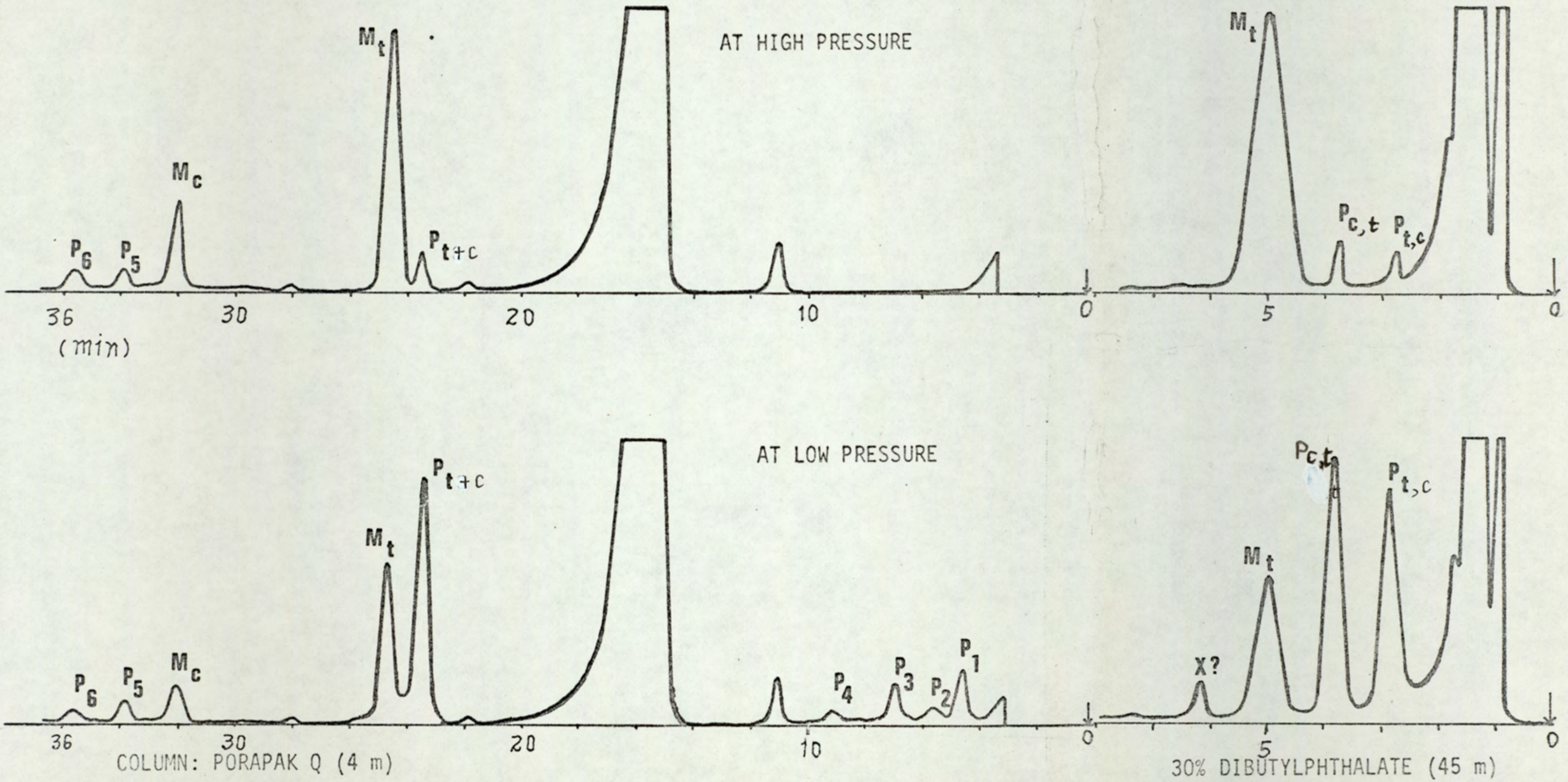


Fig.B3.1 GAS CHROMATOGRAMS FOR THE REACTION OF $O(^3P)$ + CIS-CHF=CHF

Fig. B3.2 INFRA-RED SPECTRA OF PRODUCTS FROM $O(^3P)$ + CIS - CHF = CHF

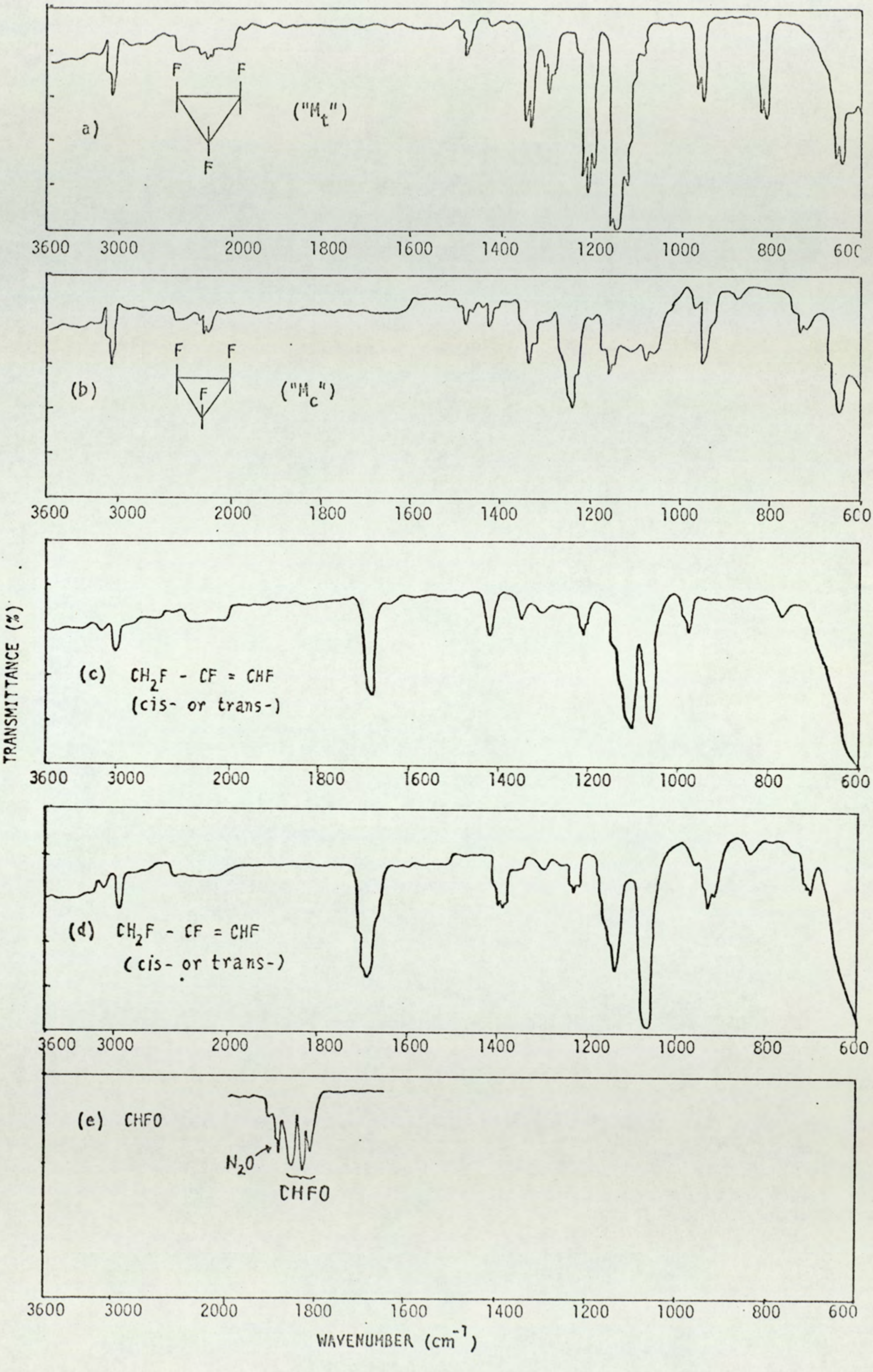


Fig. B3.3 MASS SPECTRA OF THE PRODUCTS FROM O(^{3}P) + CIS- CHF = CHF

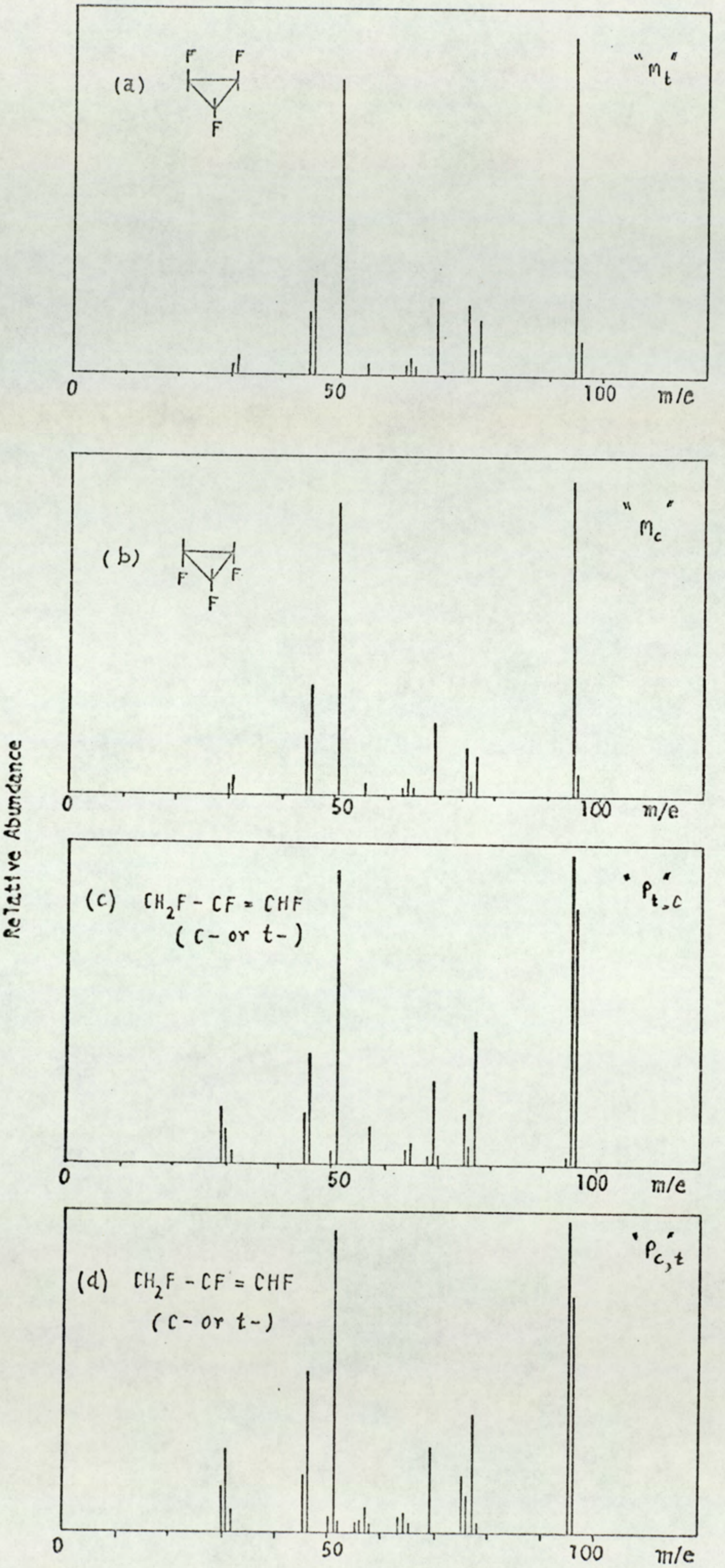


Fig. B3.4 EFFECT OF IRRADIATION TIME ON PRODUCT YIELDS.

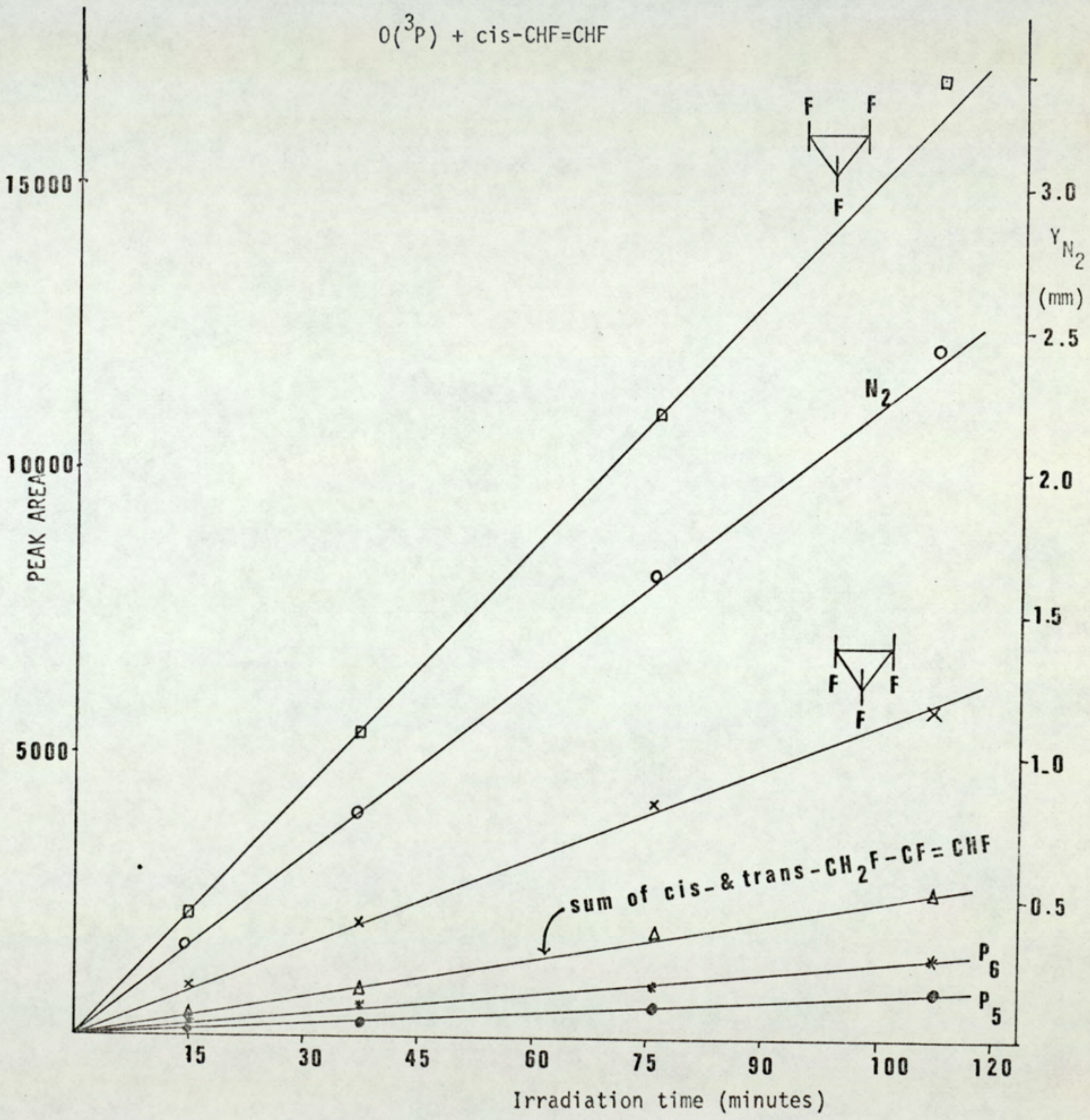


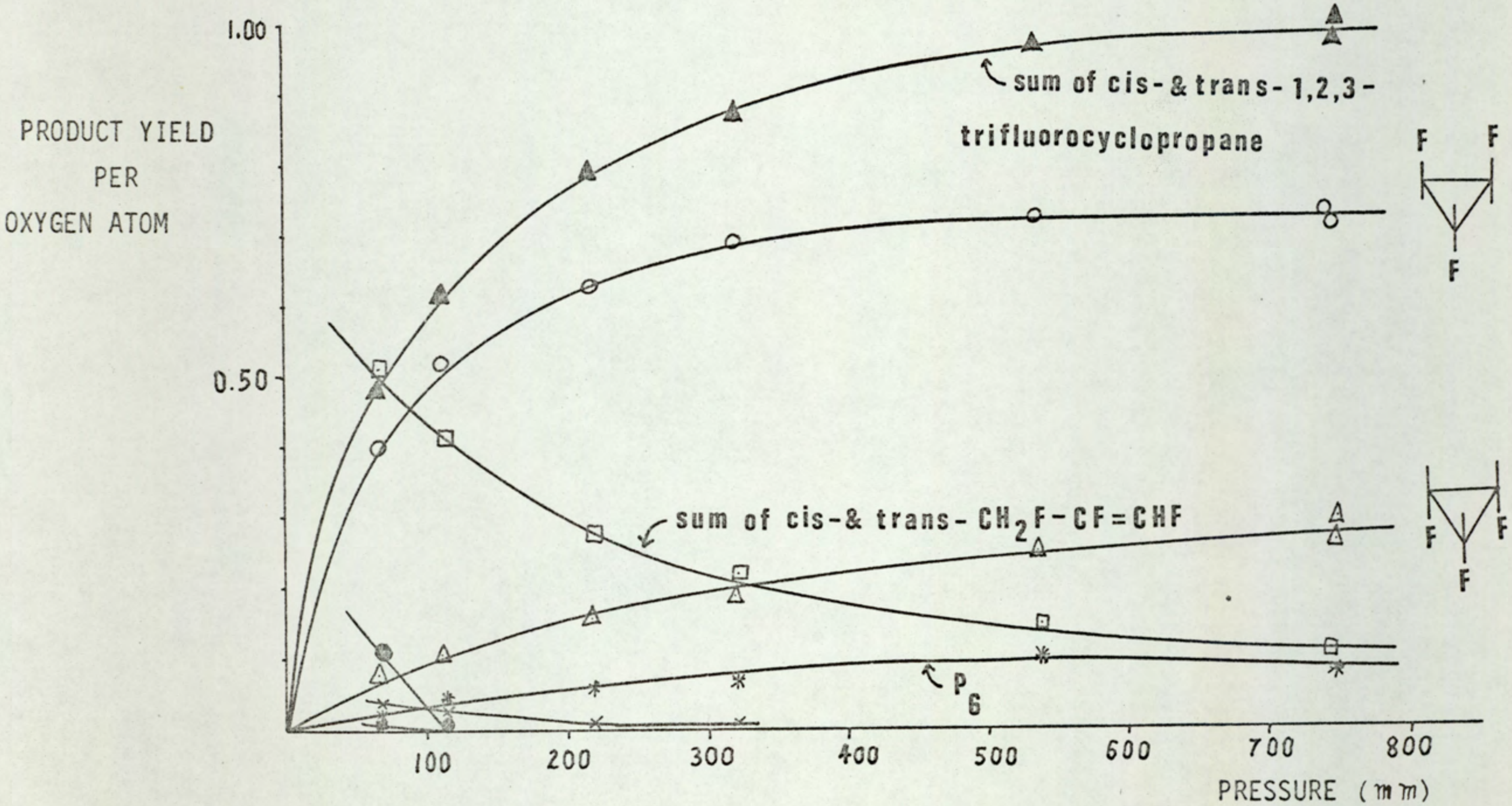
TABLE B3.1

The Effect of Pressure on Product Yields

(Quantum yields expressed as yields of products per yields of nitrogen)

Pressure (mm)	P_1	P_2	P_3	P_4	Δ (a)		(b) cis- and trans- $CH_2F.CF{=}CHF$	a + b	P_5	P_6	ϕ_{total}
					trans-	cis-					
749.0	-	-	-	-	0.72	0.28	0.10	1.10	0.04	0.06	1.20
66.0	0.10	0.02	0.04	0.01	0.40	0.07	0.52	0.99	0.05	0.02	1.23
320.5	-	-	0.007	-	0.68	0.18	0.22	1.08	0.06	0.05	1.20
113.0	0.05	0.01	0.02	0.008	0.52	0.10	0.41	1.03	0.06	0.04	1.22
536.7	-	-	-	-	0.72	0.25	0.14	1.11	0.06	0.06	1.23
218.5	-	0.005	0.01	-	0.63	0.16	0.27	1.06	0.05	0.05	1.18
742.5	-	-	-	-	0.73	0.29	0.10	1.12	0.03	0.06	1.21

Fig. B3.5 PRESSURE EFFECT ON THE YIELDS OF CHF + CIS-CHF = CHF



B3.3 EFFECT OF PRESSURE VARIATION

Variation of quantum yields of the major and minor products with pressures are shown in Figure B3.5. Using the values of the detector calibration factor in Table A3.1, the effect of pressure variation on the quantum yield of the products are summarized in the table (B3.1).

B3.4 EFFECT OF LIGHT INTENSITY

Table B3.2 shows the effect of light intensity on the product yields of this reaction. Two standard runs were carried out under the same condition as used for the pressure dependence runs. Light intensity was reduced by inserting a double layer of fine copper gauze between cell window of the reaction vessel and lamp. The transmission of the gauze at 253.7 nm has previously been measured on an SP 700 UV spectrometer and was found to be 12.5%. The reduction of the nitrogen yield indicated the reduction in the incident light intensity. The results in Table B3.2 were carried out at the irradiation time of 120 minutes, and the nitrogen yield was found to be only 0.268 mm. This corresponds to a reduction of light intensity to 7.2% compared with the standard runs.

It can be seen that the quantum yield of the products are not affected by reducing the light intensity. The reducing of light intensity on the quantum yield of formyl fluoride is assumed to have no effect, since the quantum yield of cis- and trans- 1,2,3-trifluorocyclopropane are not affected.

TABLE B3.2

The Effect of Light Intensity on Product Yields

(Quantum yields expressed as yields of products per yields of nitrogen)

Irradiation time (min)	P_{N_2} (mm)	1,2,3-trifluoro cyclopropane		the sum of cis- and trans- 1,2,3-trifluoropropylene	P_5	P_6
		cis-	trans-			
25'.45"	0.406	0.27_5	0.72	0.10_3	0.05	0.08
*120'	0.274	0.28_2	0.73	0.10	0.04_5	0.08_3
*120'	0.263	0.28	0.72_9	0.10_4	0.05_2	0.08_2
25'.45"	0.450	0.28_5	0.72_6	0.09_9	0.04_7	0.07_8

* Indicates runs with the light intensity reduced.

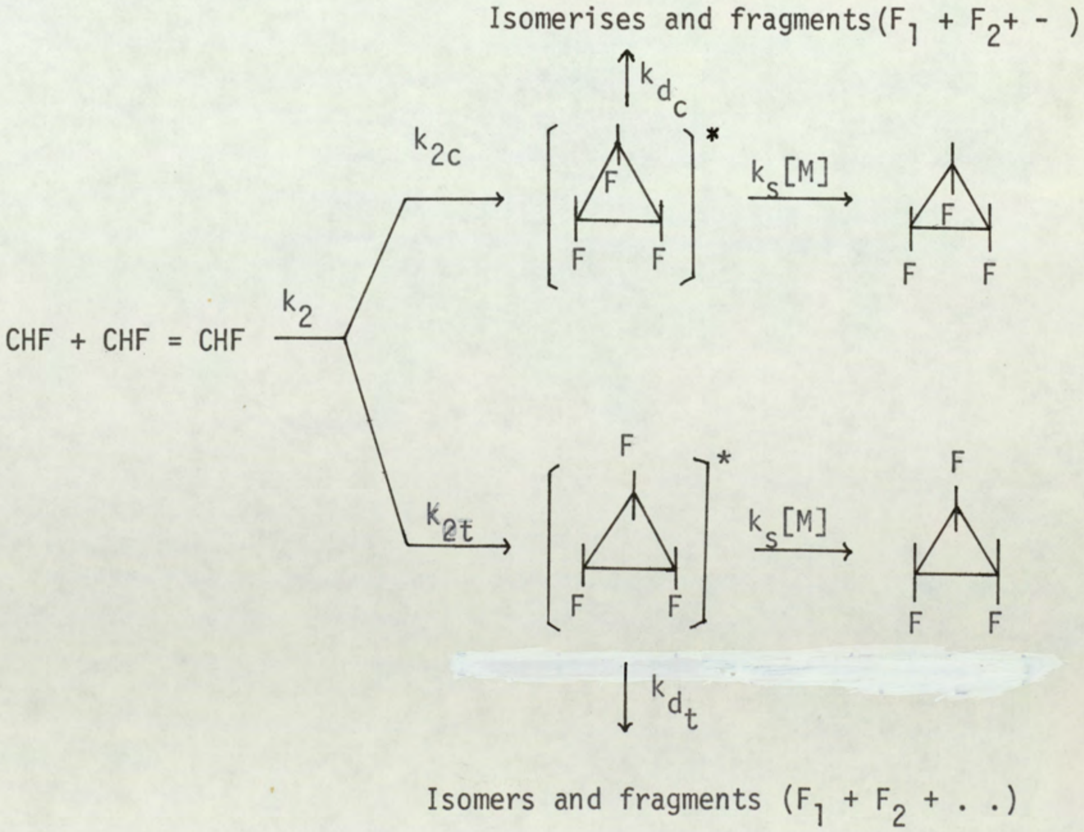
B3.5 MECHANISM OF THE REACTION OF OXYGEN ATOMS WITH CIS-CHF = CHF

The main products of this reaction are cis- and trans- 1,2,3-trifluorocyclopropane, cis- and trans- 1,2,3-trifluoropropylene. An attempt has been made to formulate a mechanism which satisfactorily explains the formation of products and corresponds to the experimental results. The main feature of the mechanism is the formation of separate "hot" cis- and trans- cyclopropanes without isomerization. The full mechanism is as follows:

$$\mathrm{Hg}(^{1}\mathrm{So}) + h\nu(253.7\ \mathrm{nm}) \longrightarrow \mathrm{Hg}^{*}\ (^{3}\mathrm{P}_{1}) \tag{1}$$

$$\mathrm{Hg}^{*}\ (^{3}\mathrm{P}_{1}) + \mathrm{N_{2}O} \longrightarrow \mathrm{Hg}(^{1}\mathrm{So}) + \mathrm{N_{2}} + \mathrm{O}(^{3}\mathrm{P}) \tag{2}$$

$$\mathrm{O}(^{3}\mathrm{P}) + \mathrm{CHF = CHF} \xrightarrow{k_{1}} \mathrm{CHFO} + \alpha\ \mathrm{CHF} \tag{3}$$



The following stationary concentrations of the intermediates are obtained by steady state application

$$[O] = R_{N_2}/k_1 \, [CHF = CHF]$$

$$[CHF] = \alpha \, R_{N_2}/k_2 \, [CHF = CHF]$$

$$[C - \Delta^*] = \alpha \, k_{2c} \; R_{N_2}/k_2(k_{dc} + k_s[M])$$

$$[t - \Delta^*] = \alpha k_{2t} \; R_{N_2}/k_2 \, (k_{dt} + k_s[M])$$

The rate of formation of the stabilized cis- and trans- cyclopropane are denoted by $R_{c\Delta}$ and $R_{t\Delta}$ respectively and Q_Δ is defined by R_Δ/R_{N_2}.

$$R_{c\Delta} = k_s[M] \, [C - \Delta^*]$$

$$Q_{c\Delta} = \alpha k_{2c} k_s [M]/k_2(k_{dc} + k_s[M])$$

$$\frac{1}{Q_{c\Delta}} = \frac{k_2 k_{dc}}{\alpha k_{2c} k_s} \cdot \frac{1}{[M]} + \frac{k_2}{\alpha k_{2c}}$$

Similarly

$$\frac{1}{Q_{t\Delta}} = \frac{k_2 k_{dt}}{\alpha k_{2t} k_s} \cdot \frac{1}{[M]} + \frac{k_2}{\alpha k_{2t}}$$

where $k_2 = k_{2c} + k_{2t}$

Since [M] represents total pressure, P, plots of $1/Q_{c\Delta}$ vs 1/P and $1/Q_{t\Delta}$ vs 1/P should be linear with ratio of slope to intercept equal to k_{dc}/k_s and k_{dt}/k_s respectively. The good linearity of these plots are obtained as shown in Figure B3.6. The plot of $1/Q_{c\Delta} + Q_{t\Delta}$ vs 1/P also gives a linear relationship (see Figure B3.6).

The lifetimes of "hot" cis- and trans- fluorocyclopropane have been estimated and are given below.

TABLE B3.3

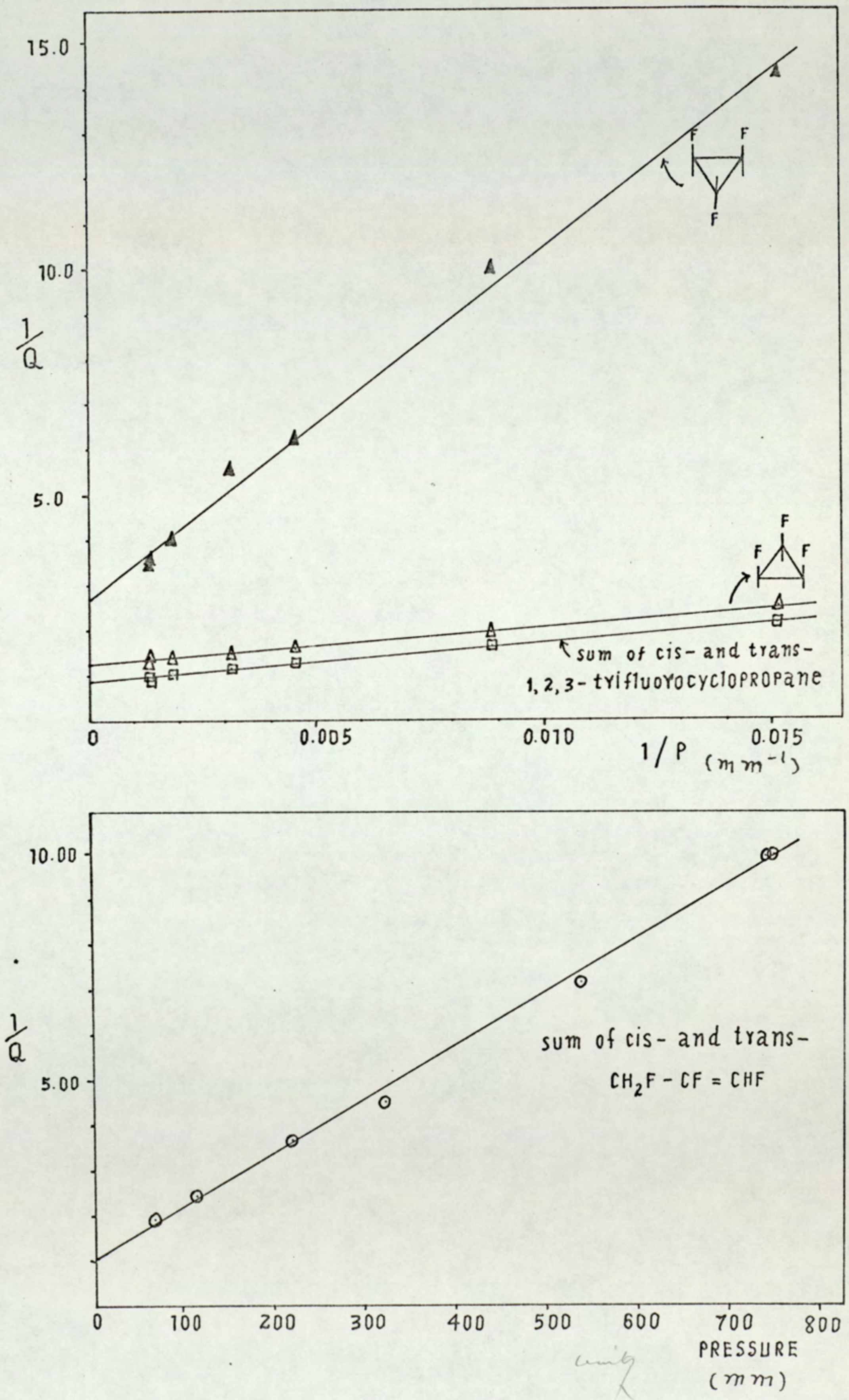
Lifetimes of "Hot" Addition Products

"Hot" products	$\frac{k_d}{k_s}$	Lifetime (sec)
trans-1,2,3-trifluorocyclopropane	65.77	9.5×10^{-10}
cis-1,2,3-trifluorocyclopropane	268.34	2.3×10^{-10}

Using $k_s = 1.6 \times 10^7$ mm^{-1} sec^{-1}

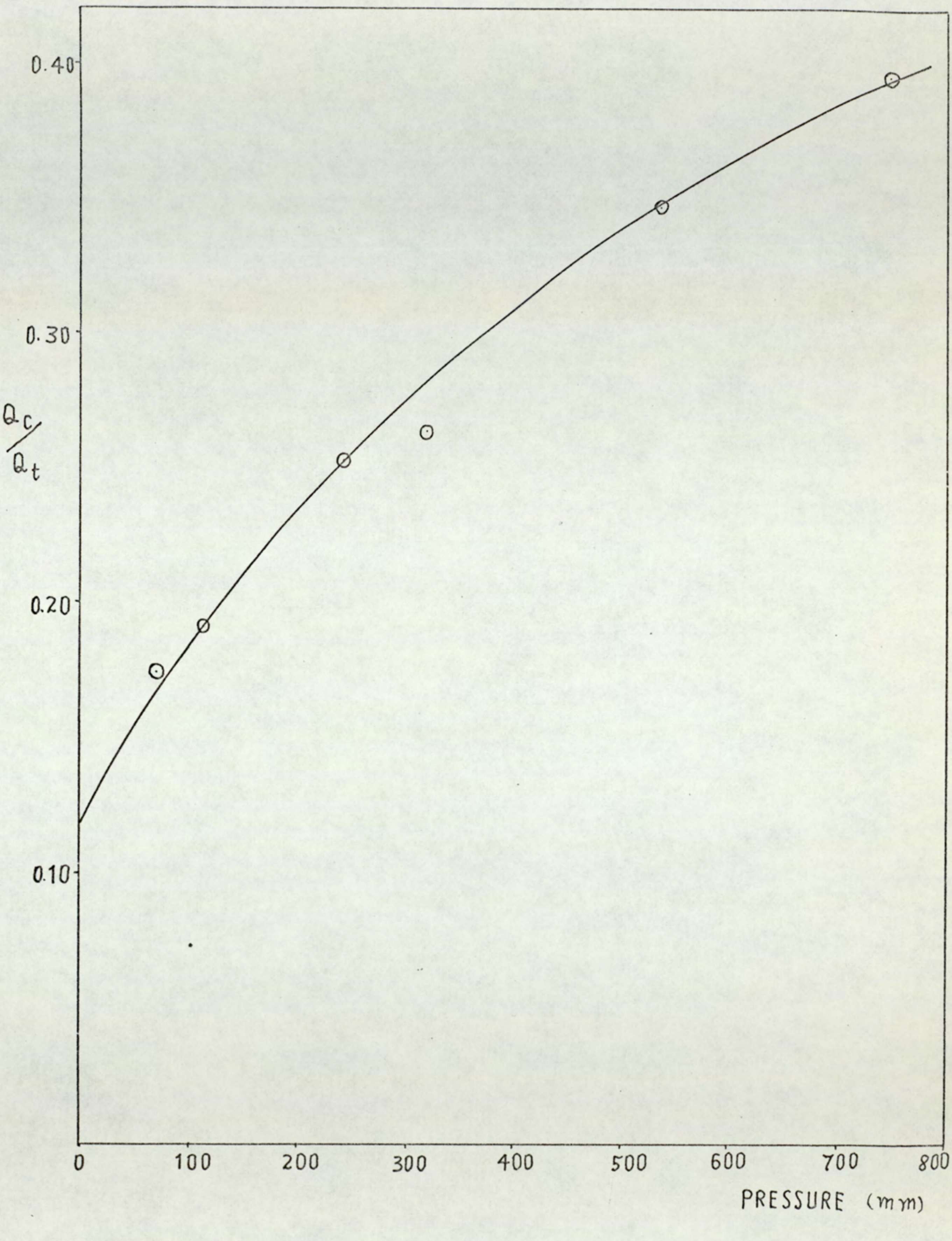
It can be seen that the lifetime of "hot" cis-trifluorocyclopropane is shorter than "hot" trans-isomer, i.e. $k_{dc\Delta} > k_{dt\Delta}$. This explains the decrease in Q_c/Q_t at lower pressures (as shown in Figure B3.7) without necessarily requiring isomerisation of the "hot" cis-cyclopropane to the "hot" trans-cyclopropane.

Fig. B3.6 PLOTS OF 1/Q AGAINST 1/P AND 1/Q AGAINST P.



unity

FIG. B3.7 PLOT OF Q_c / Q_t AGAINST P.



Consider the other products which can be formed from the "hot" fluorocyclopropane before stabilization by collision

$$\begin{tikzcd}
 & (C - \Delta)^* \arrow[r, "k_{dc}"] & F_1 + F_2 + - - - \\
CHF + CHF = CHF \arrow[ur, "k_{2c}"] \arrow[dr, "k_{2t}"'] & & \\
 & (t - \Delta)^* \arrow[r, "k_{dt}"] & F_1 + F_2 + - - -
\end{tikzcd}$$

Writing the rate of formation of F from "hot" cis- and trans-fluorocyclopropane as R_{Fc} and R_{Ft} respectively and defining Q_F as R_F/R_{N_2}.

$$R_{Fc} = k_{dc} [C - \Delta^*]$$

and $$R_{Ft} = k_{dt} [t - \Delta^*]$$

$$\frac{1}{Q_{Fc}} = \frac{k_2 k_s}{\alpha k_{2c} k_{dc}} . [M] + \frac{k_2}{\alpha k_{2c}}$$

similarly

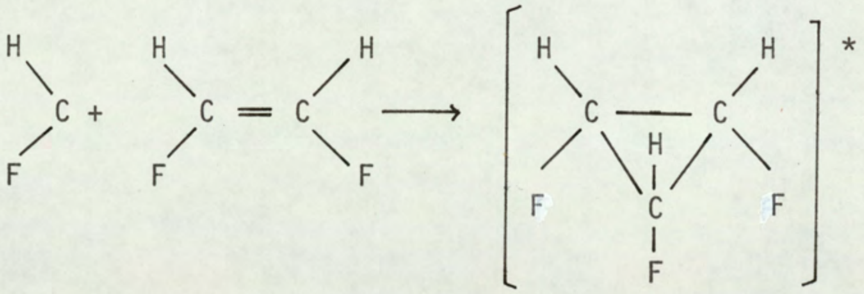
$$\frac{1}{Q_{Ft}} = \frac{k_2 k_s}{\alpha k_{2t} k_{dt}} . [M] + \frac{k_2}{\alpha k_{2t}}$$

Thus, a plot of $1/Q_{Fc}$ vs P and $1/Q_{Ft}$ vs P should be linear with ratio of slope to intercept equal to k_s/k_{d_c} and k_s/k_{dt} respectively. Unfortunately, both "hot" cis- and trans- trifluorocyclopropane decompose to give the same products in this system, therefore the plots of these equations cannot be obtained separately. However, a good linear plot of $1/Q_{F_1} + Q_{F_2}$ vs P is observed as shown in Figure B3..6.

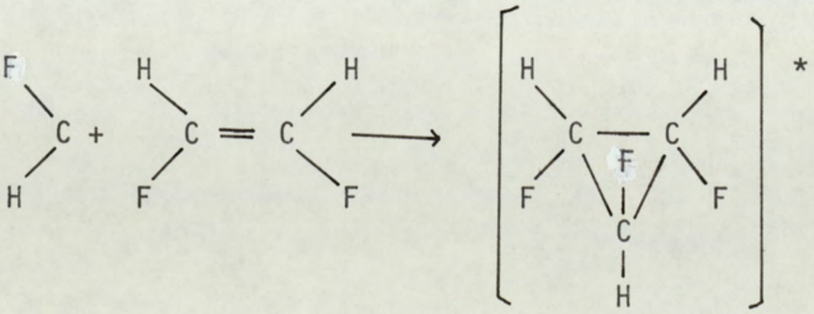
The major reaction products, cis- and trans- 1,2,3-trifluorocyclopropane, accounted for about 90% of the total addition products derived from CHF radicals at pressure greater than 550 mm Hg. The good linearity of the plots based on previous equations (see Figure B3.6) substantially confirm the validity of the mechanism proposed.

Although isomerization of the "hot" products to the other cyclopropane would be expected, none of cis- 1,2,3-trifluorocyclopropane is formed from trans- CHF = CHF. We have therefore been prepared to accept that no isomerization occurs here.

Both the "hot" cis- and trans-cyclopropane can be formed directly in this reaction due to the orientation of the CHF,



cis- 1,2,3-trifluorocyclopropane



trans-1,2,3-trifluorocyclopropane

which may be stabilized by collision to form cis- and trans-trifluorocyclopropane as the final products, or fragment to form cis- and trans-trifluoropropylene before stabilization can occur.

The results described previously showed that the lifetime of "hot" trans- 1,2,3-trifluorocyclopropane which formed from the reaction of CHF with trans- CHF = CHF is shorter than the one from the reaction of cis-isomer. This could possibly be explained in terms of the difference in the stability of cis- and trans- CHF=CHF. For the isomerization equilibrium$^{(111)}$

$$\text{cis- CHF = CHF} \rightleftharpoons \text{trans- CHF = CHF}$$

the cis-isomer is thermodynamically more stable, $\Delta H^{o}_{c\rightarrow t}$= 4180 J mole^{-1}. The transition states for both isomers may be identical or different. This situation can be represented by the following energy diagram.

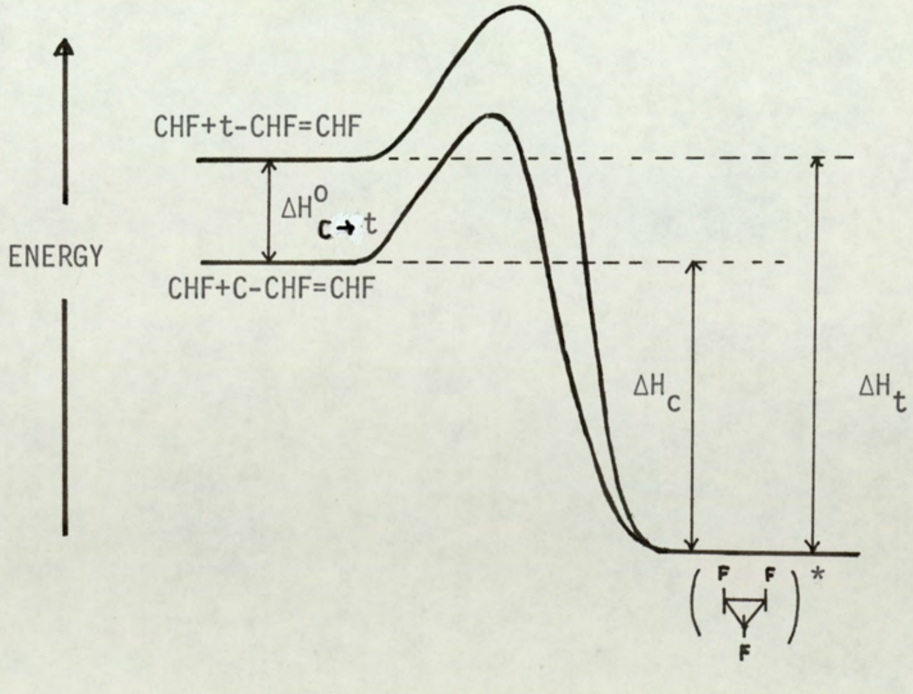


Fig. B3.8 SCHEMATIC REACTION PATHS FOR THE CHF + 1,2-DIFLUOROETHYLENE

The fact that the lifetime of "hot" product depend on the amount of excess energy and on the size of the molecule. For the molecules of equal size, the lifetime decreases with increasing amount of excess energy. From the above diagram it can be seen that $\Delta H_t > \Delta H_c$, i.e. $\tau_t < \tau_c$, as found experimentally.

B3.6 ESTIMATION OF HEATS OF REACTION

Heats of formation of CHF and cyclo-$C_3H_3F_3$ have not been reported. Rough estimates of these values can be made by selecting the compounds of similar structure whose heats of formation are known, i.e. ΔH_f^o for CHF can be obtained by taking arithmetic mean values of CH_2(368 kJ mole^{-1}) and CF_2(-163 kJ mole^{-1}).

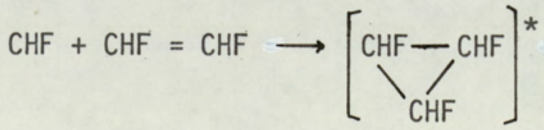
$$\Delta H_f^o \text{ for CHF } \cong 103 \pm 10 \text{ kJ mole}^{-1}$$

Similarly, ΔH_f^o for cyclo-$C_3H_3F_3$ can be estimated from the difference in heats of formation of cyclo-C_3H_6 (55 kJ mole^{-1}) and cyclo-C_3H_5F (-129 kJ mole^{-1}).

$$\Delta H_f^o \text{ for cyclo-}C_3H_3F_3 = 3(-184) + 55 = -497 \text{ kJ mole}^{-1}$$

Jones$^{(68)}$ has estimated the value of ΔH_f^o for CHF = CHF,

$$\Delta H_f^o \text{ for CHF = CHF} = -314 \text{ kJ mole}^{-1}$$



(A)

heat of reaction (A) = -497 - [103 + (-314)]
= -286 kJ mole^{-1}

A collection of heats of reaction of the addition of radicals species to ethylene and fluoroethylene is shown below.

TABLE B3.4

Heats of Reaction of the Reaction of Radicals with Olefins

Olefin	Radical	Hot Product	ΔH_f
$CH_2 = CH_2$	CH_2	cyclo-C_3H_6	-365
trans-CHF = CHF	CHF	trans-cyclo-$C_3H_3F_3$	-286
cis-CHF = CHF	CHF	cis- or trans-cyclo-$C_3H_3F_3$	-290
$CF_2 = CF_2$	CF_2	cyclo-C_3F_6	-129

Since the main mechanism of the reactions studied in this work involved unimolecular reaction process, it will be appropriate to estimate the relative rates of decomposition of the "hot" product based on the following equation$^{(137)}$.

$$k = A\left(\frac{E - E^o}{E^o}\right)^s$$

where k = rate of decomposition of the reaction

A = Pre-exponential factor

E = energy i.e. heat of reaction

E^o = activation energy

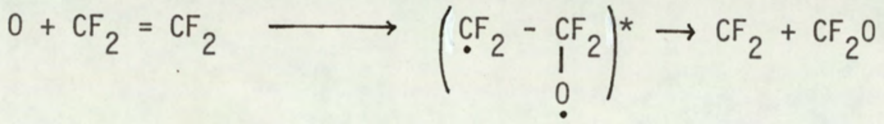
s = active vibrational modes (typically about half the total)

The activation energy is not available for the reaction of CHF + CHF = CHF. Using the plausible value of E^o = 210-230 kJ mole^{-1}, E = ΔH = 280 - 295 kJ mole^{-1} (and $E_c = E_t$ -4 kJ mole^{-1}), S = 10 - 12, the value of k_{dc}/k_{dt} was estimated as 0.60 ± 0.30. It can be seen that the calculated result is in good agreement with the experimental result (k_{dc}/k_{dt} = 0.57).

SECTION C

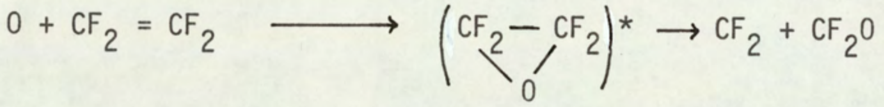
DISCUSSION AND CONCLUSIONS FOR $O(^3P)$+ 1,2-DIFLUOROETHYLENE

Heicklen$^{(57,62)}$ has reported that the reaction of oxygen atoms with tetrafluoroethylene yields carbonyl fluoride and difluoromethylene. The quantum yield for formation of carbonyl fluoride is then found to be near to unity. The structure of the oxygen containing intermediate is probably the excited biradical or epoxide.

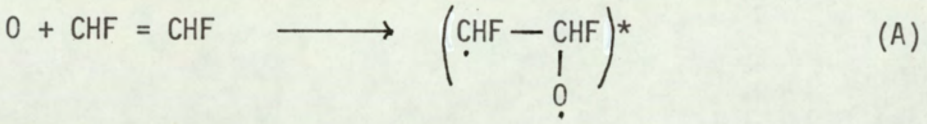


$$O + CF_2 = CF_2 \longrightarrow \left(\dot{C}F_2 - \underset{\dot{O}}{\underset{|}{CF_2}}\right)^* \longrightarrow CF_2 + CF_2O$$

or

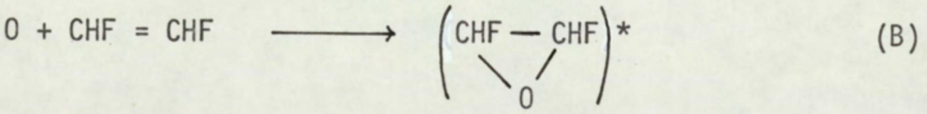


By analogy, the corresponding 1,2-difluoroethylene reaction would be

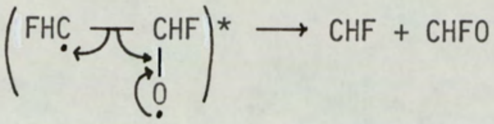


$$O + CHF = CHF \longrightarrow \left(\dot{C}HF - \underset{\dot{O}}{\underset{|}{CHF}}\right)^* \qquad (A)$$

or



No identified products of 1,2-difluoroethylene reactions had been found to be epoxide. This suggested that the intermediates (A) and (B) fragment almost completely. This is because the excited intermediate (A) or (B) is too short-lived to undergo stabilization within the pressure range investigated in this study. Since 1,2-difluoroethylene is a small molecule, its fragmentation occurs predominantly at all pressures below one atmosphere to form mainly formyl fluoride and monofluoromethylene, CHF.

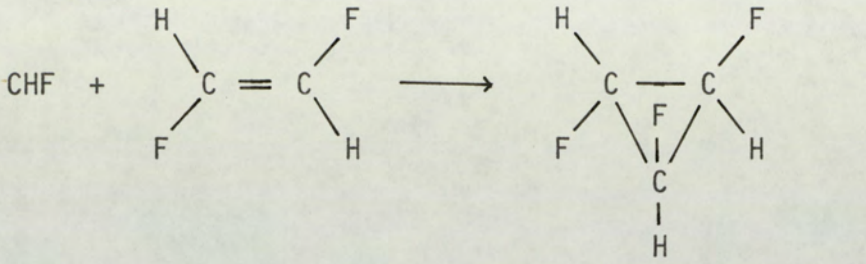


The CHF will then add to another molecule of 1,2-difluoroethylene to form a "hot" 1,2,3-trifluorocyclopropane which may be stabilized by collisional deactivation (or fragment). This has been described earlier in Section A and B.

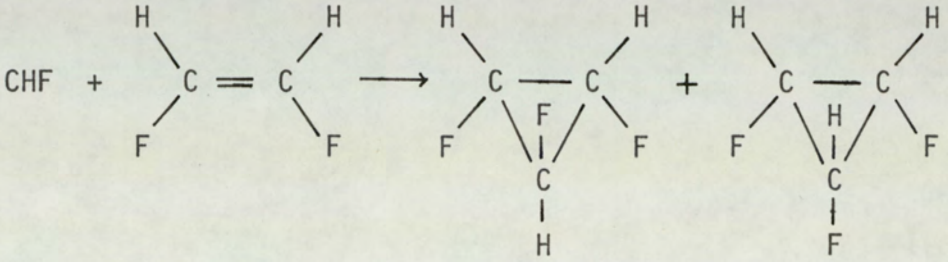
C3.1 Stereospecific Addition of CHF to 1,2-Difluoroethylene

It is known(119) that stereospecificity of the reactions of carbenes with olefinic substrates are evidence for the singlet electronic state of the reacting carbene. The reactions of singlet CF_2 with butene-2 have been found to be completely stereospecific.(136) It has also been found that singlet methylene adds to olefins stereospecifically, as described previously in Section 1.6.5). The reactions of CTF (from tritium recoil studies in CH_2F_2/T*) with cis- and trans- butene-2 have been investigated and are found to be almost entirely stereospecific. The ground electronic state of CTF has been concluded to be singlet(118).

The reactions of CHF with cis- and trans- 1,2-difluoroethylene provide a direct measurement of the yields of the stereospecific products. The stereospecificity of these reactions can be illustrated by the following schemes.



only



mainly

The observations imply that the reaction involves either

a) the simultaneous formation of both C - C bonds, or

b) that the rate of ring closure must be faster than the rate of rotation around the C - C bonds formed in first step. The explanation that the simultaneous formation of both C - C bonds seems to be more likely.

TABLE C3.1

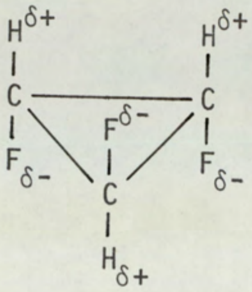
Stereospecific Addition of CHF with cis- and trans- CHF = CHF

Units

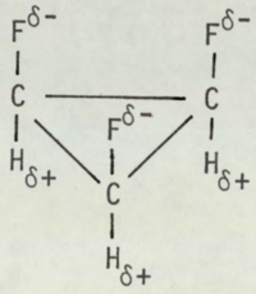
Reaction	Quantum Yield of Product *	
	trans-1,2,3-trifluoro-cyclopropane	cis-1,2,3-trifluoro cyclopropane
CHF + t - CHF = CHF	0.725 ± 0.2	≯ 0.002
CHF + cis- CHF = CHF	0.72 ± 0.2	0.28 ± 0.2

* total pressure = 750 mm.

The most stable of trans-1,2,3-trifluorocyclopropane could be explained by electron repulsion principle.

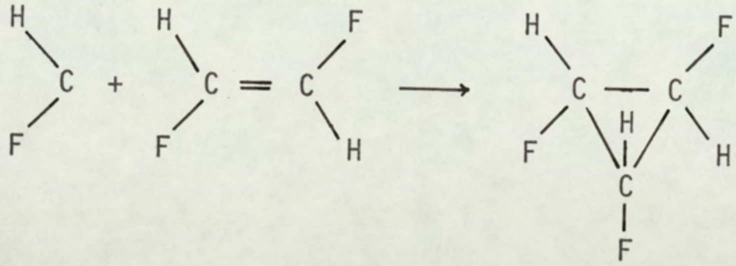


trans-1,2,3-trifluorocyclopropane



cis-1,2,3-trifluorocyclopropane

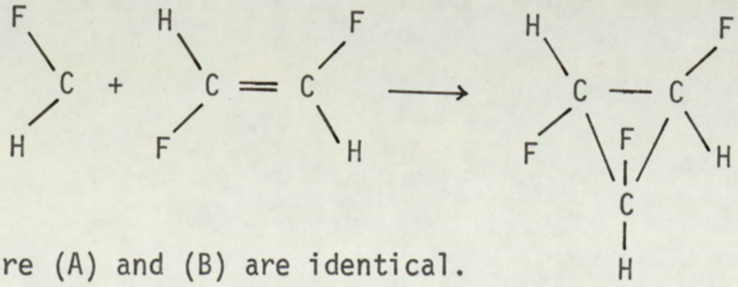
In trans-isomer, the atoms of the same relative charge are further apart from each other. This would be more stable than the situation in cis- isomer where atoms of the same relative charge are on the adjacent sites. Starting with trans-CHF = CHF, the only possibility is to form trans- adduct unless isomerization of the "hot" cyclopropane occurs. So whatever the orientation of addition of the CHF radical the product will always be trans- 1,2,3-trifluorocyclopropane:



(A)

or

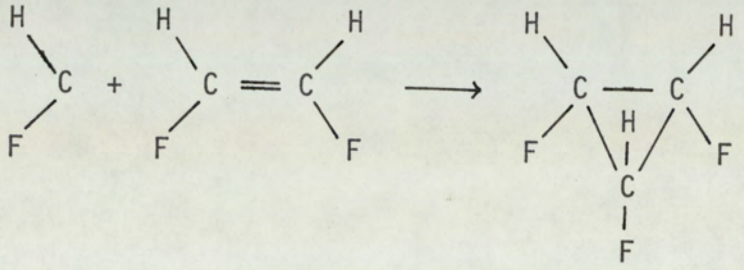
trans-trifluorocyclopropane



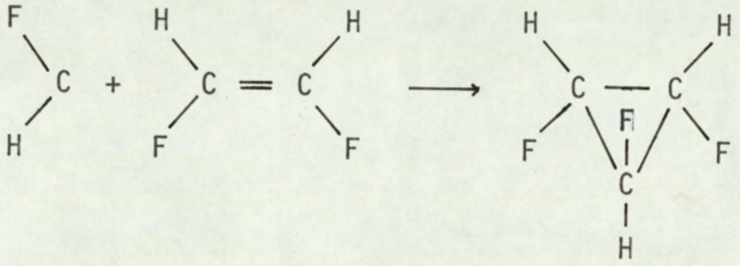
(B)

where (A) and (B) are identical.

However, starting with cis- CHF = CHF, there are two possibilities that the products can be formed in both cis- and trans- isomers due to the orientation of CHF radical.

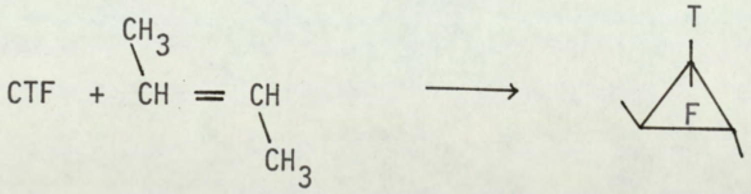

cis-trifluoro-cyclopropane

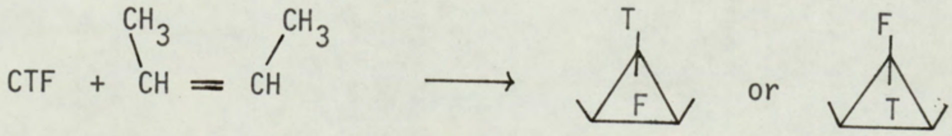
and


trans-trifluoro-cyclopropane

The trans-isomer is always formed preferentially.

The results are in good agreement with those of Tang and Rowland(118) who found that the reaction of CTF with cis- and trans-butene-2 involves single-step addition of CTF to an olefin.





C3.2 Electronic State of CHF

Tang and Rowland(118) have concluded that the CTF produced in their system is the singlet ground electronic state based on the following evidence:

a) the stereospecific reaction of CTF with olefins

b) the yield of the products are not affected by small amounts of molecular oxygen.

c) the lack of change in the observed stereospecificity of reaction in the large excess of neon.

In this study, the CHF radicals also exhibit the stereospecific reactions with 1,2-difluoroethylene and the reaction products are not affected by small amounts of molecular oxygen. This suggests that the electronic state of CHF observed in this experiment is probably the singlet state.

In principle the CHF which formed by the reaction of $O(^3P)$ with 1,2-difluoroethylene should be in triplet state by spin conservation rule.

$$O(\uparrow\uparrow) + CHF = CHF(\uparrow\downarrow) \longrightarrow CHFO(\uparrow\downarrow) + CHF(\uparrow\uparrow)$$

It is known(92) that the energy difference between singlet and triplet CHF is very small (< 5 kJ $mole^{-1}$), the intersystem crossing $CHF(\uparrow\uparrow) + M \rightarrow CHF(\uparrow\downarrow) + M$ may actually occur within the pressure range investigated in this study. Since the CHF observed in this experiment showed singlet state behaviour, this suggests that the triplet CHF formed primarily has been deactivated to singlet state almost exclusively, and the energy gap between the two states cannot be too small.

C3.3 CHF Insertion Reaction

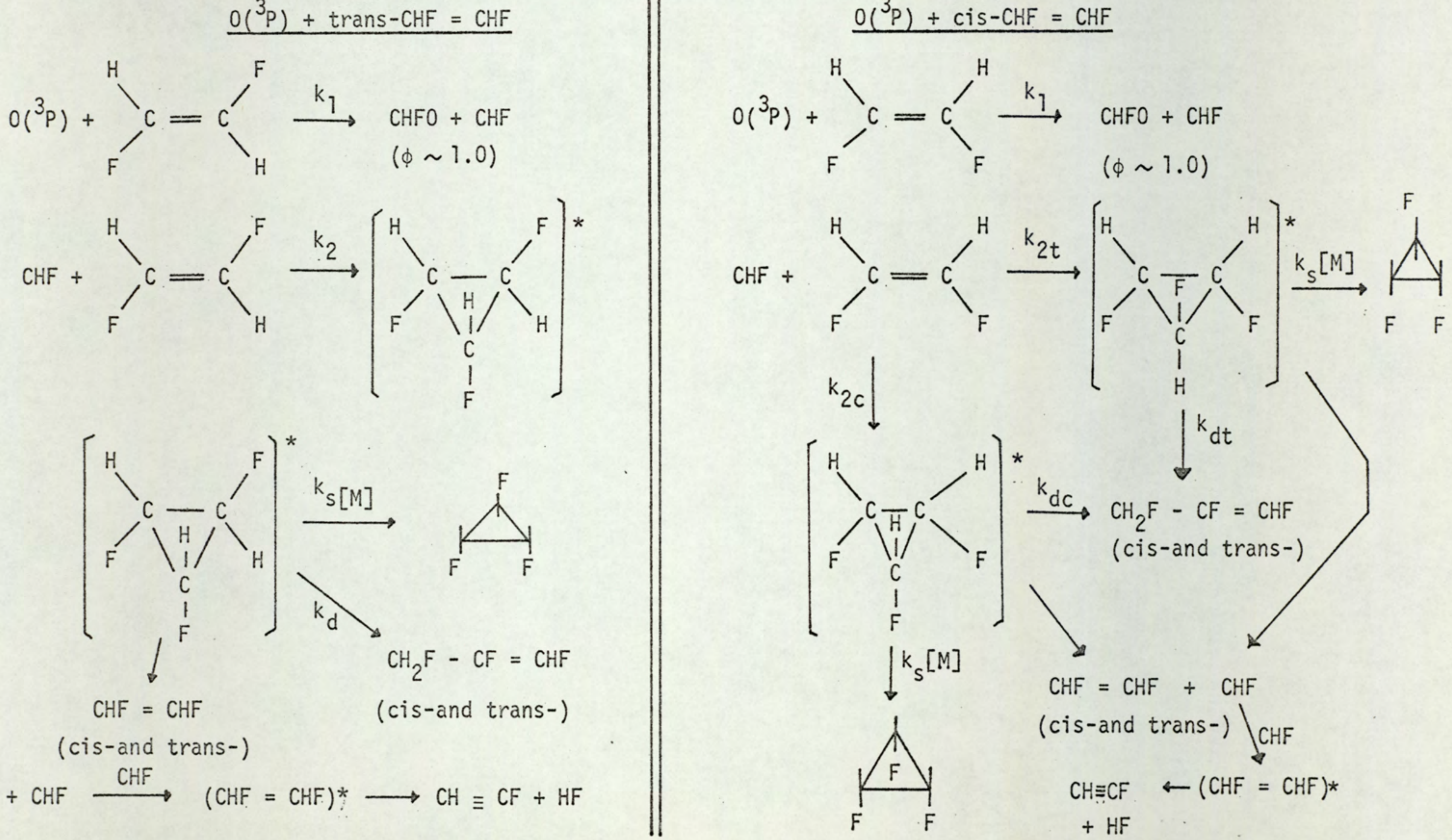
It is generally known that the singlet CH_2 inserts$^{(119)}$ into the C-H bond of ethylene to form propylene.

$$CH_2(\uparrow\downarrow) + CH_2 = CH_2 \longrightarrow CH_3 - CH = CH_2$$

It is surprising that CTF does not insert into the C-H bond of ethylene to form 3-fluoropropylene-t. No explanation has been given. The insertion reaction has always been observed in the case of unsubstituted methylene itself.

In this experiment, the formation of cis- and trans-trifluoropropylene is believed to occur by the fragmentation of "hot" trifluorocyclopropane with hydrogen atom transfer. Since these two products show a very marked pressure dependence and a good linear relation of the plot of 1/Q VS P is obtained, it is concluded that CHF does not insert into the C-H bond of 1,2-difluoroethylene.

THE PROPOSED REACTION MECHANISM OF $O(^3P)$ + 1,2-DIFLUOROETHYLENE



$O(^3P)$ + trans-CHF = CHF

$O(^3P)$ + cis-CHF = CHF

CHAPTER FOUR

REACTION OF OXYGEN ATOMS WITH TRIFLUOROETHYLENE

4.1 NATURE OF PRODUCTS

The products were collected by GLC from standard high conversion runs on the 4 m, porapak Q column. The products not isolable were investigated by various alternative techniques. The chromatograms of the reaction of oxygen atom with trifluoroethylene are shown in Figure 4.1. Using the methods of analysis described previously in Section 2.3, the following products were identified: carbonyl fluoride, formyl fluoride, cis- and trans- 1,2,3,3-tetrafluorocyclopropane, cis- and trans- 1,2,3,3-tetrafluoropropylene, cis- and trans- 1,2-difluoroethylene, pentafluorocyclopropane and tetrafluoroethylene. The method of identification and indication of the peak size of these products are given in Table 4.1.

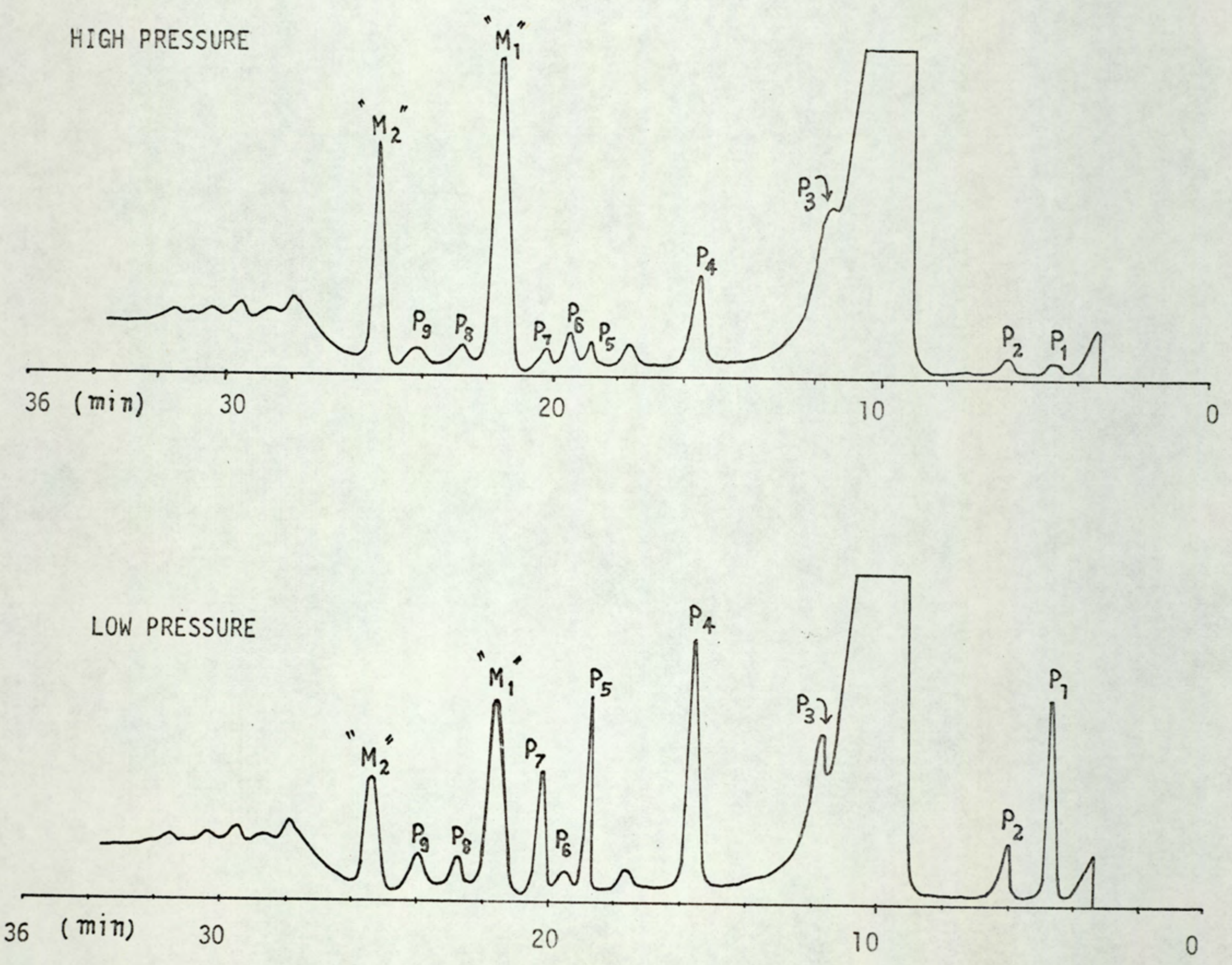
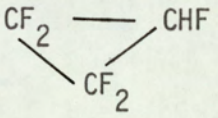
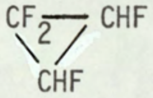
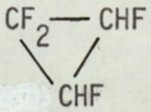


Fig. 4.1 GAS CROMATOGRAMS FOR THE REACTION OF $O(^3P) + CF_2 = CHF$

TABLE 4.1

The Reaction Products from $O(^3P) + CF_2 = CHF$

Product	Formula	Method of Identification	Peak Area (Arbitrary Unit)	
			High P. (758 cmm)	Low P. (56.8 mm)
1	$CF_2 = CF_2$	enrichment angle	750	1750
2	$CH \equiv CF$	?		
3	t-CHF = CHF	IR	1435	2420
4	c-CHF = CHF	IR	1740	3054
5	CHF_2-CF = CHF (cis- or trans)	IR and MS	492	890
6		mixed run $CF_2 = CF_2$ + $CF_2 = CHF$	685	-
7	$CH_2F - CF = CF_2$	?	120	325
M_1	t - 	IR and MS	3680	305
8	$CHF_2 - CF = CHF$ (isomer of No.5)	IR and MS	336	671
9	$CHF_2 - CF = CF_2$	?	137	332
M_2	C - 	IR and MS	2535	528

MS represents mass spectrometry

IR represents infra-red spectroscopy

Fig. 4.2 MASS SPECTRA OF PRODUCTS FROM $O(^3P) + CF_2 = CHF$

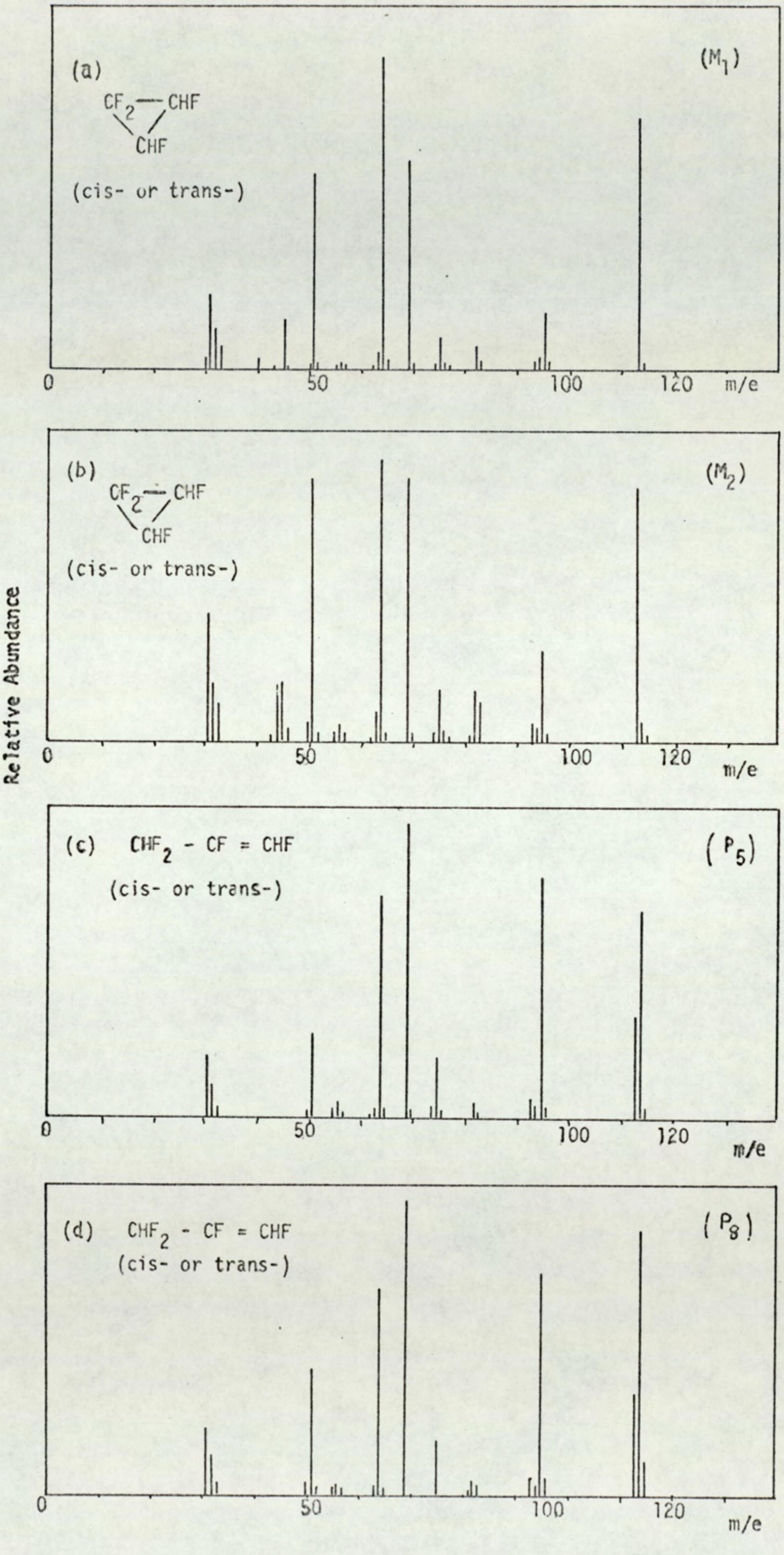
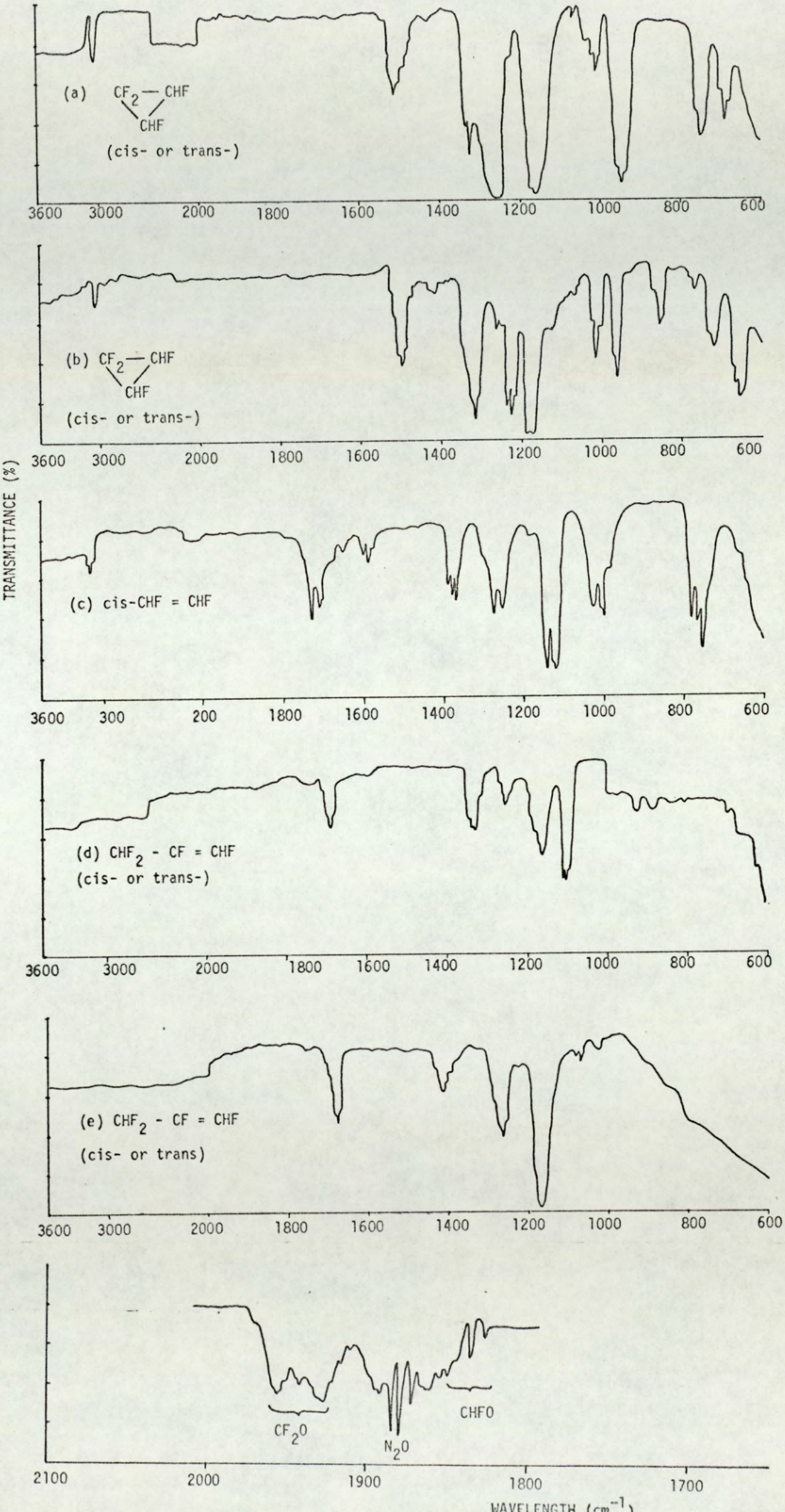


Fig. 4.3 SPECTRA OF THE PRODUCTS FROM $O(^3P) + CF_2 = CHF$



cis- and trans- 1,2,3,3-tetrafluorocyclopropanes

These two products, "M_1" and "M_2" were identified unambiguously by mass spectrometry and infra-red spectroscopy as tetrafluorocyclopropanes. Identical mass spectra of these products were obtained and were found to have molecular formulae $C_3H_2F_4$. A parent peak of molecular weight, M = 114 and a large $(P - 1)^+$ peak at M = 113 suggested the presence of cyclopropane structure. The infra-red spectra of "M_1" and "M_2" had a medium absorption band at 3060 cm^{-1} which could be assigned a $\nu(C - H)$ stretching vibration of cyclopropane and contained no band attributable to C = C stretching. Infra-red and mass spectra as well as the chemical studies strongly suggested that the compounds "M_1" and "M_2" were the isomeric cis- and trans- 1,2,3,3-tetrafluorocyclopropanes. The possible isomers of these two products can not be distinguished from the spectra available.

Carbonyl fluoride (CF_2O) and Formyl fluoride(CHFO)

The presence of carbonyl fluoride and formyl fluoride were examined by infra-red spectroscopy. The medium absorption bands at 1926, 1942, 1955 cm^{-1} and the weak bands at 1849, 1834 and 1819 cm^{-1} were observed in the infra-red spectrum of the reaction of $O(^3P) + CF_2 = CHF$ which corresponded to the carbonyl stretching vibration of CF_2O(57) and CHFO(135) respectively.

Tetrafluoropropylene

Products P_5 and P_8 were found by mass spectrometry and infra-red spectroscopy to be tetrafluoropropylenes. (see Figures 4.2 and 4.3).

Product P_7 was not collected because too small an amount of product was formed. It was believed to be another tetrafluoropropylene. The chemical studies suggested that two of these products must be cis- and trans- 1,2,3,3-tetrafluoropropylene and the other one is 1,1,2,3-tetrafluoropropylene.

Tetrafluoroethylene

It was difficult to collect this product, P_1, from the reaction mixture because its retention time was very close to nitrous oxide. However, it was identified by following alternative method.

The reaction mixture of oxygen atoms with trifluoroethylene was analysed by GLC, peak area of product P_1 was measured. A small amount of authentic sample of C_2F_4 was added into the reaction mixture, after mixing thoroughly, the mixture was again analysed on GLC, the peak area of product P_1 was found to increase. This indicated that this product must be tetrafluoroethylene.

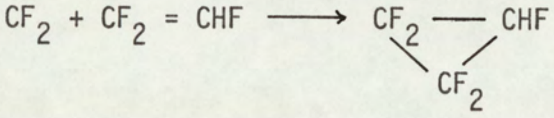
Cis- and trans- 1,2-difluoroethylenes

Product P_3 was collected and its infra-red spectrum was found to be identical to the spectrum obtained from the authentic sample of cis-1,2-difluoroethylene(131). Product P_4 peak matched the retention time of an authentic sample of trans- 1,2-difluoroethylene onto the column used. The products P_3 and P_4 must be cis- and trans- 1,2-difluoroethylene respectively.

Pentafluorocyclopropane

This compound, P_6, was not collected because of too small peak. A sample of suspected fluorocyclopropane was prepared by the reaction of oxygen atom with tetrafluoroethylene and trifluoroethylene (ratio 9:1). The reaction of $O(^3P)$ with tetrafluoroethylene(57) yields mostly carbonyl fluoride and difluoromethylene (CF_2). The CF_2 radicals then add to trifluoroethylene to yield mainly pentafluorocyclopropane by the following mechanism:

$$O + CF_2 = CF_2 \longrightarrow CF_2O + CF_2$$



The retention time of product P_6 was found to be identical to that of the cross product, pentafluorocyclopropane, which formed in the mixed run of $O(^3P) + CF_2 = CF_2/CF_2 = CHF$. It appears therefore that this product must be pentafluorocyclopropane.

Unidentified products

Product P_2 eluted after tetrafluoroethylene peak on GLC was not collected. It was thought to be monofluoroacetylene. Product P_9 with long elution time was not collected because the small quantities formed made collection of a sufficient amount for analysis very difficult. This product was probably pentafluoropropylene.

4.2 CALIBRATION RESULTS

4.2(a) CALIBRATION OF THE FLAME IONIZATION DETECTOR

The flame ionization detector was calibrated for cis- and trans- 1,2,3,3-tetrafluorocyclopropane, cis- and trans- 1,2-difluoroethylene and tetrafluoroethylene. The results are summarized in Table 4.2.

TABLE 4.2

Detector Calibration Factor

Run No.	Pressure at 23 ± 2^{o}C (mm) in V_1(3.95ml)	Pressure at 23 ± 2^{o}C (mm) in RV(760ml)	Mean area of Peak at 5=1x10^{2} (Arbitrary units)	Calibration factor
(a) 1,2,3,3-tetrafluorocyclopropane				
1	57.0	0.2964	3640	8.15×10^{-5}
2	66.9	0.3481	4460	7.80×10^{-5}
3	37.0	0.1925	1970	9.973×10^{-5}
			Mean =	8.64×10^{-5}
calibration factor for tetrafluorocyclopropane =				$8.6 \pm 1.5 \times 10^{-5}$
(b) 1,2- difluoroethylene				
	93.0	0.483	8250	5.85×10^{-5}
(c) tetrafluoroethylene				
	94.0	0.488	5280	9.25×10^{-5}

It has been assumed that cis- and trans- 1,2,3,3-tetrafluoropropene and pentafluorocyclopropane have the same response factor as cis- and trans-

1,2,3,3-tetrafluorocyclopropane. Tetrafluorocyclopropane also liquified at room temperature, the experimental uncertainty of the value of calibration factor of this compound was probably not greater than ± 10%.

4.2(b) CARBONYL FLUORIDE CALIBRATION

The IR spectrum was obtained as described in Section A3.1 for CHFO. The transmittance at 1926, 1942 and 1955 cm^{-1} which corresponded to the carbonyl stretching vibration of CF_2O(57) was noted. Heicklen(57) and Jones(68) obtained the value for the extinction coefficient of 0.013 and 0.012 $(mm\ Hg.cm)^{-1}$ for the 5.12 micron peak of carbonyl fluoride. Using the value of extinction coefficient = 0.012 $(mm\ Hg.cm)^{-1}$, the concentration of carbonyl fluoride formed in the reaction can be calculated from Beer's law.

$$\log \frac{I_o}{I_t} = \varepsilon\ C\ l$$

C = concentration = pressure of CF_2O in mm Hg.

l = cell path length = 10 cm

The quantum yield of carbonyl fluoride was calculated from the equation

$$\phi_{CF_2O} = \frac{P_{CF_2O}}{P_{N_2}}$$

and was found to be 0.60.

The reaction of oxygen atom with tetrafluoroethylene was also carried out in a similar experiment and the quantum yield of CF_2O was found to be 0.92 which agrees well with Heicklen's result(57). It seems therefore that ϕ_{CF_2O} in the reaction with CF_2=CHF is distinctly less than unity(0.6±0.1).

4.3 EFFECT OF IRRADIATION TIME

The reaction mixture of total pressure 750 mm Hg was carried out under the normal conditions used but with the irradiation time up to 2 hours (approximately 20% conversion). Variation in yields of major and minor products with irradiation time are shown in Figure 4.4.

All products except product P_9 show a linear variation with time. The rate of formation of product P_9 shows a definite increase with irradiation time.

4.4 EFFECT OF PRESSURE VARIATION

Figures 4.5a and 4.5b illustrate the variation of the quantum yields of major and minor products with total pressure respectively. The yield of products P_7 and P_9 were too small for illustration on the figure. Irradiation time of this set of experiments were of 30 minutes duration (approximately 5% conversion). The values for the yields of minor products were probably not accurate enough because of the uncertainty in measuring the overlapped peaks.

The quantum yields of all the products (except P_7 and P_9) at various pressures are summarized in Table 4.3.

It can be seen that the total quantum yield of all the products varied between 0.717 and 0.894 which may be due to the uncertainty in the calibration factors and the inaccuracy in measuring the small peak areas. The total quantum yield of the products derived from CHF radicals is approximately 0.65±0.10. This value is close to the value obtained for the quantum yield of $CF_2O(\phi_{CF_2O} \sim 0.60)$ by IR spectroscopy.

Fig. 4.4 EFFECT OF IRRADIATION TIME ON PRODUCT YIELDS.

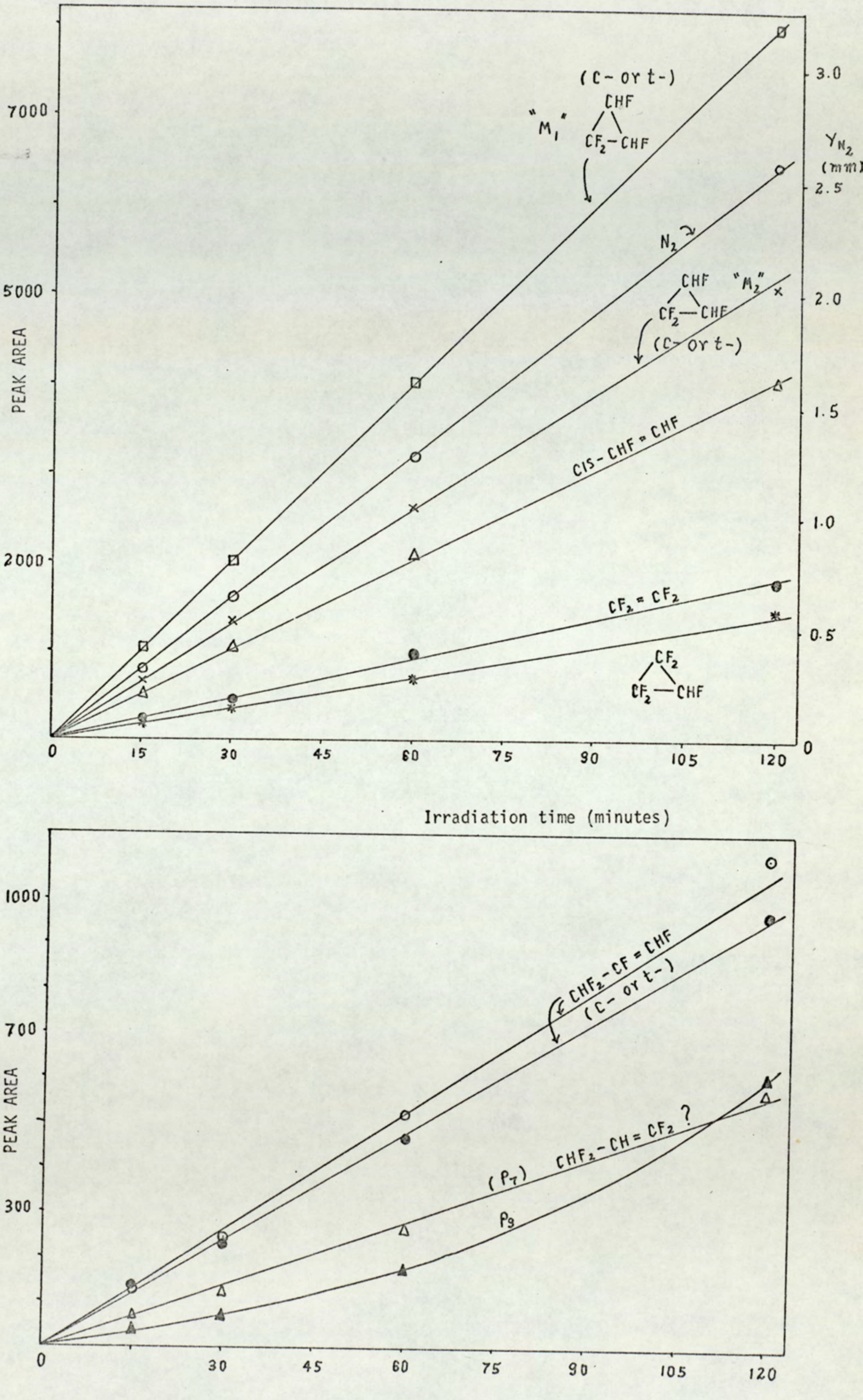
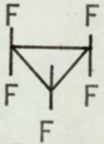


TABLE 4.3

Pressure (mm)	C_2F_4	trans- CHF = CHF	cis- CHF = CHF	P_5 CHF_2-CF=CHF cis-or trans-	P_8 CHF_2-CF=CHF cis-or trans-		tetrafluoro-cyclopropane		ϕ_{CHF}	ϕ_{total}
							(M_1)	(M_2)		
758.0	0.058	0.078	0.092	0.033	0.024	0.060	0.318	0.219	0.754	0.872
156.6	0.148	0.147	0.178	0.080	0.057	-	0.102	0.076	0.640	0.788
520.0	0.085	0.090	0.118	0.051	0.038	0.038	0.270	0.178	0.755	0.868
322.0	0.114	0.127	0.142	0.064	0.045	0.017	0.190	0.131	0.600	0.830
56.8	0.170	0.152	0.179	0.087	0.068	-	0.026	0.046	0.558	0.728
427.0	0.097	0.100	0.128	0.058	0.037	0.030	0.232	0.154	0.709	0.836
86.0	0.152	0.135	0.172	0.079	0.060	-	0.042	0.054	0.542	0.694
664.0	0.072	0.084	0.101	0.042	0.030	0.049	0.300	0.202	0.759	0.880
714.0	0.068	0.085	0.102	0.042	0.032	0.054	0.305	0.206	0.772	0.894
120.8	0.158	0.128	0.168	0.074	0.054	-	0.066	0.063	0.556	0.714

ϕ_{CHF} indicates the total quantum yield of the products derived from CHF radicals.

The Effect of Pressure on Product Yield

(Quantum yields expressed as yields of products per yields of nitrogen)

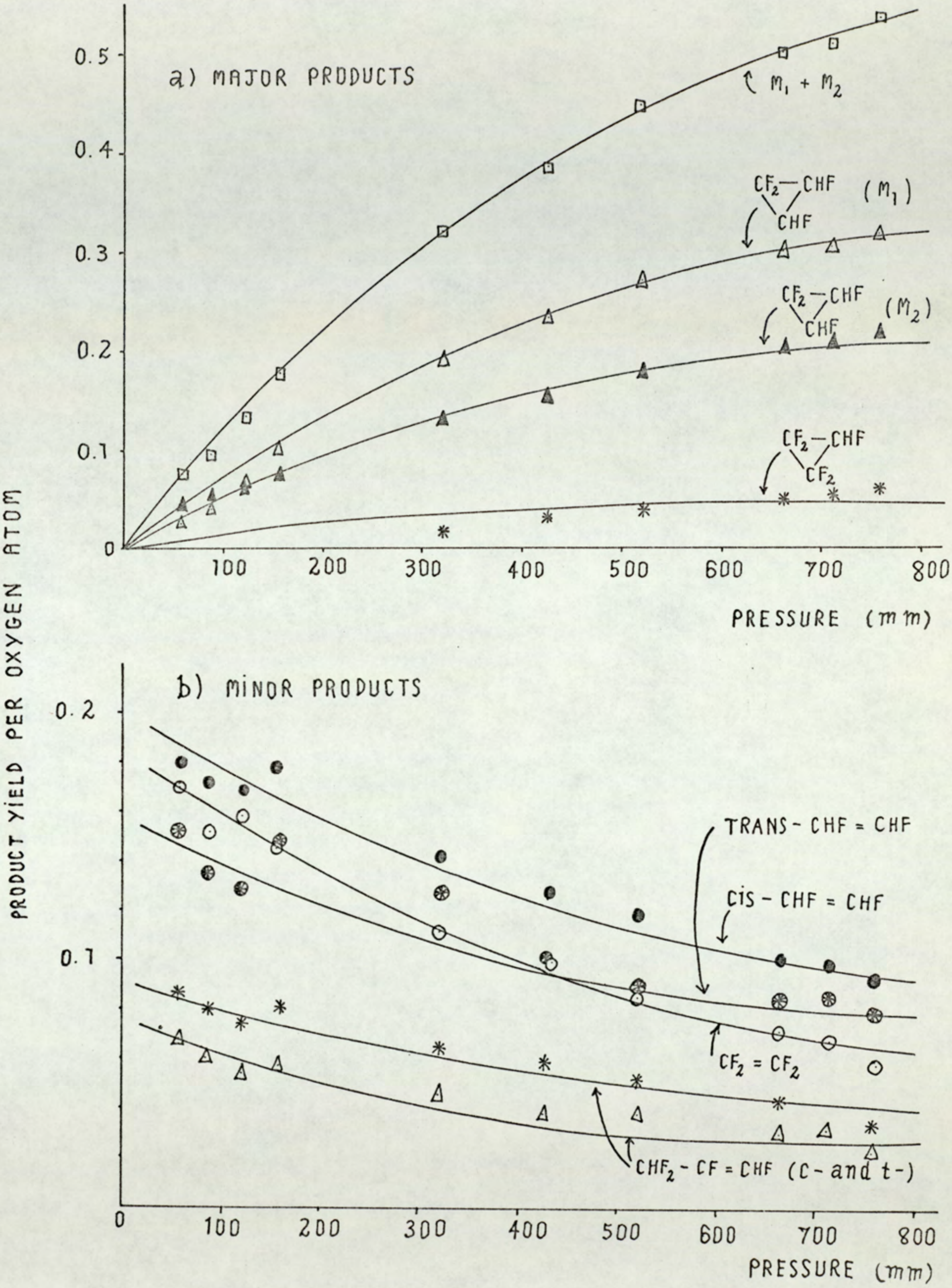


FIG. 4.5 PRESSURE EFFECT ON PRODUCT YIELD OF $O(^3P) + CF_2 = CHF$

4.5 EFFECT OF LIGHT INTENSITY

Light intensity was reduced by inserting a double layer of fine copper gauze between all the windows of the reaction vessel and lamp as described previously in Section B3.4. The effect of light intensity on the yield of products are summarized in Table 4.4.

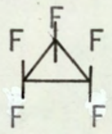
The quantum yields of all the products are not affected by reducing light intensity.

4.6 EFFECT OF MOLECULAR OXYGEN

Two standard runs were carried out under the same conditions used for the pressure dependence studies. The first run was carried out at high pressure (about 745 mm) and the second run was done at a total pressure of about 250 mm Hg. The rate of nitrogen formation was noted to be 0.02 mm (in reaction vessel) per minute for both runs. The pressure of about 9 and 5 mm Hg molecular oxygen was added to the reaction mixture at the start of the reaction. After 30 minutes irradiation, the samples were analysed by GLC. The yields of major and minor products as a function of nitrogen generated in the absence and presence of molecular oxygen are summarized later.

It can be seen in Table 4.5. that within experimental error the molecular oxygen has no effect on the observed quantum yields of all the products. It should be noted that for all runs involving addition of molecular oxygen the experimental error is greater than normal because nitrogen yields cannot be measured directly.

TABLE 4.4

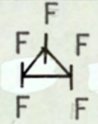
Irradiation time (min)	P_{N_2} (mm)	C_2F_4	t- CHF=CHF	c- CHF=CHF		CHF_2-CF=CHF cis-or trans	CHF_2-CF=CHF c- or t-	(M_1)	(M_2)
30'	0.60	0.070	0.080	0.102	0.060	0.043	0.029	0.318	0.219
*120'	0.41	0.068	0.082	0.104	0.057	0.044	0.030	0.317	0.220
*120'	0.39	0.065	0.077	0.098	0.064	0.050	0.028	0.319	0.223
30'	0.55	0.072	0.075	0.097	0.068	0.045	0.025	0.308	0.215

* Indicates runs with the light intensity reduced by a factor of about 7.

The Effect of Light Intensity on Pressure Yield

(Quantum yields expressed as yields of products per yields of nitrogen)

TABLE 4.5

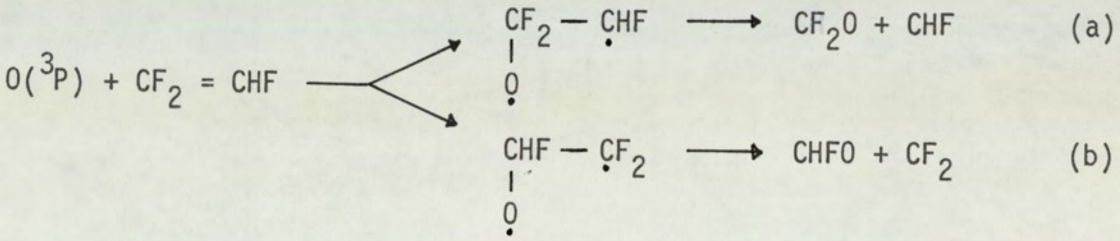
P_{TOTAL}	P_{O_2}	C_2F_4	trans- CHF=CHF t	cis- CHF=CHF		CHF_2-CF=CHF cis- or trans-	CHF_2-CF=CHF cis- or trans	$\overset{\Delta}{M_1}$	$\overset{\Delta}{M_2}$
745.0	-	0.070	0.080	0.102	0.060	0.043	0.029	0.318	0.219
745.0	9.0	0.068	0.077	0.099	0.062	0.045	0.029	0.316	0.215
253.0	-	0.130	0.126	0.156	0.001	0.072	0.052	0.154	0.110
254.0	5.0	0.140	0.124	0.152	-	0.067	0.050	0.138	0.095

Effect of Molecular Oxygen on Products Yield

(Quantum yields expressed as yields of products per yields of nitrogen)

4.7 OVERALL MECHANISTIC SCHEME

In this system, two possible primary processes may occur (analogous to CHF = CHF reaction, Chapter 3).



$$O(^3P) + CF_2 = CHF \longrightarrow \begin{cases} \dot{O}-CF_2-\dot{C}HF \longrightarrow CF_2O + CHF & \text{(a)} \\ \dot{O}-CHF-\dot{C}F_2 \longrightarrow CHFO + CF_2 & \text{(b)} \end{cases}$$

The quantum yield of 0.60 is obtained by infra-red spectroscopy for the formation of CF_2O. This result agrees well within the experimental error with the total quantum yield of the products derived from CHF radicals (Section 4.4.). The quantum yield for formation of CHFO could not be realiably measured, however weak bands at 1819, 1849 and 1834 cm^{-1} of infra-red spectrum due to the carbonyl stretching vibration of CHFO(135) are observed (see figure 4.2). Since no identified products of this reaction had been found to be epoxide, it has been assumed that the rest of oxygen atoms attach to the other carbon atom to form CHFO and CF_2 radicals in step (b).

The reaction of oxygen atoms with tetrafluoroethylene has been investigated by Heicklen et al.(57,62) and is found to follow the simple course:

$$O(^3P) + CF_2 = CF_2 \longrightarrow CF_2O + CF_2$$

The quantum yield for formation of CF_2O is found to be near to unity. (Measurement of ϕ_{CF_2O} for this reaction performed during the course of the present work gave a result of 0.92: see Section 4.2b).

Mitchell and Simons(65) have studied the reaction of oxygen atom with 1,1-difluoro-olefins by flash photolysis, the reaction of the type

$$O(^3P) + CF_2 = CXY \begin{array}{ll} \nearrow \; CF_2O + CXY & \qquad (a') \\ \searrow \; CXYO + CF_2 & \qquad (b') \end{array}$$

has been found, where X, Y = F, H, Cl and Br. The reaction type (a') is formed preferentially when X, Y = halogen. The formation of intermediate type (b') is favoured when X = H and Y = halogen, e.g. $CF_2 = CHCl$.

$$O(^3P) + CF_2 = CHCl \longrightarrow CF_2 + CHClO$$

$$CHClO \longrightarrow CO + HCl$$

The corresponding reactions with trifluoroethylene in this experiment would be expected to be

$$O(^3P) + CF_2 = CHF \longrightarrow CF_2 + CHFO$$

$$CHFO \longrightarrow CO + HF$$

In the present study, the yield of CO was found to be less than 2% of the nitrogen formation in the reaction.

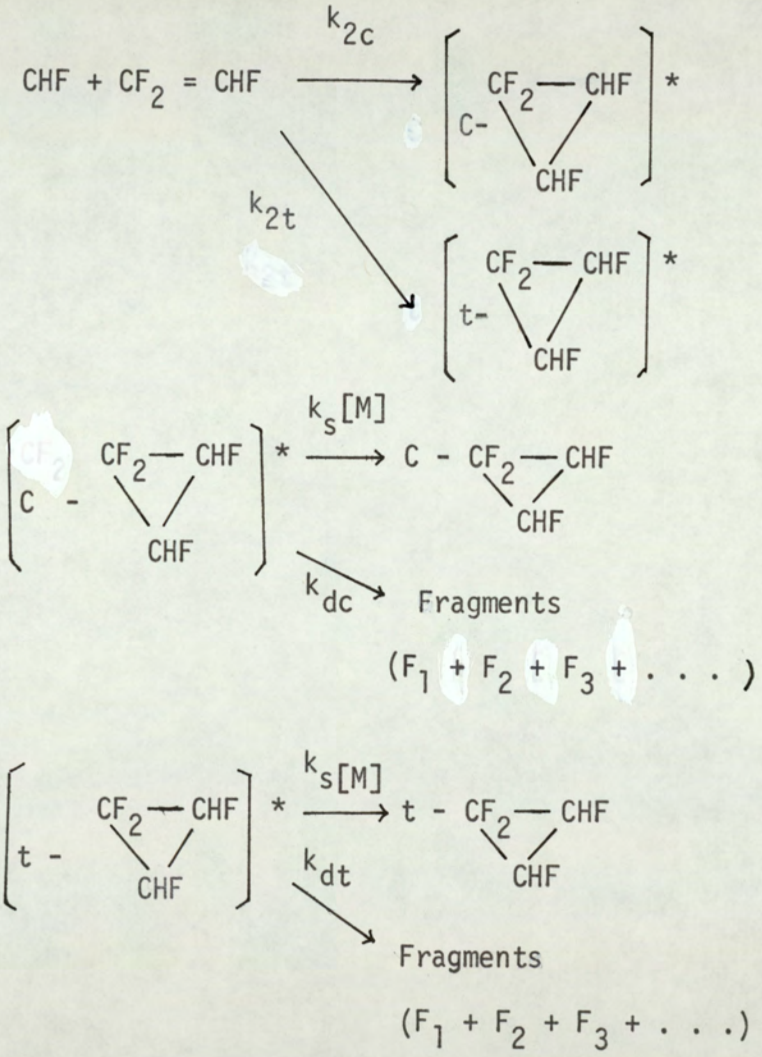
4.7(a) CHF radicals

The results described previously can be satisfactorily represented mainly as the formation of CHF radicals from the trifluoroethylene in the primary step. The CHF radicals then add to the olefin to form "hot" tetrafluorocyclopropanes which can be stabilized by collisional deactivation (or isomerize or fragment). Following the mechanism proposed for the reaction of oxygen atom with cis-1,2-difluoroethylene, the reaction with trifluoroethylene may be written as follows:

$$Hg(^1So) + h\nu(253.7\ mm) \longrightarrow Hg^*(^3P_1) \quad (1)$$

$$Hg^*(^3P_1) + N_2O \longrightarrow N_2 + Hg(^1So) + O(^3P) \quad (2)$$

$$O(^3P) + CF_2 = CHF \longrightarrow CF_2O + \alpha CHF \quad (3)$$



(4)

(4')

(5)

(5')

(6)

Steady state treatment leads to the following equations (see Section B3.5.):-

$$Q_{c\Delta} = \alpha k_{2c} k_s [M] / k_2 (k_{dc} + k_s [M])$$

$$\frac{1}{Q_{c\Delta}} = \frac{k_2 k_{dc}}{\alpha k_{2c} k_s} \cdot \frac{1}{[M]} + \frac{k_2}{\alpha k_{2c}}$$

and $$\frac{1}{Q_t} = \frac{k_2 k_{dt}}{\alpha k_{2t} k_s} \cdot \frac{1}{[M]} + \frac{k_2}{\alpha k_{2t}}$$

The plots of $1/Q_{c\Delta}$ VS 1/P and $1/Q_{t\Delta}$ VS 1/P should be linear with ratio of slope to intercept equal to k_{dc}/k_s and k_{dt}/k_s respectively as was found in the reaction with cis-CHF=CHF (Section B3.5.). The results obtained here show non-linear relationship of $1/Q_{c\Delta}$ VS 1/P and $1/Q_{t\Delta}$ VS 1/P as shown in Figure 4.6. This suggests that the mechanism of the reaction of $O(^3P) + CF_2 = CHF$ may involve the isomerization of "hot" cis-tetrafluorocyclopropane to "hot" trans-tetrafluorocyclopropane and "hot" trans- to "hot cis-tetrafluorocyclopropane.

Due to the orientation of CHF radical, both "hot" cis- and trans-tetrafluorocyclopropane can be formed directly in this reaction (as in the reaction of O + cis-CHF = CHF) and isomerization from one to each other may occur as shown on Page 138.

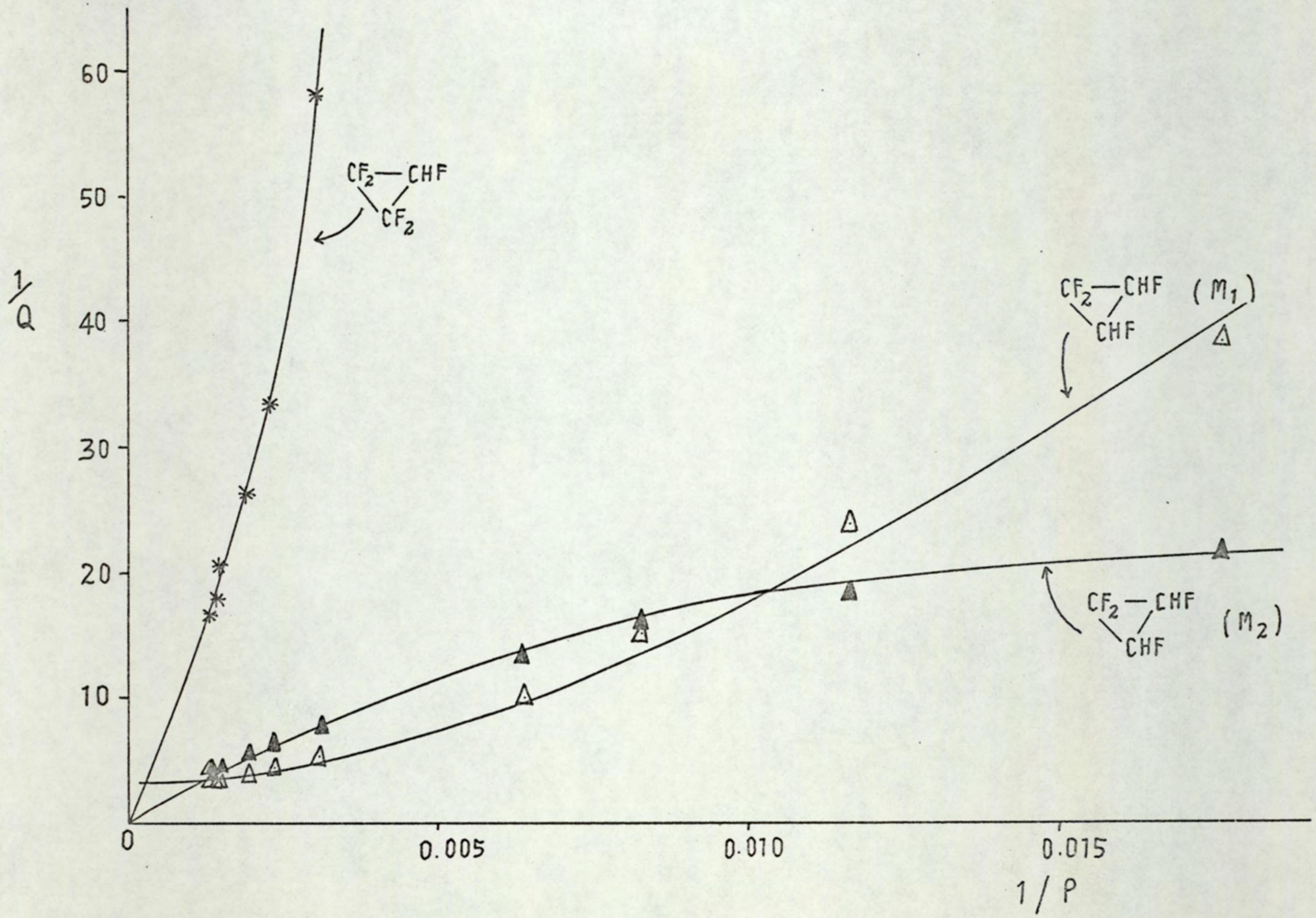
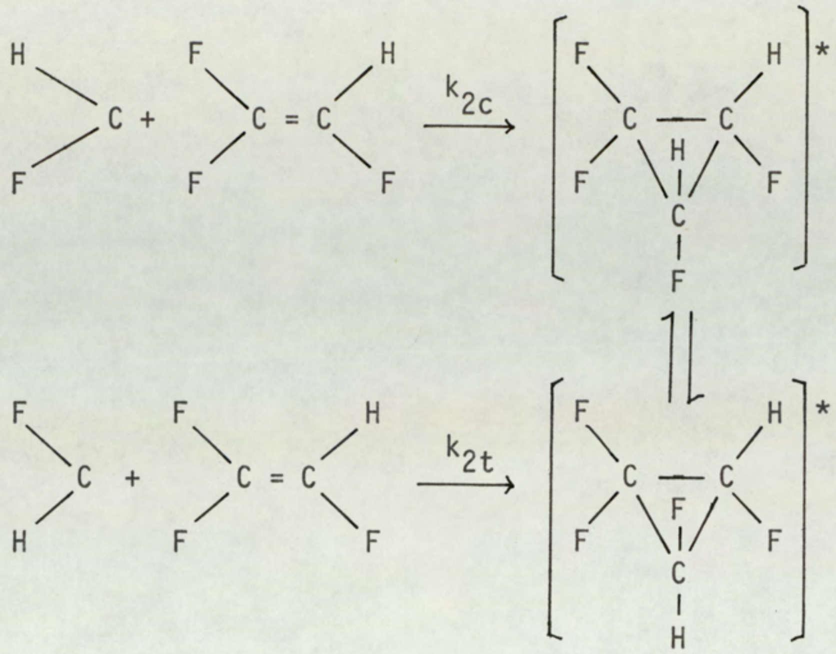
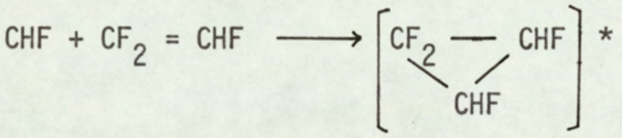


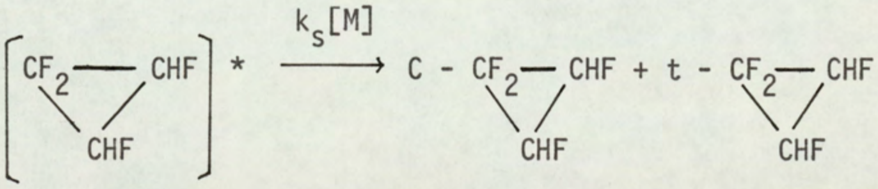
Fig 4.6 PLOTS OF 1/Q AGAINST 1/P (mm^{-1})



As figure 4.8 shows, a good linear plot of $1/Q_{c\Delta} + Q_{t\Delta}$ VS 1/P is observed. This reaction may be obtained by the following simple mechanism:



cis- and trans-



cis-and trans-

Steady state treatment leads to the equation (see Section A3.4):-

$$\frac{1}{Q_{c\Delta} + Q_{t\Delta}} = \frac{1}{\alpha}\frac{k_d}{k_s}\cdot\frac{1}{[M]} + \frac{1}{\alpha}$$

where [M] represents total pressure.

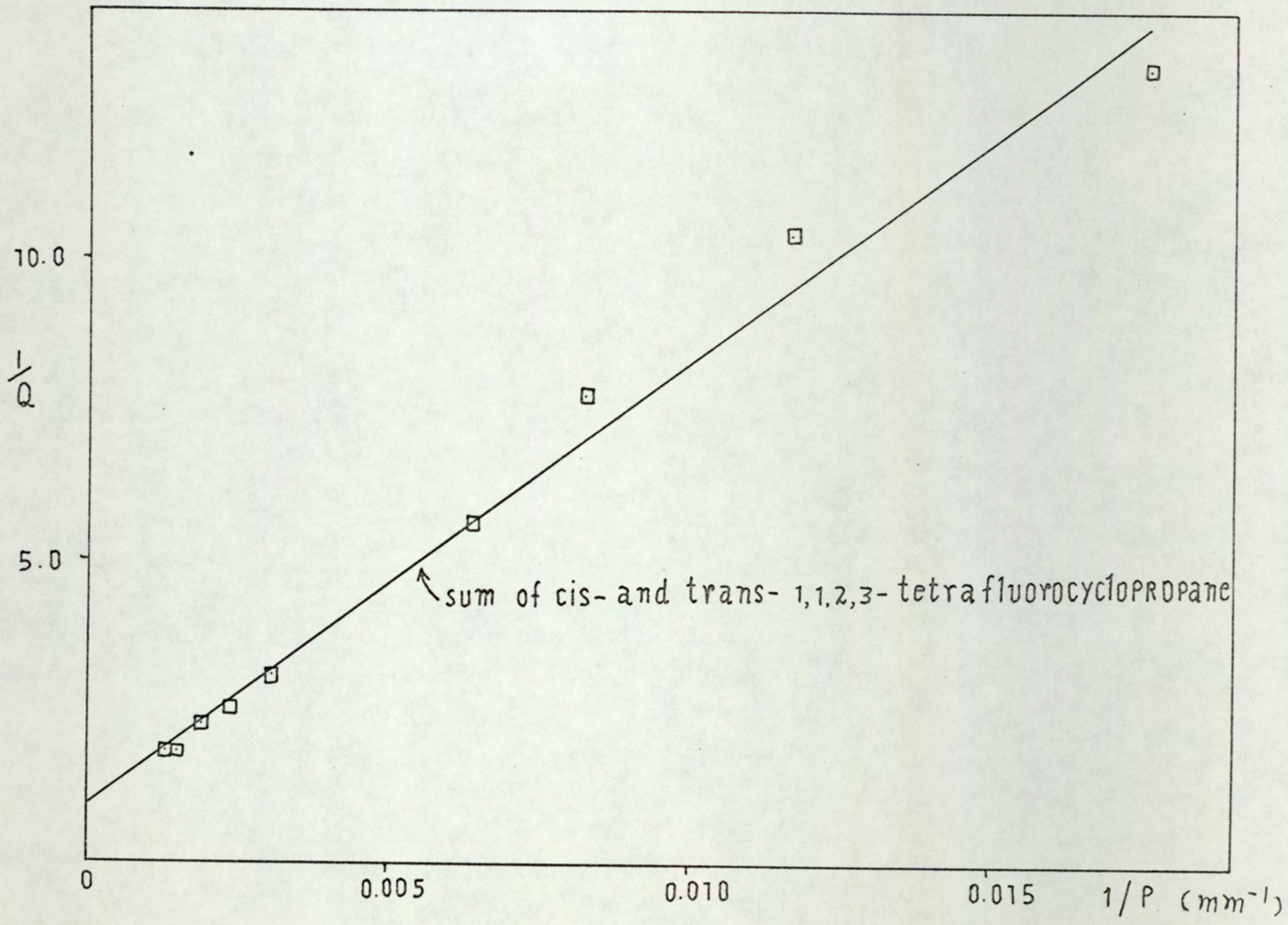


FIG 4.8 PLOT OF 1/Q AGAINST 1/P

This simplified mechanism ignores the distinction between the cis- and trans- "hot" products and therefore takes no account of the isomerization of the two "hot" products. Although the individual stabilized products cannot be separated in this mechanism, the total of these products is well represented quantitatively.

The plots of 1/Q of the minor products VS P are linear with a large scatter of points (see figure 4.7). Unfortunately the quantitative results for the lifetimes of the separated cis- and trans- "hot" tetrafluorocyclopropanes cannot be estimated because the mechanism of the reaction is too complicated.

Although it has not been possible to verify the structures of the tetrafluorocyclopropanes conclusively, we believe these products to be the isomeric cis- and trans-1,2,3,3-tetrafluorocyclopropanes. The formation of these isomers involves isomerization and stabilization by collision of "hot" cis- and trans- tetrafluorocyclopropane.

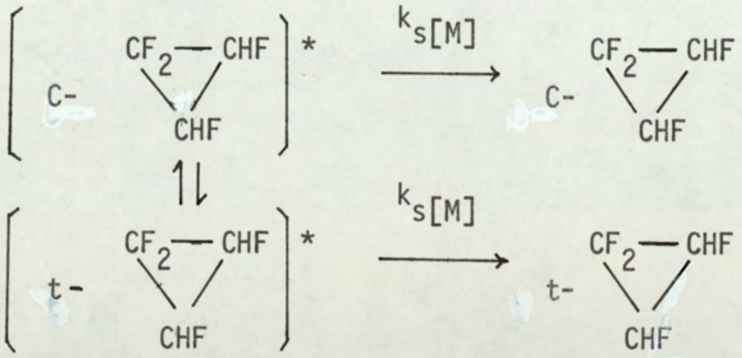
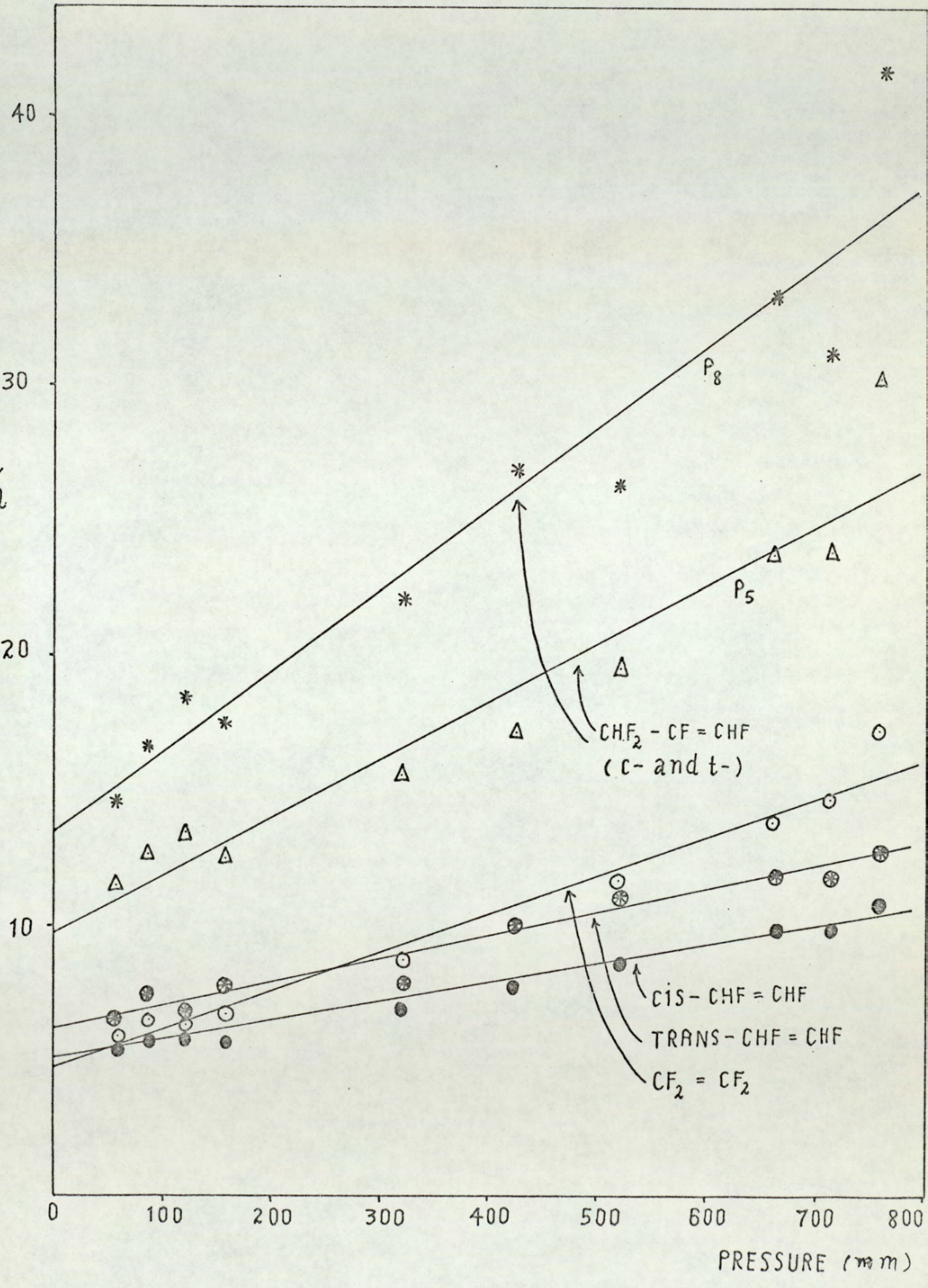
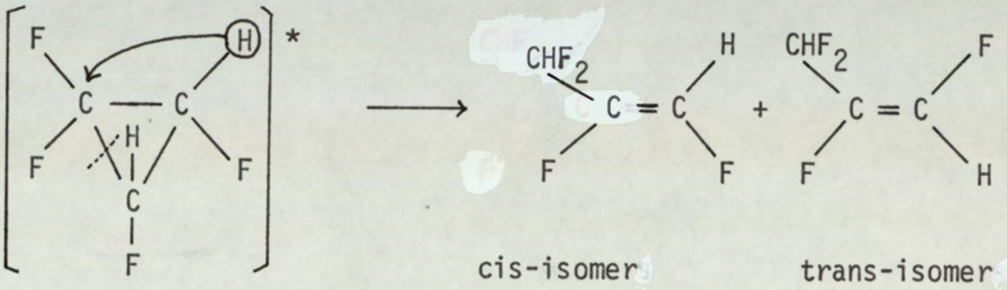


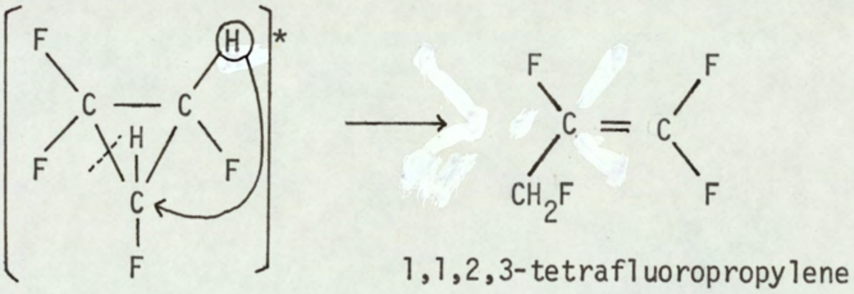
FIG. 4.7 PLOTS OF 1/Q AGAINST P.



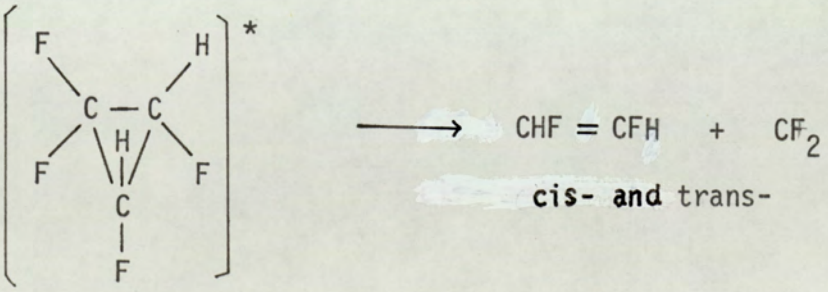
The "hot" cyclopropanes may then undergo fragmentation before the stabilization can occur. The fragmentation involves ring opening and hydrogen atom transfer, e.g.



Hydrogen atom transfer to the other carbon atom may occur:-

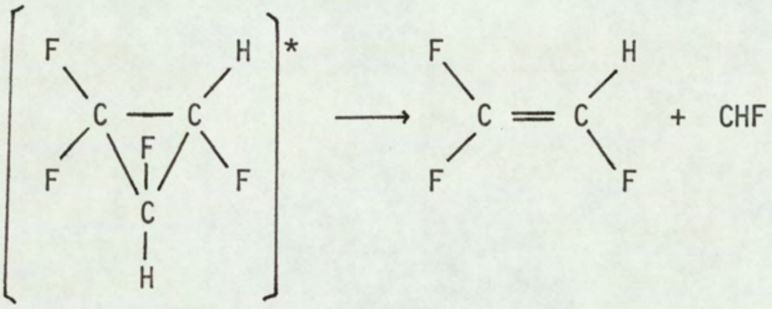


It is possible that the CF_2 elimination can occur in this reaction as found in the reaction of methylene with tetrafluoroethylene(116). The CF_2 elimination from "hot" tetrafluorocyclopropane gives cis- and trans- 1,2-difluoroethylene as found experimentally.



As the results of pressure dependence studies show, the yields of both cis- and trans- 1,2-difluoroethylene decreased with increasing pressure (see Figure 4.5b), there is a good reason to believe that both cis- and trans- 1,2-difluoroethylene are mostly formed by the above mechanism. Tetrafluoropropylenes accounted for about 40% of cis- and trans- 1,2-difluoroethylene, this suggests that the elimination of CF_2 radicals from "hot" tetrafluorocyclopropane is preferentially formed than isomerization to form tetrafluoropropylenes.

The "hot" tetrafluorocyclopropane may also eliminate some CHF radicals to form trifluoroethylene.



Unfortunately, this reaction cannot be observed experimentally because the presence of starting olefin, trifluoroethylene, prevented this observation.

CHF radicals may recombine to form "hot" cis- and trans- 1,2-difluoroethylene. These "hot" products may be very short-lived and are likely to undergo fragmentation to form mainly monofluoroacetylene even at atmospheric pressure.

$$CHF + CHF \longrightarrow (CHF = CHF)^*$$

$$(CHF = CHF)^* \longrightarrow CH \equiv CF + HF$$

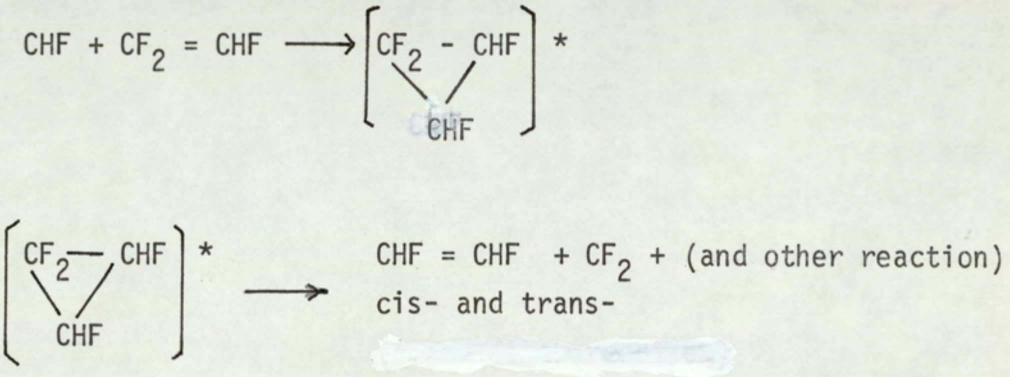
4.7b CF_2 radicals

In this reaction system, two possible sources of CF_2 radicals arise:-

(i) Primary process (b)

$$O + CF_2 = CHF \longrightarrow CHFO + CF_2$$

(ii) Elimination from "hot" tetrafluorocyclopropane:



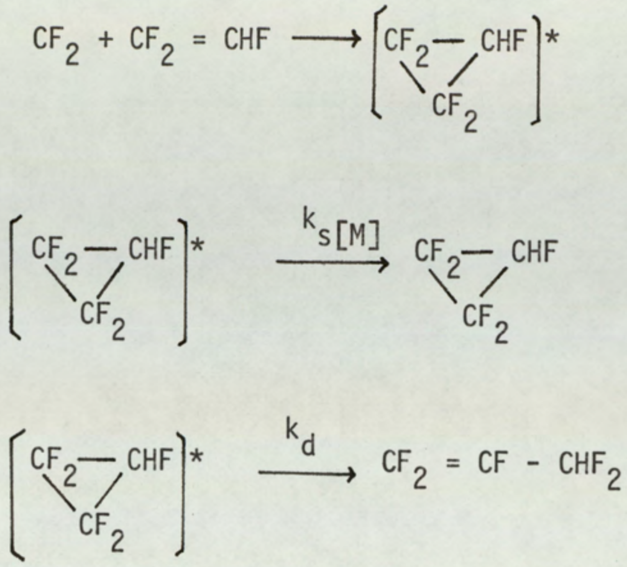
The CF_2 radicals can undergo two types of reaction:-

1. Recombination of CF_2 radicals to form "hot" tetrafluoroethylene which can be stabilized by collision.

$$CF_2 + CF_2 \longrightarrow (CF_2 = CF_2)^*$$

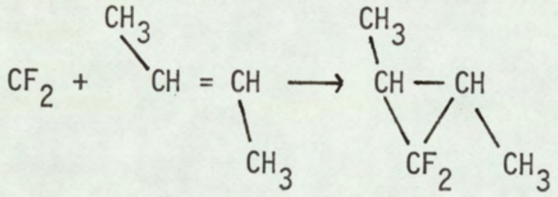
$$(CF_2 = CF_2)^* \xrightarrow{k_s[M]} CF_2 = CF_2$$

2. Addition of CF_2 radicals to trifluoroethylene to form "hot" pentafluorocyclopropane which again can be stabilized by collision (or isomerize or fregmant):



These two types of reaction have also been observed in the reaction of CF_2 (by photolysis of CF_2N_2) with butene-2(136).

$$CF_2N_2 + h\nu \longrightarrow CF_2 + N_2$$



and $$CF_2 + CF_2 \longrightarrow CF_2 = CF_2$$

4.8 Conclusion

For the details studied of reaction of oxygen atoms with trifluoroethylene, the following conclusion can be made:-

1. The primary reactions of $O(^3P)$ with trifluoroethylene were observed to be:-

$$O + CF_2 = CHF \longrightarrow \begin{cases} CF_2O + CHF & (\phi = 0.6 \pm 0.1) \\ CHFO + CF_2 & (\phi = ?\ ) \end{cases}$$

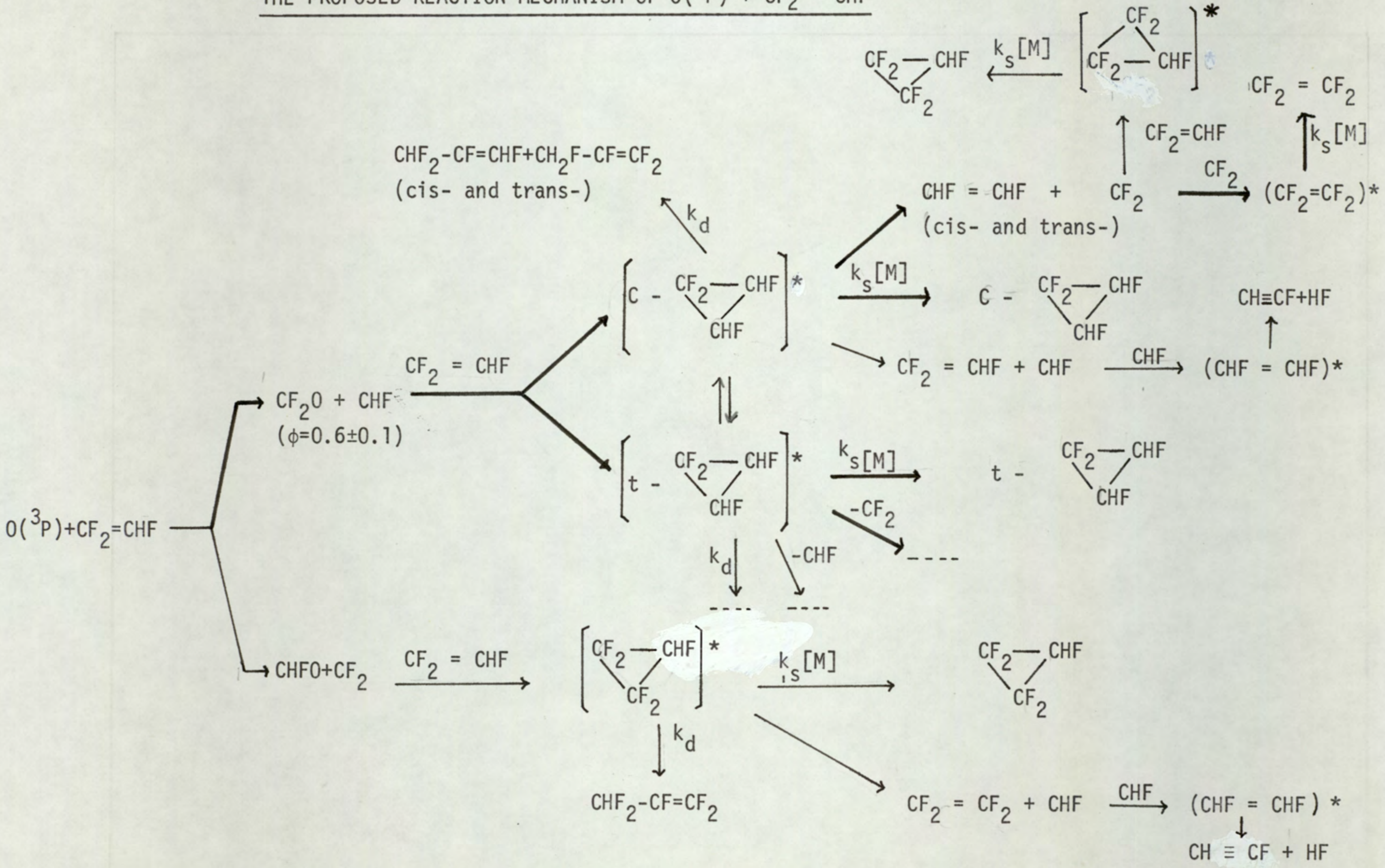
2. CHF radicals add to trifluoroethylene to form "hot" tetrafluorocyclopropanes which will preferentially eliminate CF_2 radicals than isomerize to form tetrafluoropropenes.

3. CF_2 radicals which formed in the primary process and eliminated from "hot" cyclopropanes can also undergo recombination to form tetrafluoroethylene and addition to trifluoroethylene to form pentafluorocyclopropane.

4. The electronic state of both CHF and CF_2 are observed to be singlet as the products formed in this reaction system are not affected by a small amount of molecular oxygen.

See overall scheme shown diagrammatically on the following page.

THE PROPOSED REACTION MECHANISM OF $O(^3P) + CF_2 = CHF$



Heavy line represents the main course of the reaction

CHAPTER FIVE

REACTIVITY OF MONOFLUOROMETHYLENE RADICALS WITH FLUOROETHYLENES

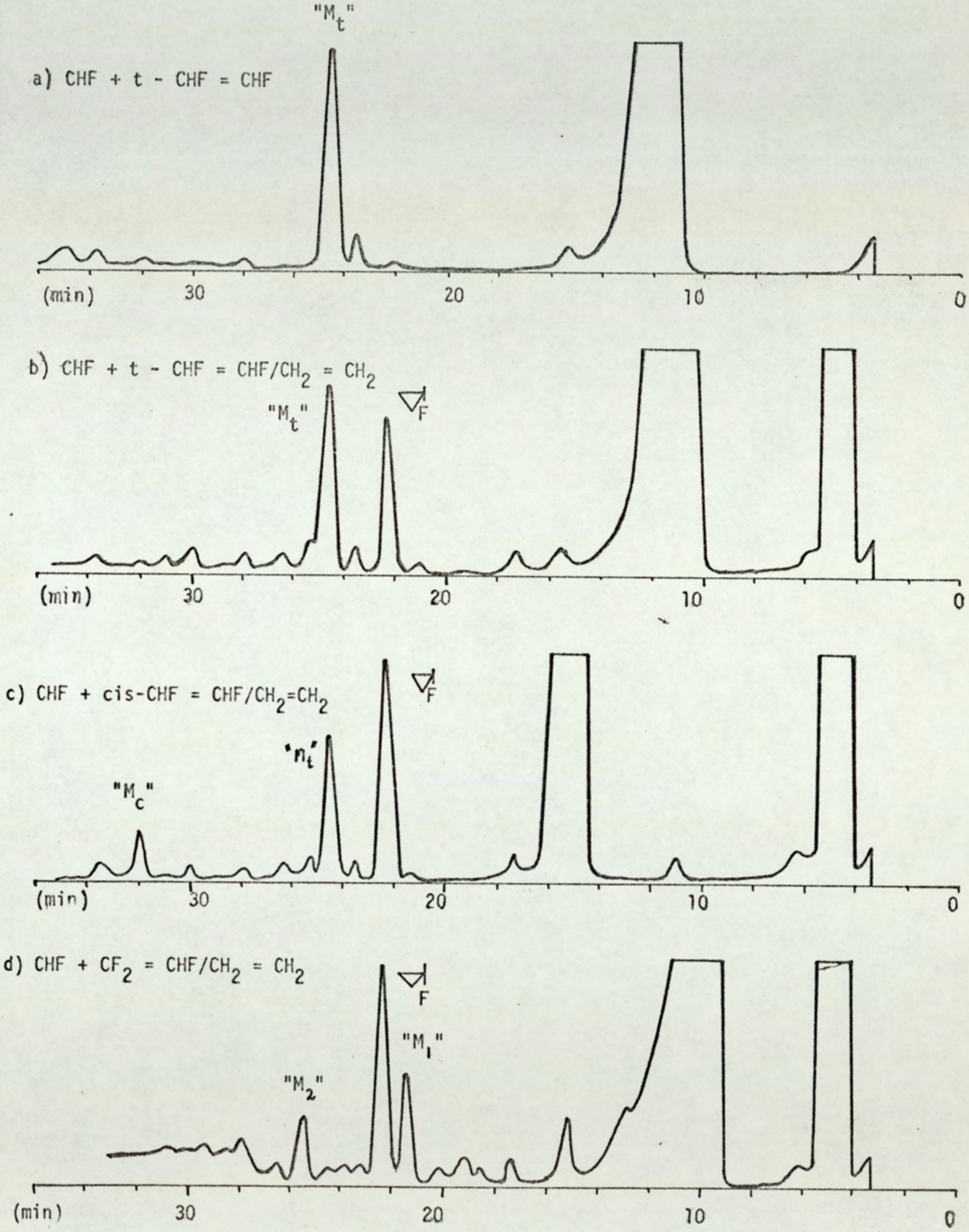
5.1 INTRODUCTION

In the previous chapters (3 and 4) it was found that the reactions of $O(^3P)$ + CHF = CHF and $O(^3P)$ + CF_2 = CHF produced CHF radicals. The obtained CHF radicals reacted with the fluoroethylene to give the corresponding fluorocyclopropane. The fluoroethylenes mentioned above will be treated as reference olefin. Following the detailed studies of these reactions, the systems were used to investigate relative reactivities of CHF radicals with all the fluoroethylenes using the competitive method. Details of the investigation will be given in this chapter. The competitive method used has already been described in detail in Chapter 2 (section 2.3a.2). All the kinetic runs (standard and competitive) were carried out at room temperature (23 ± 2^oC) and were kept at high total pressure (750 ± 10 mm Hg) in order to minimise decomposition of the fluorocyclopropane products.

5.2 NATURE OF CROSS PRODUCTS

All samples of the competitive reactions were analysed by G.L.C. under the same conditions used in Chapters 3 and 4. The chromatograms of all competitive runs are compared in Figures 5.1a and 5.1b with chromatograms of the standard runs. It can be seen that the retention time of the new products formed in the competitive reactions of CHF + CHF = CHF / CH_2 = CH_2 and CHF + CF_2 = CHF / CH_2 = CH_2 (see

Fig. 5.1(a) G.L.C. SEPARATION SHOWING "CROSS PRODUCTS" FORMED FROM



----.continued

Fig. 5.1(b)

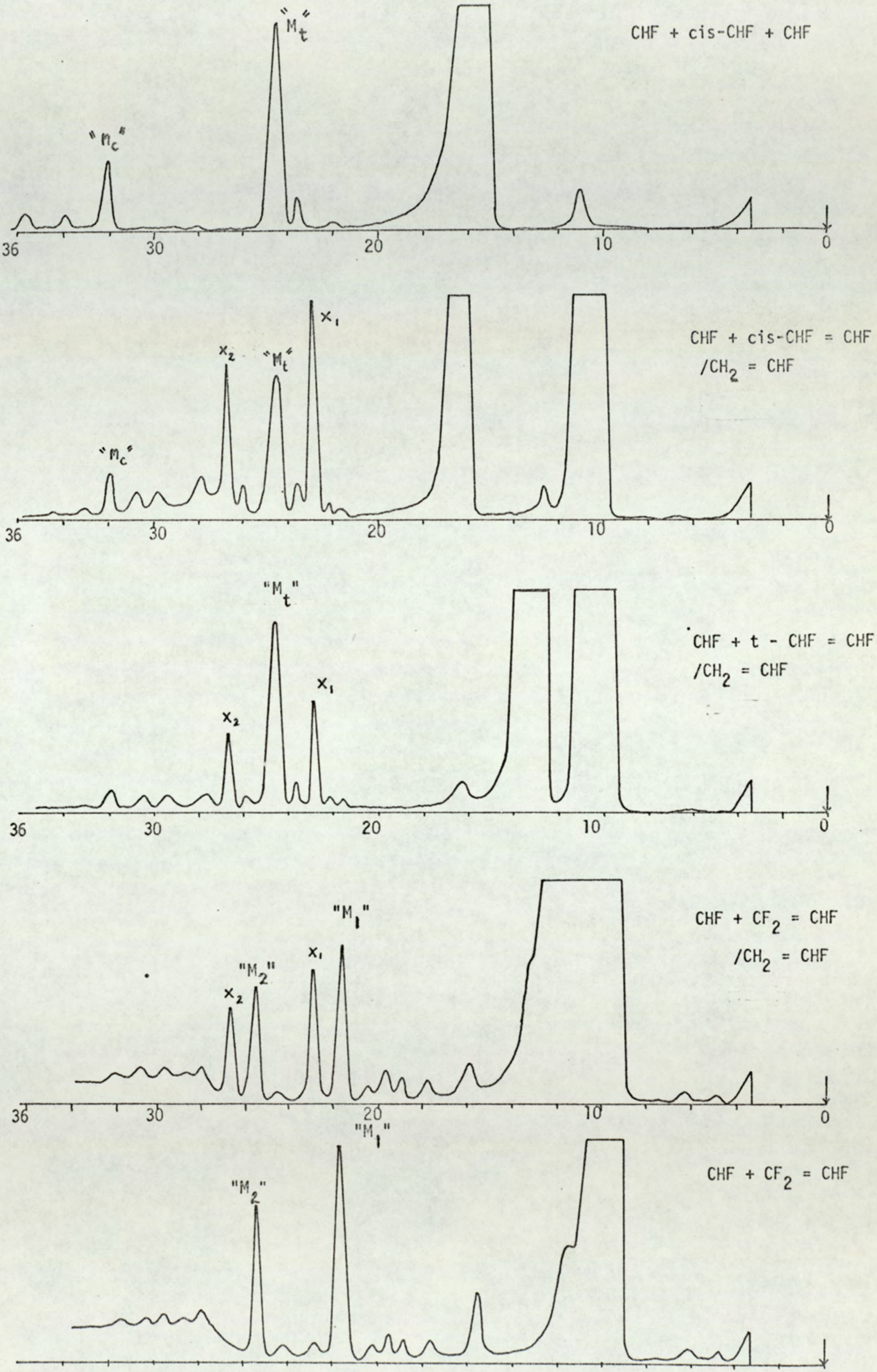
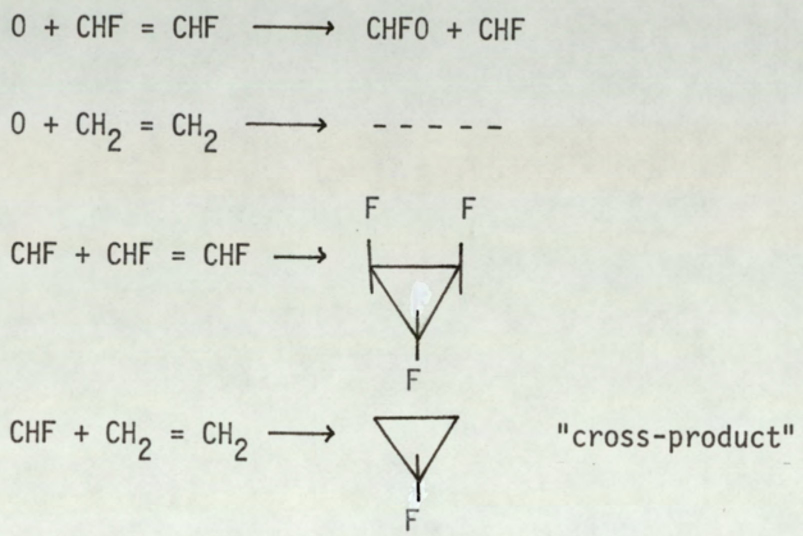


Figure 5.1a) are identical. (From now on these new products will be referred to as "cross-products"). The cross-products are probably formed by the following mechanism.

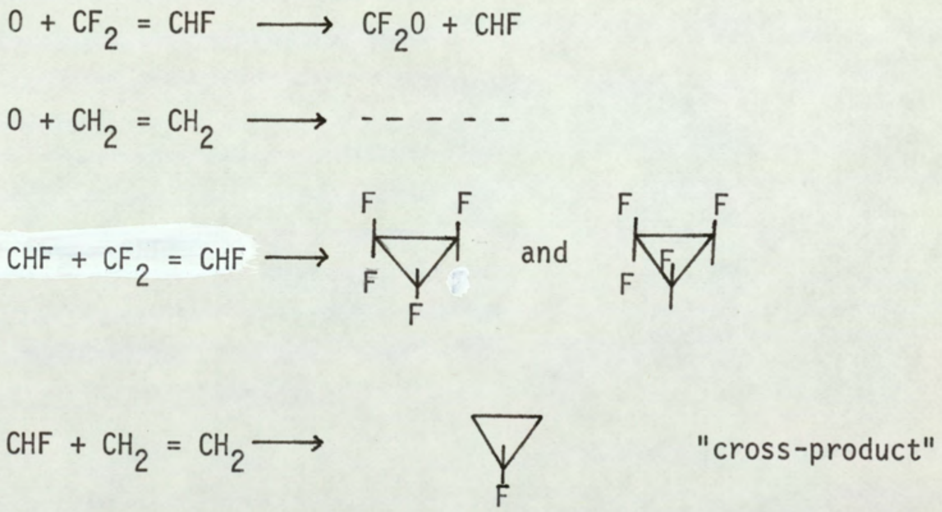

$O + CHF = CHF \longrightarrow CHFO + CHF$

$O + CH_2 = CH_2 \longrightarrow$ - - - - -

$CHF + CHF = CHF \longrightarrow$

$CHF + CH_2 = CH_2 \longrightarrow$ "cross-product"

and


$O + CF_2 = CHF \longrightarrow CF_2O + CHF$

$O + CH_2 = CH_2 \longrightarrow$ - - - - -

$CHF + CF_2 = CHF \longrightarrow$ and

$CHF + CH_2 = CH_2 \longrightarrow$ "cross-product"

Similar reactions were also observed for the use of $CH_2 = CHF$ as a competing olefin (see Figure 5.1b). The cross-products formed as shown in Figure 5.1b were believed to be cis- and trans- 1,2-difluorocyclopropanes according to the mechanism proposed on the preceding page.

In order to support the mechanism proposed for the formation of cross-products, a cross-product formed by the reaction of $CHF + CF_2 = CHF$ / $CF_2 = CH_2$ was collected and was identified by means of infra-red and mass spectrometry to be a trifluorocyclopropane (see Figures 5.2 and 5.3). Both IR and mass spectra are consistent with 1,1,2-trifluorocyclopropane.

It should be noted that the mass spectrun of this cross-product is different from that of 1,2,3-trifluorocyclopropane. The peak at m/e = 46 shows (as expected) that CF_2 elimination in the molecule of 1,1,2-trifluorocyclopropane occurs more readily than in 1,2,3-trifluorocyclopropane, (see Figure 5.3)

This suggests that the cross-products must be formed by addition of CHF radicals to the competing olefins and this proves the validity of the proposed mechanism. The cross-products of all the competitive reactions were gathered in Table 5.1.

FIG. 5.2 a) G.L.C. SEPARATION SHOWING CROSS PRODUCT FROM $CHF + CF_2{=}CHF/CF_2{=}CH$

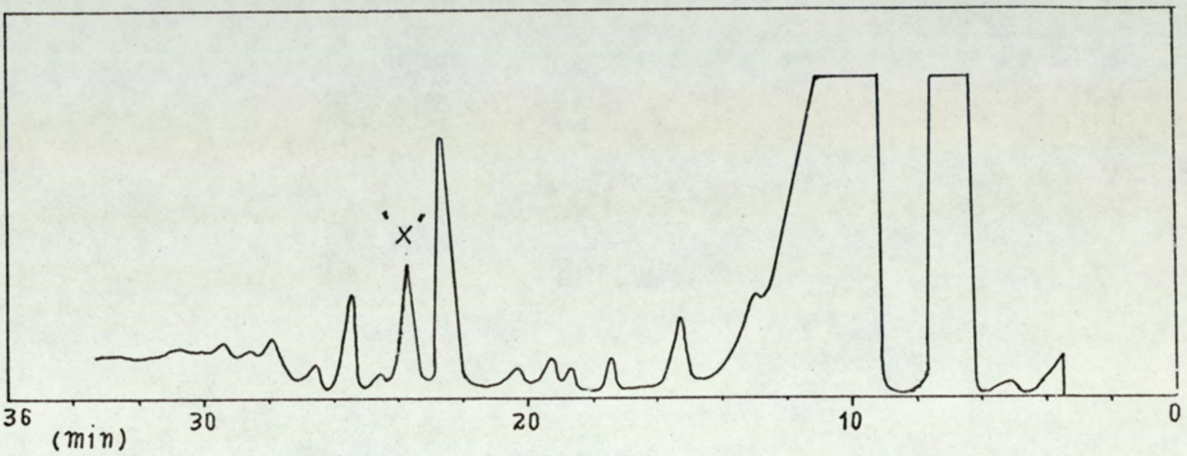


FIG. 5.2 b) INFRA-RED SPECTRUM OF CROSS PRODUCT FROM $CHF + CF_2{=}CHF/CF_2{=}C$

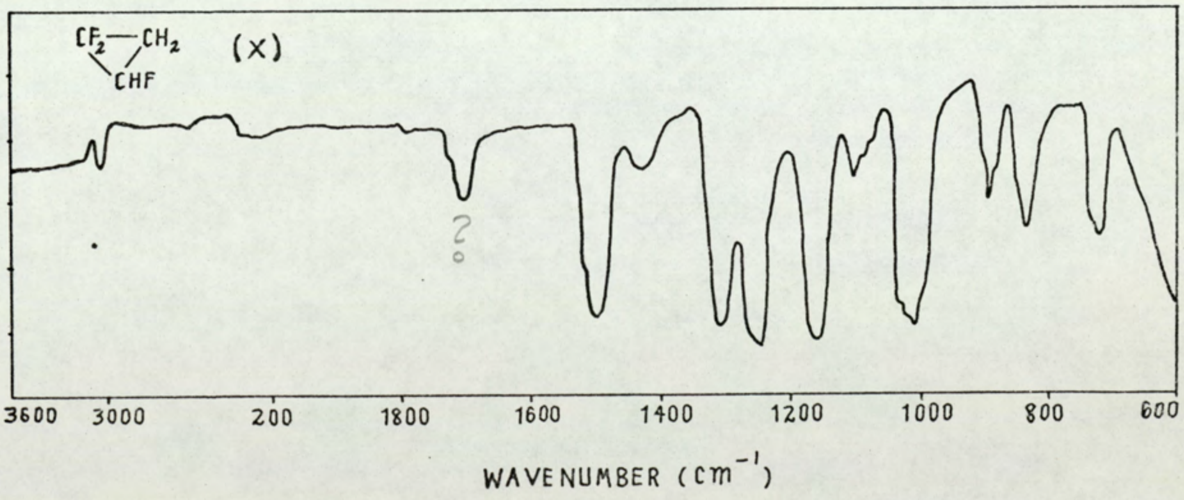


Fig. 5.3 MASS SPECTRUM OF THE CROSS PRODUCT FORMED FROM CHF + CF_2 = CHF/CF_2 = CH_2 COMPARED WITH 1,2,3-TRIFLUOROCYCLOPROPANE.

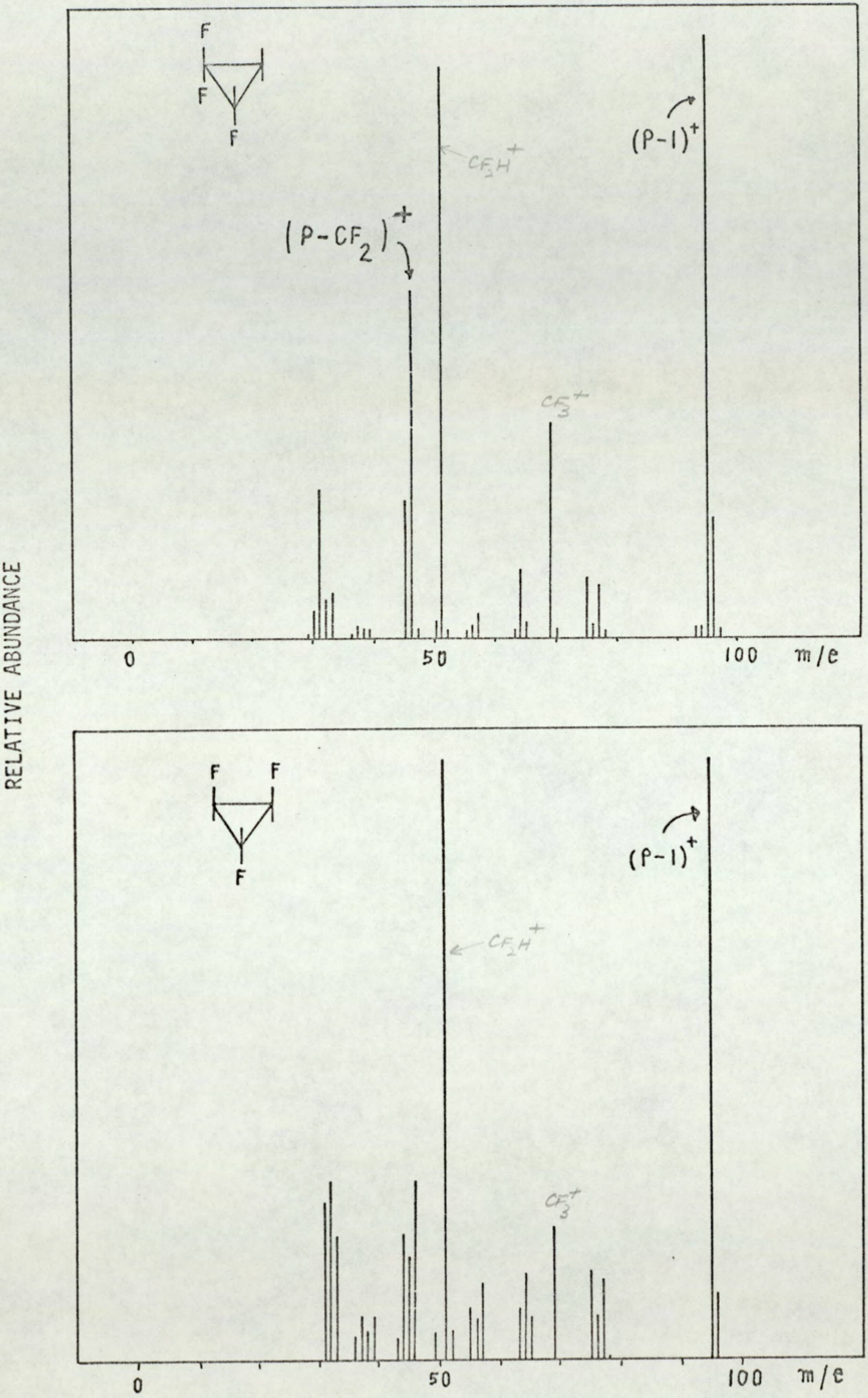
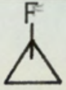
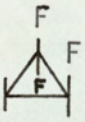


TABLE 5.1

Cross-Products From The Reactions of CHF + Fluoroethylenes

Competitive reactions	Cross-products
$CHF + CF_2 = CHF/CH_2 = CH_2$	 (Cross-product obtained with same G.L.C. retention time in each case)
$CHF + cis\text{-}CHF = CHF/CH_2 = CH_2$	
$CHF + trans\text{-}CHF = CHF/CH_2 = CH_2$	
$CHF + CF_2 = CHF/CH_2 = CHF$	 and  (x_1 and x_2 in fig.5.1b) (Cross-product obtained with same G.L.C. retention time in each case)
$CHF + cis\text{-}CHF = CHF/CH_2 = CHF$	
$CHF + trans\text{-}CHF = CHF/CH_2 = CHF$	
$CHF + CF_2 = CHF/CH_2 = CF_2$	 (Identified by means of IR and mass spectra for an isolated sample)
$CHF + CF_2 = CHF/CF_2 = CF_2$	

5.3 DERIVATION OF RATE EQUATIONS

When mixtures of cis- or trans-1,2-difluoroethylene or trifluoroethylene and other olefin are irradiated in the presence of excess nitrous oxide, the reaction scheme can be written as follows:

(a) $Hg(^1So) + h\nu\ (253.7\ nm) \longrightarrow Hg^*\ (^3P_1)$

(b) $Hg^*(^3P_1) + N_2O \longrightarrow Hg(^1So) + N_2 + O(^3P)$

(c) $O(^3P) + CHF = CHF\ (1) \xrightarrow{k_1} \alpha_1 CHFO + \alpha_1 CHF$

(d) $O(^3P) + \text{olefin}(2) \xrightarrow{k_2} \alpha_2\ \text{Products} + \ldots$

(e) $CHF + CHF = CHF\ (1) \xrightarrow{k_3} \alpha_3$

(f) $CHF + \text{olefin}\ (2) \xrightarrow{k_4} \alpha_4\ \text{Cross-products}$

where α represents the fraction of oxygen atom and CHF radical reacting with the olefin to produce product P.

Then $R_{CP} = \alpha_3 k_3[CHF][ol_1]$ (1)

Steady state treatment leads to the following stationary concentrations.

$$[O] = R_{N_2}/(k_1[ol_1] + k_2[ol_2]) \tag{2}$$

$$[CHF] = \frac{\alpha_1 k_1[O][ol_1]}{(k_3[ol_1] + k_4[ol_2])} \tag{3}$$

substituting (2) into (3)

$$[CHF] = \frac{\alpha_1 k_1[ol_1].R_{N_2}}{(k_1[ol_1] + k_2[ol_2])(k_3[ol_1] + k_4[ol_2])} \tag{4}$$

where R_{N_2} is the rate of formation of nitrogen in this system, and R_{CP} is the rate of formation of fluorocyclopropane in reaction (e). Substituting (4) into (1)

$$\frac{R_{CP}}{R_{N_2}} = \alpha_1\alpha_3/(1 + \frac{k_2}{k_1}\ \frac{[ol_2]}{[ol_1]})\ (1 + \ \frac{k_4}{k_3}\ \frac{[ol_2]}{[ol_1]}) \qquad (5)$$

Both the detector calibration and the α values can be eliminated by performing calibration experiments with the olefins individually, but otherwise under the same conditions used in the mixed runs.

If detector calibration factor is f, let A be the peak area corresponding to the formation product P in reaction (e), then f_{CP} is defined by

$$P_{CP} = f_{CP}\ A_{CP}$$

define $\quad R_{CP} = P_{CP}/t$ and $R_{N_2} = P_{N_2}/t, \quad Q_{CP} = \frac{A_{CP}}{P_{N_2}}$

$$\frac{R_{CP}}{R_{N_2}} = \frac{P_{CP}}{P_{N_2}} = \frac{f_{CP}.A_{CP}}{P_{N_2}} = Q_{CP}f_{CP} \qquad (6)$$

(this defines Q_{CP})

α values in equation (5) are determined in experiments with single olefins (denoted by *) by comparison with the yield of nitrogen

$$\frac{R^*_{CP}}{R^*_{N_2}} = \alpha_1\alpha_3 = Q^*_{CP}.f_{CP}$$

$$Q^*_{CP} = \frac{\alpha_1\alpha_3}{f_{CP}} \qquad (7)$$

Substituting (6) and (7) into (5):

$$Q_{CP}.f_{CP} = \alpha_1\alpha_3/(1 + \frac{k_2}{k_1}\frac{[ol_2]}{[ol_1]})(1 + \frac{k_4}{k_3}\frac{[ol_2]}{[ol_1]})$$

$$Q_{CP} = \frac{\alpha_1\alpha_3}{f_{CP}}/(1 + \frac{k_2}{k_1}\frac{[ol_2]}{[ol_1]})(1 + \frac{k_4}{k_3}\frac{[ol_2]}{[ol_1]})$$

$$\frac{Q_{CP}}{Q^*_{CP}} = \frac{1}{(1 + \frac{k_2}{k_1}\frac{[ol_2]}{[ol_1]})(1 + \frac{k_4}{k_3}\frac{[ol_2]}{[ol_1]})}$$

The last expression is obtained as

$$\frac{1}{Q_{CP}(1 + \frac{k_2}{k_1}\frac{[ol_2]}{[ol_1]})} = \frac{1}{Q^*_{CP}} + \frac{1}{Q^*_{CP}}\frac{[ol_2]}{[ol_1]} \cdot \frac{k_4}{k_3} \qquad (8)$$

It should be noted that the above equation derived was based on the assumption that the concentration of the two olefins remain constant throughout the irradiation period. However, it is possible to correct for the small amount of olefins consumed by calculating the final concentrations of each olefins and using a mean value for calculating the relative rate constants.

For most determinations of the relative rate constants in the present work equation (8) was used. In the case of the reference reactions in which both cis- and trans- cyclopropane products were produced, the sum of the yield of these two products was used to determine the ratio of the rate constants. The relative rate constants (k_2/k_1) for the reaction of oxygen atoms with all fluoroethylenes have previously been measured by Moss$^{(70)}$.

Considering equation (8), a plot of $1/Q_{CP}\left(1 + \frac{k_2}{k_1}\,\frac{[ol_2]}{[ol_1]}\right)$ vs $[ol_2]/[ol_1]$ should be linear with the ratio of slope to intercept equal to k_4/k_3. The good linear plots imply the validity of the equation derived (equation 8) as shown in Figures 5.4 - 5.6 in Section 5.4.

5.4 RESULTS OF RELATIVE RATE CONSTANTS FOR CHF RADICALS WITH THE FLUOROETHYLENES AT 23±2^{o}C

All relative rate constants, k_3/k_4, present in Tables 5.4 and 5.3 were estimated by using equation (8) with a least squares treatment. The rate constants quoted in Table 5.2 are relative to various fluoroethylenes and all measurements are shown graphically at the end of this section. The error in k_3/k_4 for ± 10% change in k_1/k_2 are also shown. Detailed results are collected in the Appendix. The rate constants for the reaction of CHF radicals with propylene and all the fluoroethylenes relative to ethylene are summarized in Table 5.3. The last column of Table 5.3 shows the values of k_2/k_1 (or k_1/k_2) for the reactions of $O(^3P)$ with fluoroethylenes which were used to calculate the relative rate constants (k_3/k_4) in the present work.

TABLE 5.2

Results for Relative Rate Constants for CHF + Fluoroethylenes

Reference	Olefin	$\frac{K_{reference}}{K_{olefin}}$	$\frac{K_{olefin}}{K_{reference}}$	Error in K_{ref}/K_{ol} for ± 10% change in k_2/k_1	
$CF_2 = CHF$	$CH_2 = CH_2$	0.1085	9.2113	0.1118	0.1055
$CF_2 = CHF$	$CH_2 = CHF$	0.2594	3.8536	0.2668	0.2530
$CF_2 = CHF$	$CH_2 = CF_2$	0.6561	1.5239	0.6800	0.6365
$CF_2 = CHF$	$CF_2 = CF_2$	3.7471	0.2668	10.3950	2.2016
t-CHF = CHF	CH_3-CH = CH_2	0.0665	15.0232	0.0735	0.0606
t-CHF = CHF	$CH_2 = CH_2$	0.1666	5.9996	0.1752	0.1586
t-CHF = CHF	$CH_2 = CHF$	0.4890	2.0446	0.5109	0.4674
C-CHF = CHF	$CH_2 = CH_2$	0.0894	11.1741	0.0942	0.0849
C-CHF = CHF	$CH_2 = CHF$	0.2599	3.8465	0.2768	0.2437

TABLE 5.3

Relative Rate Constant for CHF + Fluoroethylenes

Olefin	$K_{olefin}/K_{C_2H_4}$	$K_{olefin}/K_{C_2H_4}$ * (O^3P)
$CH_3 - CH = CH_2$	2.51 ± 0.007	5.30
$CH_2 = CH_2$	1.00	1.00
$CH_2 = CHF$	0.42 ± 0.003	0.38
cis-CHF = CHF	0.10 ± 0.005	0.54
trans-CHF = CHF	0.18 ± 0.008	0.32
$CF_2 = CHF$	0.11 ± 0.003	0.57
$CF_2 = CF_2$	0.03 ± 0.02	1.60

* MOSS, S.J., Trans.Faraday Soc., 65, 415 (1969)

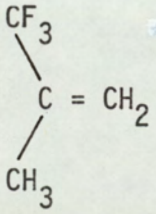
The internal check on relative rate constants for CHF radicals with fluorinated ethylenes are quoted in the Table below. The values measured from different sources of CHF radicals are in satisfactory agreement within the experimental uncertainty.

TABLE 5.4

Relative Rate Constant for CHF Reacting with CH_2CHF and CH_2CH_2

Reference	Relative $k(CH_2CHF/CH_2CH_2)$
cis- $CHF = CHF$	0.34_4
trans- $CHF = CHF$	0.34_1
$CF_2 = CHF$	0.41_8

Relative Rate Constant for CHF Reacting with cis-and trans-$CHF = CHF$

Reference	Relative k(cis-/trans- $CHF = CHF$)
$CH_2 = CHF$	0.54
$CH_2 = CH_2$	0.53_3
 $(CF_3)(CH_3)C = CH_2$	0.53_2*

* MOSS, S.J., Unpublished result

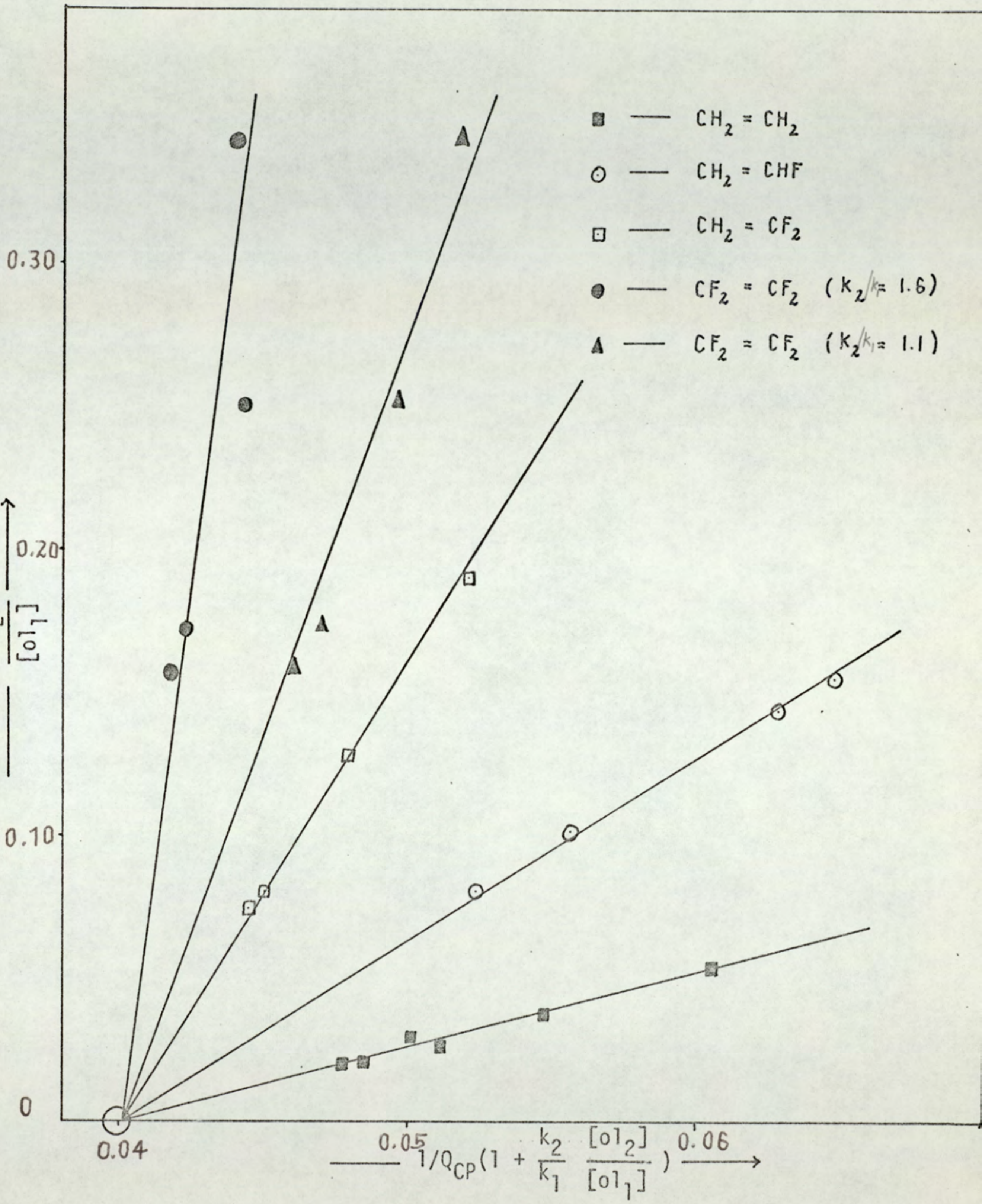


Fig. 5.4 PLOTS OF EQUATION (8) (USED CF_2 = CHF AS A REFERENCE OLEFIN)

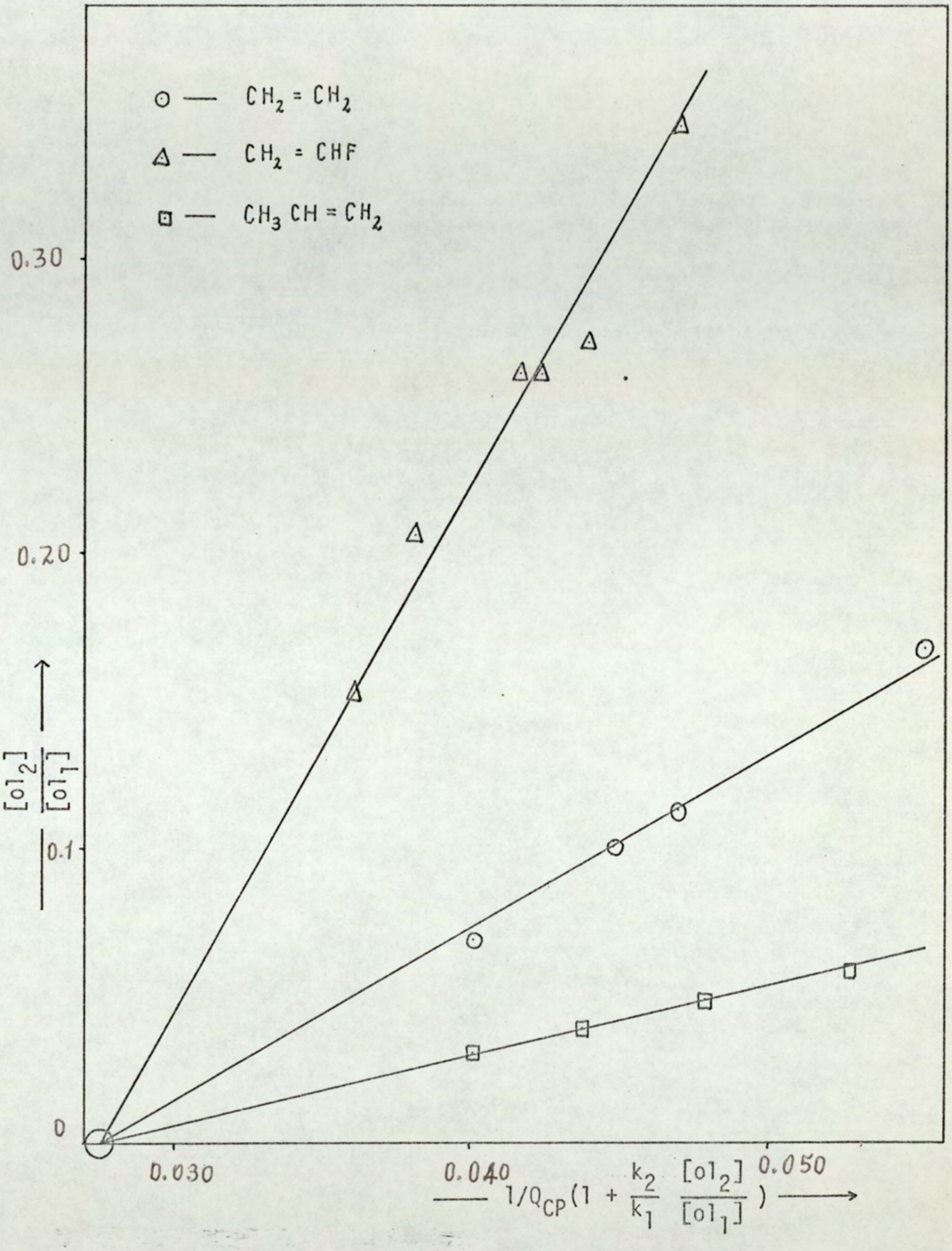


Fig. 5.5 PLOTS OF EQUATION (8) (USED TRANS-CHF=CHF AS A REFERENCE OLEFIN)

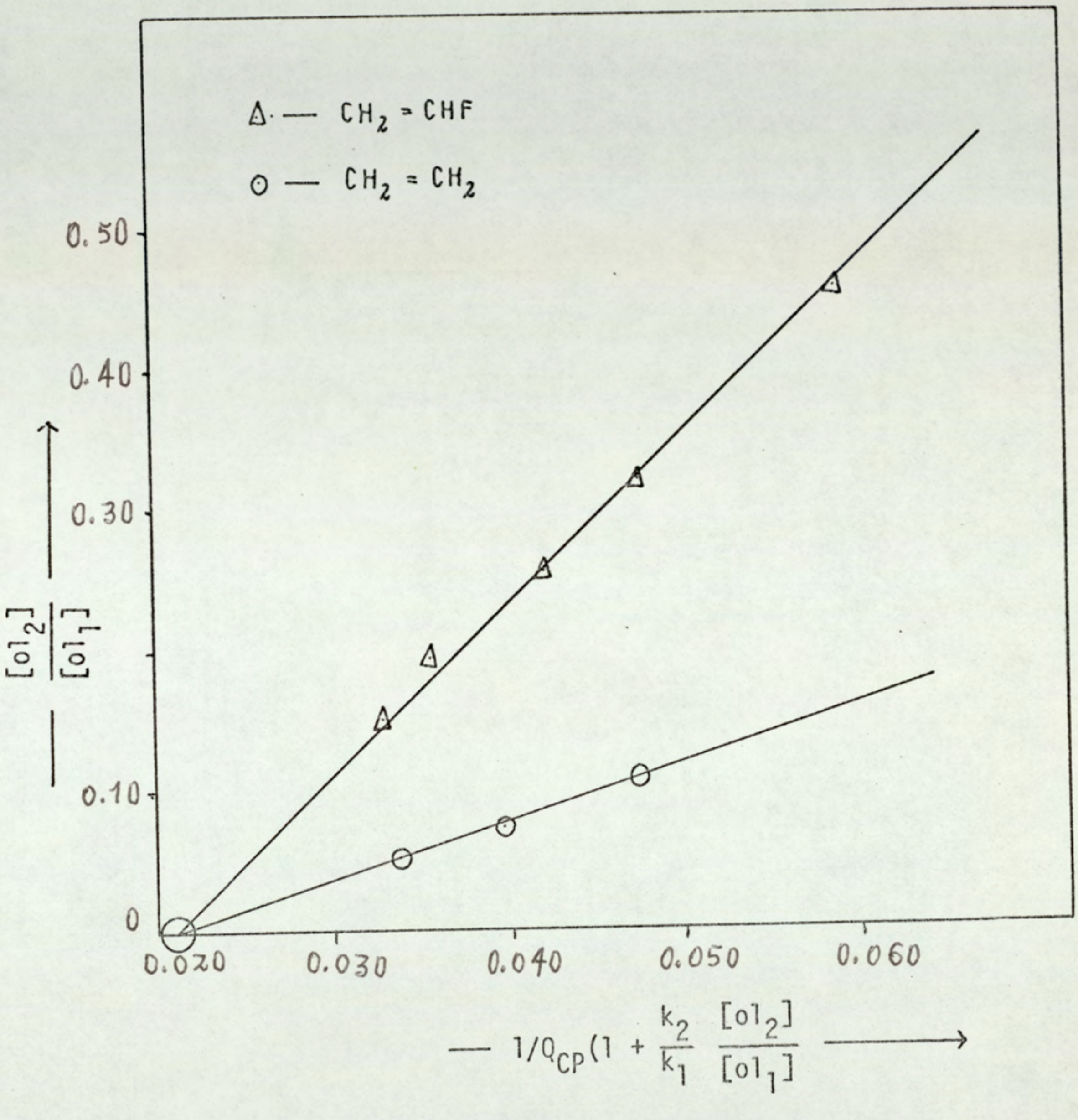


Fig. 5.6 PLOTS OF EQUATION (8) (USED CIS-CHF=CHF AS A REFERENCE OLEFIN)

5.5 RELIABILITY OF THE METHOD

The experimental method used for the measurement of the relative rate constants in this work is reasonably reliable because:-

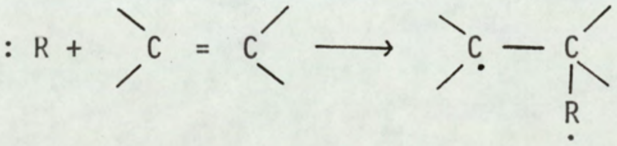
1. A good straight line plots in Figs.5.4 - 5.6 imply the validity of the expression used.

2. Good agreement in the internal check for the relative rate constants of the reaction of CHF + fluoroethylene (see Table 5.4).

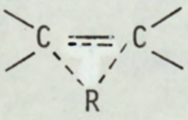
3. The method used in this work was entirely different from that of Rowland(118), but the results obtained for the rate constants of the reaction with propylene in both cases are compatible. (In this work $k_{propylene}/k_{ethylene} = 2.5$; $k_{propylene}/k_{ethylene} = 2.2$ (118)).

5.6 CORRELATION OF RATES WITH CALCULATED PHYSICAL PROPERTIES OF THE FLUORINATED ETHYLENES

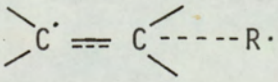
For addition of the reaction type



there are two possible structures of the transition state i.e., a Π-complex (A) and a σ-complex (B)



(A)



(B)

In the case of the activation energies not being known, the physical properties calculated by the application of molecular orbital theory such as bond order, excitation energy, atom localization energy etc., usually have been correlated with the logarithms of rate constants obtained at one temperature. The logarithms of the reaction rate constants are proportional to the free energy of activation, or the activation energy if the pre-exponential factors in the Arhenius rate equation are constant.

The physical properties of an olefin associated with the double bond as a whole are the excitation energy, the Π-bond order and the ionization potential. If the logarithms of the rate constants for the addition reaction of an atom or radical with a series of olefins are found to correlate well with the above properties, then the reaction generally proceeds through a Π-complex at the top of the potential energy curve. This observation has been found to be the case with, for example, oxygen atoms, peracetic acid and dibromocarbene(71).

The other properties associated with individual atoms in the molecule are the atom localization energy, charge density and maximum free valence. If the logarithms of the rate constants are related to these atomic properties, then it is likely that a σ-complex transition state is formed.

Kilcoyne(121) has calculated a number of useful parameters of these physical properties using simple Hückel molecular orbital theory.

TABLE 5.5

Parameters calculated by M.O.Theory for the Fluoroethylenes

Molecule	charge density		Atom Localization Energy		Maximum Free Valence		Excitation Energy	Bond Order	I.P* (ev)	log k
	q_1	q_2	L_1	L_2	F_1	F_2		P_{12}		
$CH_2 = CH_2$	1.000	1.000	2.200	2.200	0.732	0.732	2.200	1.000	10.66	0.000
$CH_2 = CHF$	1.093	0.934	2.629	2.159	0.591	0.742	2.134	0.983	10.45	-0.379
$CH_2 = CF_2$	1.179	0.872	3.077	2.121	0.478	0.777	2.076	0.962	10.45	-0.782
t-CHF = CHF	1.031	1.031	2.578	2.578	0.590	0.590	2.062	0.969		-0.745
c-CHF = CHF										-1.00
$CF_2 = CHF$	1.121	0.972	3.018	2.533	0.461	0.593	2.000	0.951	10.33	-0.967
$CF_2 = CF_2$	1.065	1.065	2.966	2.966	0.449	0.449	1.926	0.935	10.12	-1.538

* Lifshitz, C and Iong, F.A., J.Phys.Chem, 67, 2463 (1963)

The results obtained must be treated as highly approximate because the calculation ignores all non-bonded interaction and regards all C-H and all C-F bonds as identical. The results are shown in Table 5.5. and explanatory note for each physical properties are given.

(i) Excitation energy (ε)

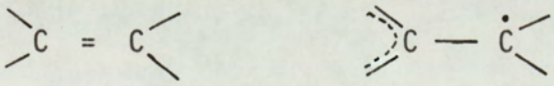
This property is associated with the double bond as a whole. Ideally, it should be the difference in energy of the ground state molecule (olefin) and the lowest excited triplet state. If the excitation energy is calculated by using Hückel theory, then it is the difference in energy of ground state and the average of the lowest excited singlet and triplet states of the olefin. This is because the Hückel theory does not take into account electron spin.

(ii) Π-bond order ($P_{\mu\nu}$)

A correlation between rate data for the addition of an atom or radical with this property of olefin would indicate a Π-complex transition state. $P_{\mu\nu}$ is a measure of the Π-electron density in the bond between carbon atoms μ and ν, i.e. it is a measure of charge in the Π-bond between atom μ and ν.

(iii) Atom localization energy (I_{μ})

This is the energy required to localise a Π-electron completely on carbon atom μ of the double bond by the following process:-



iv) Maximum free valence (F_μ)

This can be regarded as a measure of the "available valence" at atom μ. Therefore it is related to the simplicity of forming an incipient bond at this atom.

In the present study an attempt has been made to correlate the logarithms of the rate constants of the reaction of CHF radicals and a series of fluoroethylenes with the various physical properties listed in Table 5.5, the results are illustrated graphically in Figures 5.7 - 5.10.

It can be seen that a reasonably linear relationship exists between the plots of logarithms of the relative rate constants against the excitation energy, bond order and ionization potential of the fluorinated ethylenes (see Figures 5.7 and 5.8). No correlation has been found with the other parameters as shown in Figures 5.9 and 5.10. This suggests the reactions of CHF radicals with fluoroethylenes proceed through a Π-transition state rather than σ-type.

5.7 COMPARISONS OF CHF RADICALS WITH OTHER ATOMS AND RADICAL SPECIES

The relative rate constants for the reaction of CHF radicals with all the fluorinated ethylenes are compared in Table 5.6 with relative rate constants for other atoms and radical species.

Fig. 5.7 PLOT OF $\log_{10}k$ AGAINST IONIZATION POTENTIAL.

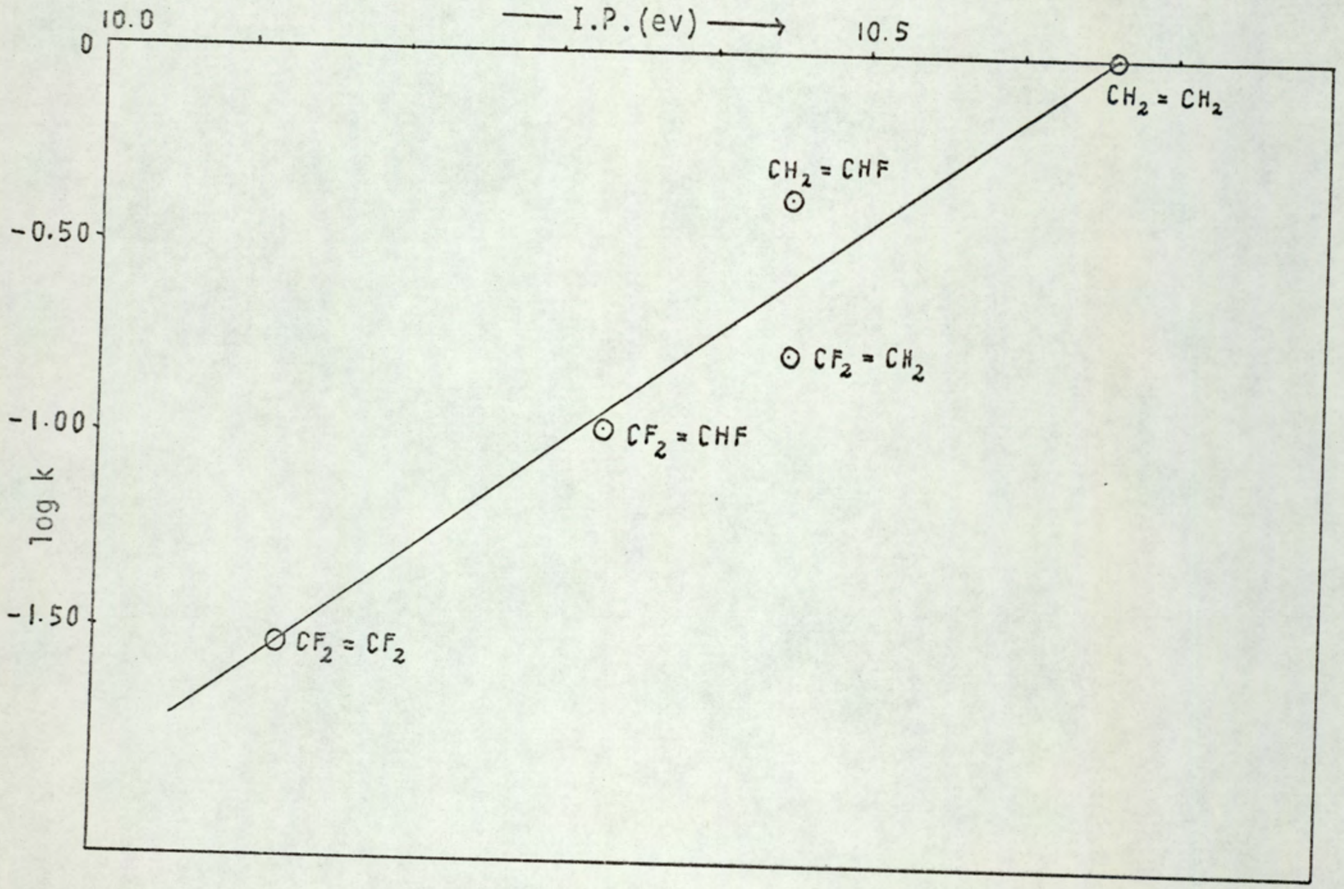
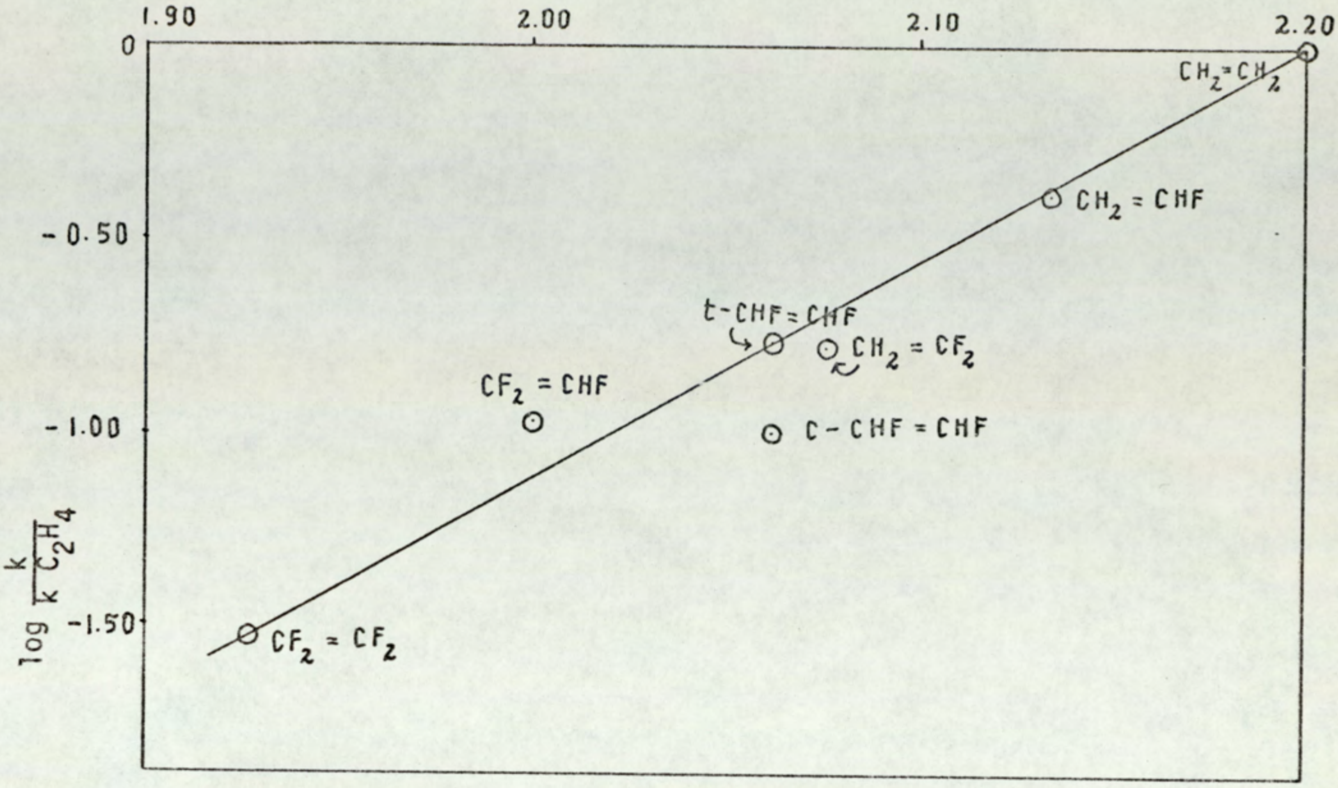
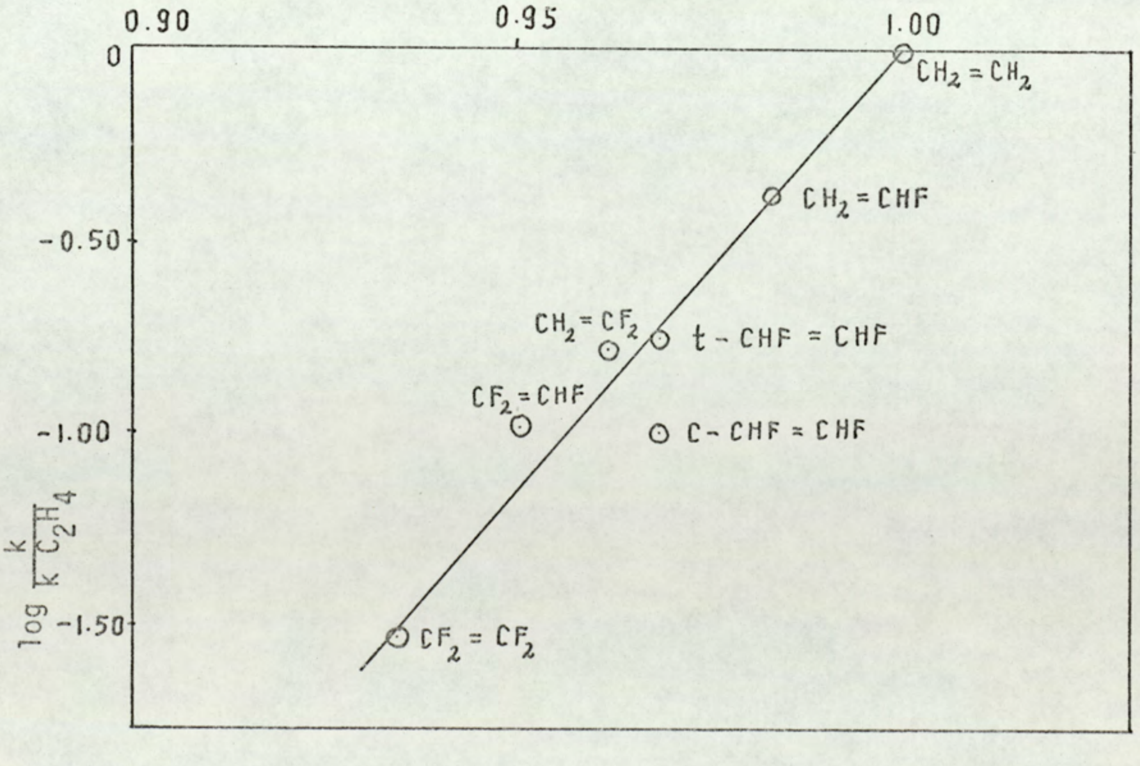


Fig. 5.8 PLOTS OF $\log_{10}k$ AGAINST BOND PROPERTIES

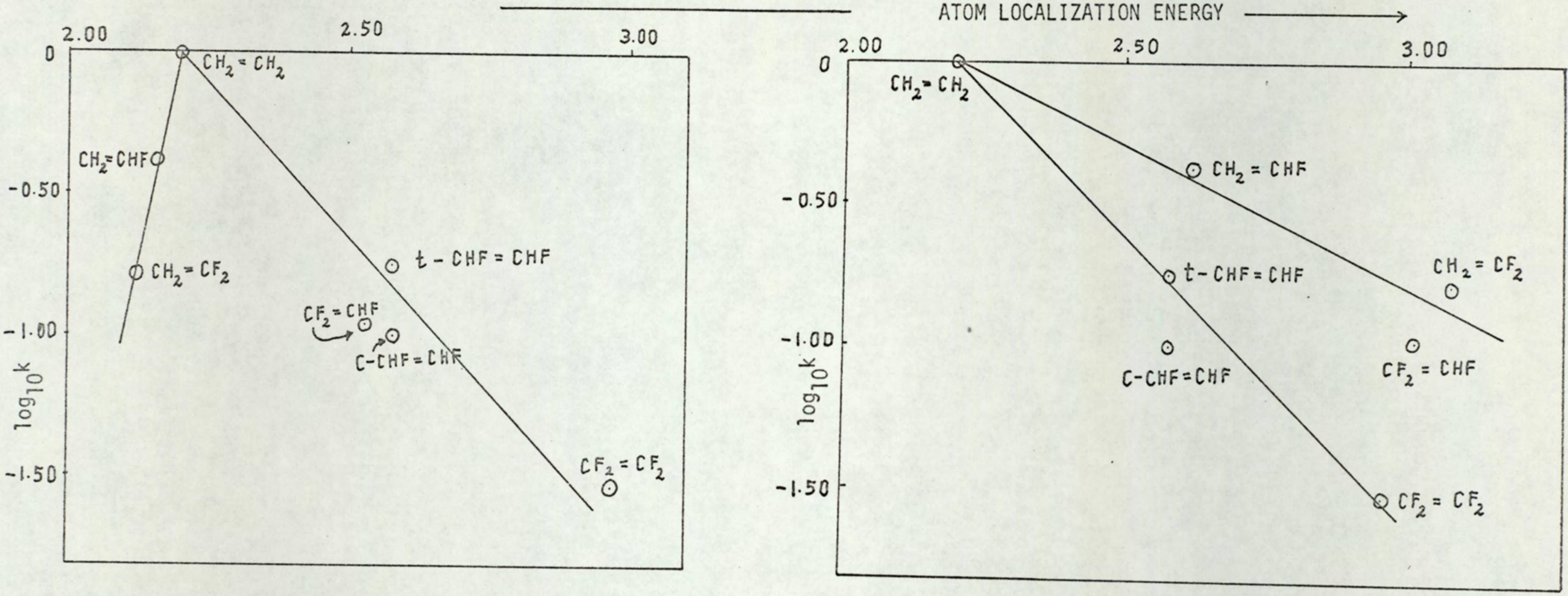


(a) EXCITATION ENERGY ⟶



(b) BOND ORDER ⟶

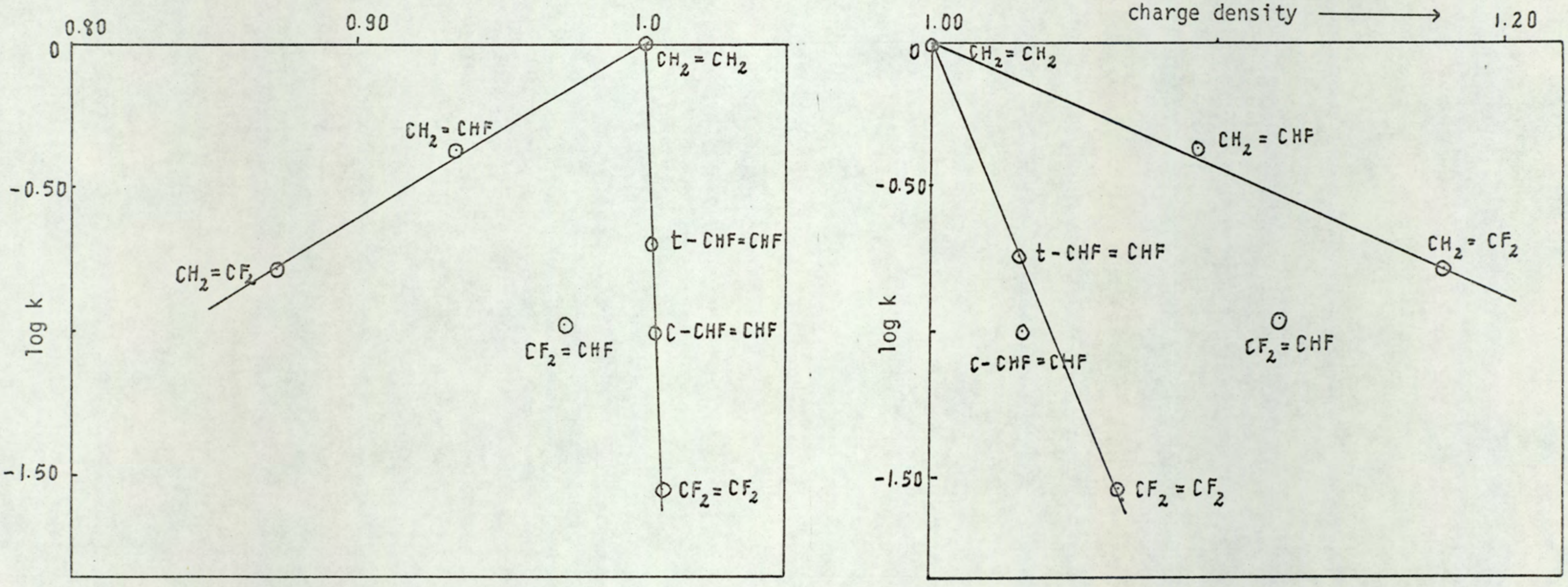
Fig. 5.9 PLOTS OF $\log_{10}k$ AGAINST ATOM LOCALIZATION ENERGY.



(a) LESS SUBSTITUTED CARBON

(b) MORE SUBSTITUTED CARBON

Fig. 5.10 PLOTS OF $\log_{10}k$ AGAINST CHARGE DENSITY



(a) LESS SUBSTITUTED CARBON

(b) MORE SUBSTITUTED CARBON

TABLE 5.6

Relative Reactivities for Addition to the Fluoroethylenes at 23±2°C

Olefins	CHF	CH_2	$Hg(^3P_1)$	H	C_3F_7	CF_3	$C\,Cl_3$	$S(^3P)$	$O(^3P)$	CH_3	I.P. (ev)
$CH_2 = CH_2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	10.66
$CH_2 = CHF$	0.42	0.60	0.79	0.51	0.10	0.47	0.68	0.42	0.38	0.36	10.45
$CH_2 = CF_2$	0.17	0.30	0.62	0.42	0.03	<0.47	0.12	0.10	0.22	0.09	10.45
cis-CHF = CHF	0.10			0.07					0.32		
trans-CHF = CHF	0.18			0.10					0.54		
$CF_2 = CHF$	0.11	0.16	0.41	0.07	0.01		0.05	0.07	0.57	1.46	10.33
$CF_2 = CF_2$	0.03	0.10	0.21	0.09	0.02	0.12	0.23	0.09	1.60	10.2	10.12
References	this work	114	123	121	141	142 132	140	139	70	138	125

As can be seen, the species such as H, CH_2, Hg($^3P_1$), CF_3, C_3F_7 and S(^3P) show the same trends in reactivities as are exhibited by CHF radical reactions. The reactivities of these species and CHF radical progressively decrease with decreasing fluorine substitution.

The correlation between atom and different radical can be obtained by the plot of logarithms of rate constants of the reactions of atom or radical with olefin against each other. A linear relationship of the free energy plot suggests the similar transition state of the reaction. An analysis of log-log plots for the species listed in Table 5.6 provides the following information:

1. A good correlation between rates of methylene, Hg($^3P_1$) and CHF radical with the fluoroethylenes as shown in Figure 5.11.

2. An approximate correlation of the CF_3, C_3F_7, C Cl_3, H and S(^3P) reactions. Tedder and Walton(141) have pointed out that the reaction of C Cl_3, CF_3 and C_3F_7 with fluoroethylenes follow the same trend.

3. No correlation of oxygen atoms and CH_3 rates with other species.

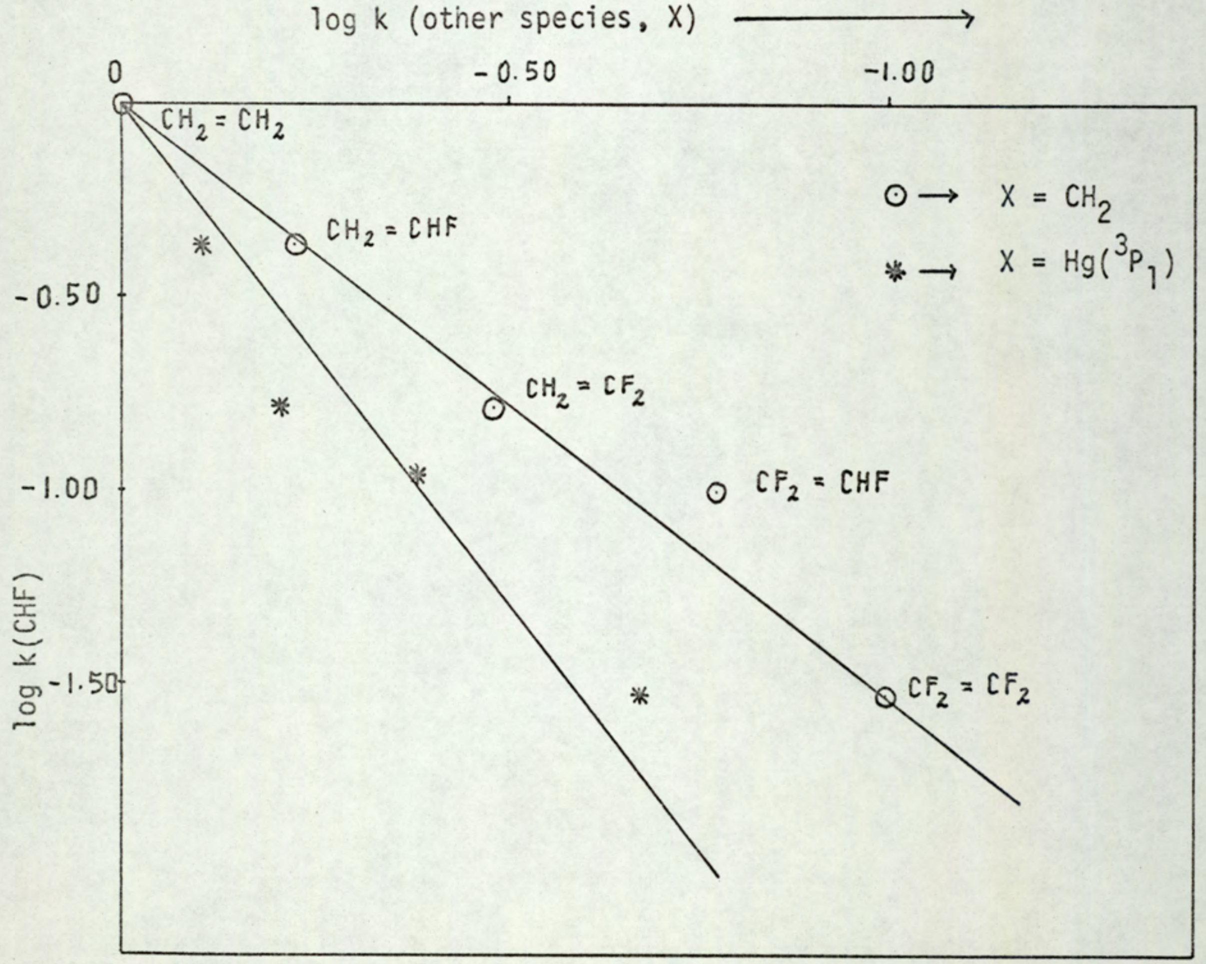


Fig. 5.11 FREE ENERGY PLOTS FOR CH_2, $Hg(^3P_1)$ AND CHF RADICAL REACTION WITH FLUOROETHYLENE

3.8 DISCUSSION

The results obtained for the relative rate constants for the addition of CHF radicals to fluoroethylenes (see Table 5.3) show a general trend as the fluorine substitution is increased, the relative rate decreases. Therefore, it is apparent that in the reaction with CHF radical, substitution of fluorine at the carbon atom of a double bond deactivates the reacting molecule.

The changes in electron density of the organic molecule on substitution can be described by means of the inductive and mesomeric properties of the substituents(14). In the case of fluorine atom the overall inductive effect is electron withdrawing (-I), and the mesomeric effect (which only occurs in unsaturated molecules) is electron donating (+M). Thus, there are two competing effects when fluorine is substituted at the carbon atom of a double bond. In the case of fluorine, the inductive effect may be greater than the mesomeric effect because of its high electronegativity, resulting in an overall withdrawal of electron from the carbon-carbon double bond.

The substitution of electron withdrawing fluorine atoms in ethylene cause deactivation with respect to attack by CHF radicals. This suggests that the rate of reaction of CHF radicals with fluoroethylenes is controlled by the Π-bond order of the molecule. The explanation for this can be made on the supposition that CHF primarily attacks the Π-electrons of a double bond and that substitution with highly electronegative fluorine atoms reduces the Π-electron density and hence the reactivity.

It can be seen in Table 5.3 that the relative rate constant for the reaction of $O(^3P)$ atoms decreases progressively with increasing fluorine substitution and reaches a minimum for 1,1 and 1,2-difluoroethylenes. Further fluorination increases the reactivity of fluoroethylenes toward $O(^3P)$ atoms. In contrast, the relative rate for the addition of CHF radicals to a series of fluoroethylenes decreases regularly.

It can be seen from the above information for oxygen atoms and CHF radicals that the mechanisms of addition of the two species are very different. The explanations are consistent with a Π complex transition state for CHF radicals and a σ complex(68) for oxygen atoms.

The evidences supported a <u>Π complex</u> for the reaction of CHF radicals and are as follows:

1. The free energy plots (log-log plot) for the rate of addition of CHF radicals to fluoroethylenes against the rate of CH_2 and $Hg(^3P_1)$ reactions reveal a reasonably linear relationship (see Figure 5.11). These could indicate that the factors controlling the rate of CH_2 and the rate of quenching of $Hg(^3P_1)$ atoms by fluorinated ethylenes are the <u>same</u> as those controlling the rate of addition of CHF radicals to them. It has been pointed out(22) that the quenching site of $Hg(^3P_1)$ atoms is at the doubly bonded carbon atoms. It is therefore reasonable to conclude that the CHF radicals primarily attack at the carbon-carbon double bond of the

fluoroethylenes as a whole and hence the Π complex is being formed.

2. As the logarithms of rates of the addition of CHF radicals to fluorinated ethylenes correlate well with the Π bond order, excitation energy and ionization potential (see Figures 5.7 - 5.8), there is a good reason to believe that the reaction proceeds through a Π transition state.

3. It has been shown in Chapter 3 that CHF radicals add to fluorinated ethylenes stereospecifically. This suggests the biradical intermediate is not involved in this reaction, and CHF attacks at the carbon-carbon double bond as a whole resulting in the formation of Π complex transition state. The observed results probably relate to the reaction of <u>singlet</u> CHF.

The correctness of the conclusion made in this chapter depends on the reliability of the calculated results presented in Table 5.5. Further studies on temperature dependence to obtain the values for the pre-exponential factors and the activation energy leading to more understanding of the transition state are desirable.

APPENDIX

Detailed quantitative results for the series of competitive runs investigating the relative rate constants for CHF + fluorinated ethylenes are given.

VNF represents vinyl fluoride ($CH_2 = CHF$)

DFE represents 1,2-difluoroethylene

TFE represents trifluoroethylene

P_{N_2} represents pressure of nitrogen in a volume of 3.95 ml at 23±2°C.

Pol represents pressure of olefin in the reaction vessel (760 ml) at 23±2°C.

Q represents Quantum yield of product. $= \frac{\text{Peak area}}{\text{yields of nitrogen}}$

$CHF + CF_2 = CHF/CH_2 = CHF$

P_{TOTAL} (mm)	P_{TFE} (mm)	P_{YNF} (mm)	$\frac{P_{TFE}}{P_{VNF}}{}_I$	$\frac{P_{TFE}}{P_{VNF}}{}_F$	$\frac{P_{TFE}}{P_{TFE}}{}_M$	$\frac{P_{VNF}}{P_{TFE}}{}_M$	Q_{M_1}	Q_{M_2}	$Q_{M_1}+Q_{M_2}$	$\frac{1}{Q(Ax+1)}$ obs	$\frac{1}{Q(Ax+1)}$ calc.	$\frac{K_4}{K_3}$
740.0	18.15	-	-	-	-	-	15.10	10.00	25.10	0.0398	0.0402	-
742.0	18.57	-	-	-	-	-	14.63	9.76	24.39	0.0410	0.0402	-
739.0	19.70	-	-	-	-	-	14.09	10.48	24.53	0.0407	0.0402	-
742.0	17.4	-	-	-	-	-	14.67	10.45	25.12	0.0398	0.0402	-
744.5	22.58_2	2.73	9.5230	9.9524	9.7377	0.10269	10.12	6.66	16.78	0.0557	0.0561	3.7513
745.0	18.57_2	2.95_8	6.2797	6.5874	6.4335	0.15543	8.404	5.562	13.966	0.0648	0.0643	3.9330
747.5	30.44_4	2.52_5	12.0568	12.5341	12.2954	0.08133	10.89	7.20	18.09	0.0524	0.0528	3.7165
744.5	20.31	3.0_2	6.7085	7.0342	6.8713	0.14553	8.66	5.84	14.50	0.0628	0.0628	3.8569

$K_{3/K_4} = 0.2594$

$K_{4/K_3} = 3.8536$

$CHF + CF_2 = CHF/CH_2 = CH_2$

P_{TOTAL} (mm)	P_{TFE} (mm)	P_2 (mm)	$\frac{P_{TFE}}{P_2}_I$	$\frac{P_{TFE}}{P_2}_F$	$\frac{P_{TFE}}{P_2}_M$	$\frac{P_2}{P_{TFE}}_M$	Q_{M_1}	Q_{M_2}	$Q_{M_1}+Q_{M_2}$	$\frac{1}{Q(Ax+1)}$	$\frac{1}{Q(Ax+1)}$	$\frac{K_4}{K_3}$
730.2	27.336	0.658	41.5440	48.7664	45.1552	0.02214	11.96	7.864	19.824	0.0485	0.0485	9.2287
735.0	25.52	0.74_9	34.0782	39.7702	36.9242	0.02708	11.15	7.52	18.67	0.0511	0.0503	9.9034
735.0	55.34_3	1.74_5	31.7151	33.6951	32.7051	0.03057	11.19	7.73	18.92	0.0501	0.0516	7.9867
732.0	65.21_3	1.37	47.6010	50.3696	48.9853	0.02041	12.06	8.10	20.16	0.0778	0.0478	9.1976
752.0	30.64_8	1.78_3	17.1917	19.5737	18.3827	0.05439	9.241	5.807	15.048	0.0606	0.0605	9.2776
749.0	43.58_9	1.74_2	25.0253	27.7179	26.3716	0.03791	10.45	6.64	17.09	0.0548	0.0543	9.5159

$K_{3/K_4} = 0.1085$

$K_{4/K_3} = 9.2113$

$CHF + CF_2 = CHF/CH_2 = CF_2$

P_{TOTAL} (mm)	P_{TFE} (mm)	P_{VNF} (mm)	$\frac{P_{TFE}}{P_{VNF}}_I$	$\frac{P_{TFE}}{P_{VNF}}_F$	$\frac{P_{TFE}}{P_{VNF}}_M$	$\frac{P_{VNF}}{P_{TFE}}_M$	Q_t	Q_c	$Q_c + Q_c$	$\frac{1}{Q(Ax+1)}$	$\frac{1}{Q(Ax+1)}$	$\frac{K_4}{K_3}$
734.4	22.42	1.665	13.4654	13.4252	13.4453	0.07437	12.98	8.85	21.83	0.0445	0.0448	1.4218
740.0	16.348	2.091	7.8182	7.7794	7.7988	0.12822	11.89	7.94	19.83	0.0480	0.0481	1.5064
740.0	17.4	-	-	-	-	-	14.67	10.45	25.12	0.0398	0.0402	-
735.0	18.15	-	-	-	-	-	15.10	10.00	25.10	0.0398	0.0402	-
734.5	18.57	-	-	-	-	-	14.63	9.76	24.39	0.0410	0.0402	-
742.5	19.70	-	-	-	-	-	14.05	10.48	24.53	0.0407	0.0402	-
736.0	15.872	1.286	12.3421	12.2863	12.3142	0.08120	12.580	8.94	21.52	0.0450	0.0452	1.4631
732.5	10.119	1.917	5.2785	5.2294	5.2540	0.19033	10.527	7.313	17.84	0.0522	0.0519	1.5585

$K_{3/K_4} = 0.6561$ $K_{4/K_3} = 1.5239$

$CHF + CF_2 = CHF/CF_2 = CF_2$

P_{TOTAL} (mm)	P_{TFE} (mm)	P_2 (mm)	$\frac{P_{TFE}}{P_2}\ _I$	$\frac{P_{TFE}}{P_2}\ _F$	$\frac{P_{TFE}}{P_2}\ _M$	$\frac{P_2}{P_{TFE}}\ _M$	Q_{M_1}	Q_{M_2}	$Q_{M_1}+Q_{M_2}$	$\frac{1}{Q(Ax+1)}$	$\frac{1}{Q(Ax+1)}$	$\frac{K_4}{K_3}$
738.0	19.9740	3.19_5	6.2510	6.4028	6.3269	0.15805	9.85	6.75	16.60	0.0417	0.0420	0.2175
745.0	11.48	4.01_2	2.8615	2.9548	2.9082	0.34385	6.92_5	4.65_9	11.57_9	0.0439	0.0440	0.2599
742.0	16.03_9	2.82_6	5.6745	5.8602	5.7674	0.17338	9.52	6.38	15.90	0.0423	0.0422	0.2806
742.0	13.27_3	3.39	3.9125	4.0470	3.9797	0.25126	8.06	5.48	13.54	0.0433	0.0430	0.2928

$K_{3}/K_4 = 3.7471$

$K_{4}/K_3 = 0.2668$

CHF + cis-CHF=CHF/CH_2 = CHF

P_{TOTAL} (mm)	P_{TFE} (mm)	P_{VNF} (mm)	$\frac{P_{DFE}}{P_{VNF}}_I$	$\frac{P_{DFE}}{P_{VNF}}_F$	$\frac{P_{DFE}}{P_{VNF}}_M$	$\frac{P_{VNF}}{P_{DFE}}_M$	Q_t	Q_c	$Q_t + Q_c$	$\frac{1}{Q(Ax+1)}$	$\frac{1}{Q(Ax+1)}$	$\frac{K_4}{K_3}$
742.5	12.6	-	-	-	-	-	33.686	12.85	46.536	0.0214	0.0213	-
750	14.8799	2.8181	5.2801	5.5629	5.4215	0.18444	16.065	6.826	22.891	0.0358	0.0364	3.6947
750.0	6.1258	2.8902	2.1195	2.2668	2.1931	0.45595	7.8544	3.1436	10.998	0.0589	0.0586	3.8770
744.0	20.8834	3.1977	6.5307	6.7990	6.6648	0.15004	18.04	7.63	25.67	0.0330	0.0336	3.6751
750.0	10.3211	3.3875	3.0468	3.2105	3.1286	0.3196	10.707	4.493	15.20	0.0476	0.0475	3.8720
753.0	10.5	-	-	-	-	-	32.39	13.172	45.862	0.0218	0.0213	-
751.0	11.8987	3.1232	3.8097	4.0284	3.9191	0.25516	12.80	5.37	18.17	0.0422	0.0422	3.8478

K_{3}/K_{4} = 0.2599 K_{4}/K_{3} = 3.8465

CHF + cis-CHF = CHF/CH$_2$ = CH$_2$

P_{TOTAL} (mm)	P_{TFE} (mm)	$P_{C_2H_4}$	$\frac{P_{DFE}}{P_{C_2H_4}}{}_{I}$	$\frac{P_{DFE}}{P_{C_2H_4}}{}_{F}$	$\frac{P_{DFE}}{P_{C_2H_4}}{}_{M}$	$\frac{P_{C_2H_4}}{P_{DFE}}{}_{M}$	$Q_{t-\nabla}$	$Q_{c-\nabla}$	$Q_t + Q_c$	$\frac{1}{Q(Ax+1)}$	$\frac{1}{Q(Ax+1)}$	$\frac{K_4}{K_3}$
742.5	12.6	-	-	-	-	-	33.686	12.85	46.536	0.0214	0.0216	-
753.0	10.5	-	-	-	-	-	32.39	13.172	45.862	0.0218	0.0216	-
747.0	23.603	1.9028	12.4043	14.5833	13.4938	0.07410	15.01	5.43	20.44	0.0397	0.0395	11.2655
748.0	20.336	2.3809	8.5412	10.0174	9.2713	0.10776	11.538	4.16	15.698	0.0476	0.0477	11.1454
752.5	33.973	1.8764	18.1052	20.6824	19.3938	0.05156	18.18	7.11	25.29	0.0340	0.0341	11.1107

$K_4/K_3 = 11.1741$ $K_3/K_4 = 0.0894$

$CHF + trans\text{-}CHF = CHF/CH_2 = CHF$

P_{TOTAL} (mm)	P_{DFE} (mm)	P_{VNF} (mm)	$\left(\frac{P_{DFE}}{P_{VNF}}\right)_I$	$\left(\frac{P_{DFE}}{P_{VNF}}\right)_F$	$\left(\frac{P_{DFE}}{P_{VNF}}\right)_M$	$\left(\frac{P_{VNF}}{P_{DFE}}\right)_M$	$Q_{t-\nabla}$	$\frac{1}{Q(Ax+1)}$	$\frac{1}{Q(Ax+1)}$	$\frac{K_4}{K_3}$
742.0	9.9665	2.7169	3.6683	3.7235	3.6959	0.27056	19.087	0.0440	0.0428	2.1994
740.5	12.098	3.1755	3.8097	3.8420	3.8258	0.26137	20.2537	0.0417	0.0423	1.9566
739.5	12.8557	2.6668	4.8206	4.5694	4.8450	0.20639	22.80	0.0382	0.0392	1.8798
742.0	9.47	-	-	-	-	-	35.99	0.0277	0.0275	-
740.0	9.7369	2.5515	3.8161	3.8625	3.8393	0.26046	19.96	0.0423	0.0422	2.0521
742.5	16.2715	2.5058	6.4934	6.5551	6.5243	0.15327	24.986	0.0361	0.0362	2.0179
748.0	15.80	-	-	-	-	-	35.344	0.0282	0.0275	-
749.0	11.42	-	-	-	-	-	36.079	0.0277	0.0275	-
744.0	12.65	-	-	-	-	-	37.17	0.0269	0.0275	-
744.0	8.7345	3.0271	2.8854	2.9283	2.9068	0.34401	17.077	0.0471	0.0469	2.0599

$K_3/K_4 = 0.4890$ $K_4/K_3 = 2.0446$

CHF + trans-CHF = CHF/CH_2 = CH_2

P_{TOTAL} (mm)	P_{DFE} (mm)	$P_{C_2H_4}$ (mm)	$\frac{P_{DFE}}{P_{C_2H_4}}$ I	$\frac{P_{DFE}}{P_{C_2H_4}}$ F	$\frac{P_{DFE}}{P_{C_2H_4}}$ M	$\frac{P_{C_2H_4}}{P_{DFE}}$ M	$Q_t - \nabla$	$\frac{1}{Q(Ax+1)}$	$\frac{1}{Q(Ax+1)}$	$\frac{K_4}{K_3}$
742.0	9.47	-	-	-	-	-	35.99	0.0277		-
748.0	15.80	-	-	-	-	-	35.344	0.0282		-
749.0	11.42	-	-	-	-	-	36.079	0.0277		-
744.0	12.65	-	-	-	-	-	37.17	0.0269		-
749.0	28.03	2.03	13.8075	14.7665	14.2892	0.06999	22.044	0.0401	0.0394	6.3426
755.5	20.1409	2.3785	8.4678	9.1251	8.7965	0.11368	17.549	0.0470	0.0467	6.0919
755.0	12.3445	2.119	5.6136	6.2738	5.9437	0.16824	13.784	0.0553	0.0558	5.8774
746.0	23.2223	2.4313	9.5513	10.2642	9.9078	0.10093	18.80	0.0448	0.0446	6.0570

K_{3/K_4} = 0.1666

K_{4/K_3} = 5.9996

$CHF + t\text{-}CHF = CHF/CH_3CH = CH_2$

P_{TOTAL} (mm)	P_{DFE} (mm)	$P_{C\ H}$ (mm)	$\frac{P_{DFE}}{P_{C_3H_6}}$ I	$\frac{P_{DFE}}{P_{C_3H_6}}$ F	$\frac{P_{DFE}}{P_{C_3H_6}}$ M	$\frac{P_{C_3H_6}}{P_{DFE}}$ M	$Q_t - \nabla$	$\frac{1}{Q(Ax+1)}$	$\frac{1}{Q(Ax+1)}$	$\frac{K_4}{K_3}$
742.0	9.47	-	-	-	-	-	35.99	0.0277	0.0275	-
748.0	15.80	-	-	-	-	-	35.344	0.0282	0.0275	-
749.0	11.42	-	-	-	-	-	36.079	0.0277	0.0275	-
744.0	12.65	-	-	-	-	-	37.17	0.0269	0.0275	-
745.5	29.0050	1.2805	22.6513	27.9154	25.2833	0.03955	16.45	0.0439	0.0439	14.8467
758.0	21.3476	1.2393	17.2533	23.2452	20.2493	0.04938	14.06	0.0479	0.0480	14.9111
744.5	17.1431	1.2181	14.0736	19.4373	16.7554	0.05968	11.93	0.0528	0.0523	15.3461
746.0	28.8193	1.0403	27.7028	35.4987	31.6007	0.03164	18.99	0.0401	0.0407	14.4230

$K_{3/K_4} = 0.0665$ $K_{4/K_3} = -5.0232$

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