THE REACTIONS OF OXYGEN ATOMS WITH SOME PARTIALLY FLUORINATED OLEFINS.

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SUMMARY

A detailed study was undertaken of the reaction of ground state oxygen atoms with the fluoroethylenes and with 1,1,2 trifluorobutene-1.

The $O(^3P)$/ fluoroethylene study yielded the following rate constants and Arrhenius parameters relative to ethylene.

OLEFIN	$k_{ol}/k_{C_2H_4}$		$\frac{A_{ol}}{A_{C_2H_4}}$	$E_{ol} - E_{C_2H_4}$ (kJmol.$^{-1}$)
	23°C	150°C		
CH_2=CH_2	(1.0)	(1.0)	(1.0)	(1.0)
CH_2=CHF	0.40	0.52	1.04	2.43
CH_2=CF_2	0.22	0.30	0.72	3.01
cisCHF=CHF	0.31	0.45	1.26	3.51
transCHF=CHF	0.56	0.71	1.43	2.38
CHF=CF_2	0.57	0.66	1.08	1.63
CF_2=CF_2	1.70	1.33	0.88	-1.55

Reactivity differences between the cis and trans isomers of 1,2 difluoroethylene have been attributed to a combination of entropic and enthalpic factors. An attempt to relate reaction rates to various bond and atomic properties of the fluoroethylenes indicated that formation of a σ transition complex is probably the rate determining process.

The reaction of ground state oxygen atoms with 1,1,2 trifluorobutene-1 yields 1 fluoropropene (cis and trans isomers) and carbonyl fluoride with quantum yields near to unity. Minor products identified included ethane, ethylene, propane, fluorocyclopropane and propionyl fluoride. In sharp contrast to the reactions of non-fluorinated olefins with oxygen atoms, epoxide formation was not significant in this system. The main primary process is thought to be formation of carbonyl fluoride and ethylfluorocarbene CH_3CH_2CF:, fluorocyclopropane and 1 fluoropropene being products of the isomerisation of this carbene.

Addition of oxygen to the system left the yield of 1 fluoropropene unchanged but greatly increased yields of propionyl and carbonyl fluoride. This behaviour has been attributed to the reaction of the biradical, $CH_3CH_2^{\cdot}CF-CF_2O^{\cdot}$, with molecular oxygen to yield ultimately 1 fluoropropene, carbonyl fluoride and propionyl fluoride.

The reaction schemes proposed satisfactorily explain major and minor product formation both in the presence and absence of molecular oxygen.

CHAPTER ONE

INTRODUCTION

1.1 PHOTOSENSITISATION

The process of photosensitisation consists of absorption of light energy by a strongly absorbing substance, the "photosensitiser", and transfer of this energy by collision to a compound only weakly absorbing in the spectral range considered.

Photosensitisation offers the obvious advantage of inducing chemical reactions in substances which do not absorb a sufficient amount of light energy in a particular spectral region. When light has been absorbed by the sensitiser, a competitive situation is created. The light energy can either be spontaneously re-emitted or can be dissipated by collision with another molecule (either the photosensitiser or a different molecule). The latter process is termed "quenching".

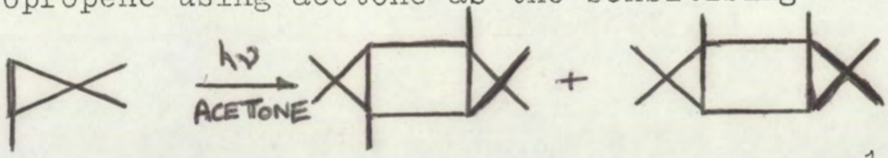
Photosen~~is~~sitisers in the gas phase have to fulfil the following requirements:

1) A relatively high vapour pressure at the temperature considered, is essential for sufficient molecules to be able to absorb in the gas phase.

2) The potential photosensitiser must have readily accessible excited states (singlet or triplet) of suitable energy for the purpose considered.

If we are interested in bringing about chemical reactions, 1 and 2 above limit the metal photosensitisers to mercury, cadmium and zinc.[1]

An example of a reaction photosensitised by an organic molecule is the dimerisation of 1,3,3trimethylcyclopropene using acetone as the sensitising molecule.[2]



The triplet state of acetone is about 330kJ mol.$^{-1}$ above the ground state.

In the field of inorganic photosensitisers, an example is the mercury photosensitised decomposition of nitrous oxide.[3]

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

1.2 MERCURY PHOTOSENSITISATION

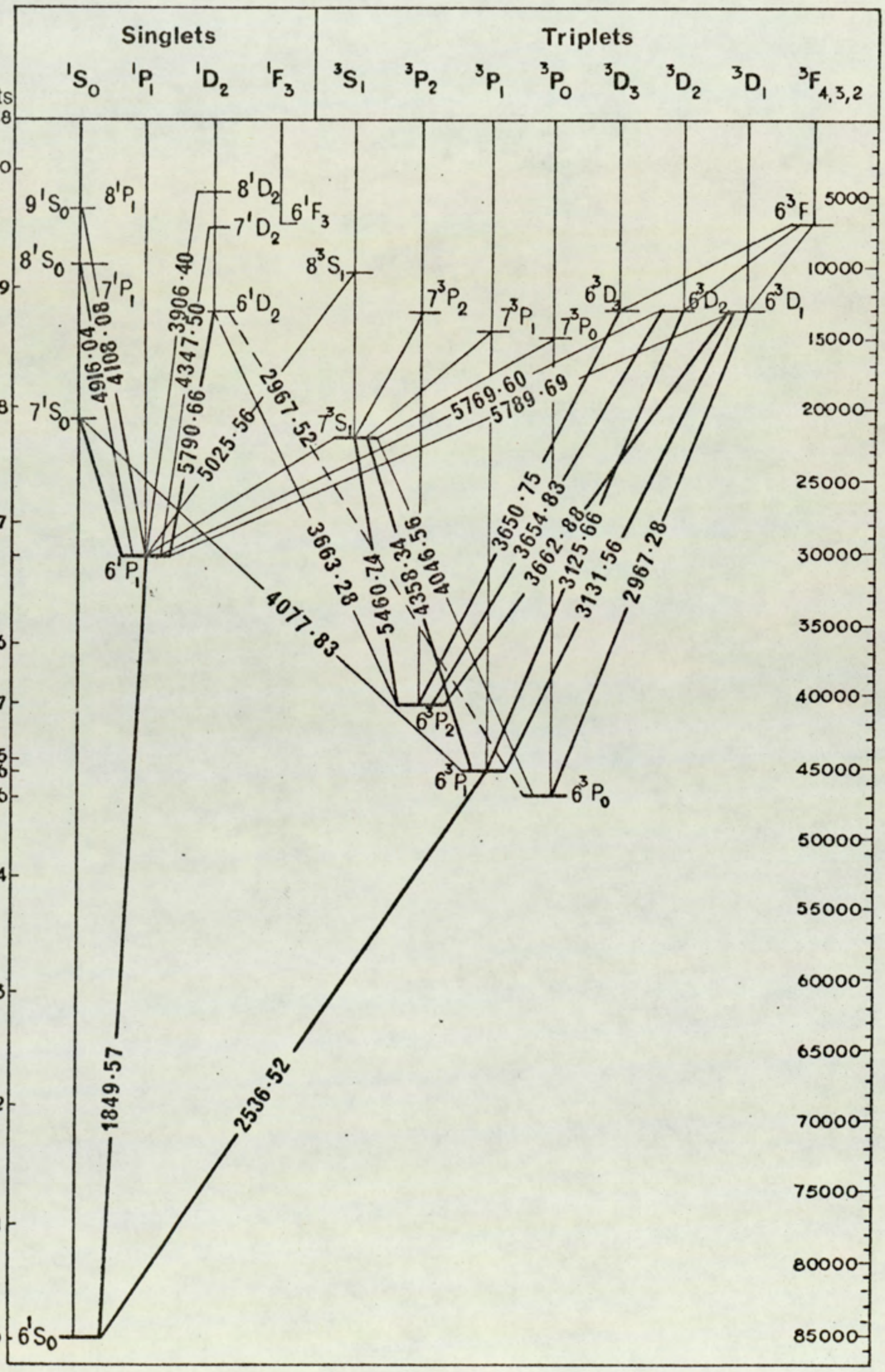
Mercury is particularly usefulfrom a photosensitisation point of view for the following reasons:

1) It is not very reactive and hence does not usually react chemically with other substances in the system.

2). It has an appreciable vapour pressure at ambient temperatures (1.5 x 10^{-3}mm. at 23°C).

3) It has an easily accessible triplet state 6($^3P_1$) 469 kJ mol.$^{-1}$ above the ground state. This is of sufficient energy to induce many chemical reactions (see fig. 1.1).

A low pressure mercury lamp emits mainly 2537 and 1849 Å radiation corresponding to the transitions Hg 6($^1S_0$) $\longrightarrow$ Hg 6($^3P_1$) and Hg 6($^1S_0$) $\longrightarrow$ Hg 6($^1P_1$). However, 1849 Å radiation is absorbed strongly by ordinary quartz and atmospheric oxygen. Almost all the useful radiation from a low pressure mercury lamp is at 2537 Å. For absorption of 2537 Å radiation by the mercury in the reaction cell to be effective, it is



ENERGY LEVELS OF MERCURY

FIG 1.1

essential that the line shapes of absorbing and emitting systems should match as closely as possible. In the high pressure mercury lamp, the line shape is considerably broadened by collisions (collision broadening). In addition, the 2537 Å line is almost entirely absent due to re-absorption of this line by ground state mercury atoms in the lamp. This phenomenon is termed "self-absorption" and is minimised by using a low pressure lamp.

When mercury is excited by 2537 Å radiation to the $6(^3P_1)$ state, three types of quenching are possible

$$1)\ Hg(^3P_1) + A \longrightarrow Hg(^3P_o) + A\ (21\text{kJ mol.}^{-1})$$

$$2)\ Hg(^3P_1) + A \longrightarrow Hg(^1S_o) + A^*(469\text{kJ mol.}^{-1})$$

$$3)\ Hg(^3P_1) + A \longrightarrow Hg(^1S_o) + A_1 + A_2$$

$$\text{or}\ \ HgA_1 + A_2$$

where A is the quenching molecule.

Process 1 is quenching of the triplet mercury state to the metastable $6(^3P_o)$ level. (See fig.1.1) Transitions from this state to the ground state are strictly forbidden and hence species in this state are relatively long lived ($\simeq 10^{-3}$sec.). Metastable quenching takes place with the transfer of only 21 kJ mol.$^{-1}$ of energy to the quenching molecule and hence this process can rarely induce chemical reaction. For a number of years the extent of metastable quenching by various gases has been a matter of controversy, due principally to the difficulty of quantitatively monitoring the metastable population levels. Many early workers[4,5] used a detection method **based on the** ability of metastable atoms to induce emmission of electrons from a metal surface. More recent work using this method has been carried out by Darwent and Hurtubise.[6] An alternate method of detection of metastable mercury atoms (6^3P_0) is by their absorbtion of 4047 Å (corresponding to the transition $Hg(6^3P_0) \rightarrow Hg(7^3S_1)$). This method has been used by Kimbell and Le Roy.[7] However, it would appear that more reliable work has been carried out by Callear and Norrish[8] using the flash photolysis technique. Excitation takes place by absorption of continuous light and the absorption spectrum noted at intervals after the flash. For the purpose of discussion the recent work of Callear and Hedges[9] has been accepted as the most reliable. The method is flash photolysis, using a special lamp constructed to produce an intense flash of mercury resonance radiation. Briefly their findings were that metastable atom yields in H_2, D_2, NO, N_2O, O_2 H_2S, C_2H_2, CH_3Br, HBr, HCl and HCN are less than 1% (i.e. fractional quenching of $Hg(^3P_1)$ to $Hg(^3P_0)$); significant yields of $Hg(^3P_0)$ were observed with N_2, C_2H_6, CH_4, C_3H_8 and CO.

Process 2 is direct quenching of $Hg(^3P_1)$ to the ground state, with transfer of 469kJ mol.$^{-1}$ to the quenching molecule. This energy raises the quenching molecule to an excited electronic state (as with CS_2).

Process 3 involves the transfer of the energy, again with quenching to the ground state, but in this case the quenching molecule fragments. An example of this is quenching by hydrocarbon molecules in which the energy is sufficient to break the C-H bond, with the formation of a hydrogen atom and alkyl radical. Excess energy after rupture is manifest as excess kinetic energy of the fragments. It is possible for one of the fragments to form a complex with the mercury atom. Callear and Hedges[9] have observed, spectroscopically, HgH in the mercury photosensitised decomposition of hydrogen presumably formed by the process

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

1.2a Quenching Cross Sections

1) Physical method

If we consider the 3 quenching acts mentioned previously together, then the following reaction scheme can be written;

$$\text{a)}\quad Hg6(^1S_o) + 2537\text{ Å} \longrightarrow Hg\ 6(^3P_1)$$

$$\text{b)}\quad Hg6(^3P_1) \xrightarrow{k_f} Hg\ 6(^1S_o) + h\nu\ (2537\text{Å})$$

$$\text{c)}\quad Hg6(^3P_1) + M \xrightarrow{k_q} Hg\ 6(^1S_o) + \ldots\ldots$$

If the rate of a) is R_i, then by steady state theory

$$\frac{d([Hg(^3P_1)])}{dt} = R_i - k_f[Hg(^3P_1)] - [Hg(^3P_1)][M]k_q = 0$$

$$[Hg(^3P_1)] = R_i / (k_f + k_q[M])$$

Hence the rate of the fluorescence reaction b) is

$$k_f[Hg(^3P_1)] = R_i k_f / (k_f + k_q[M]) = R_f$$

If in the absence of M, $R_f = R_f o = R_i$

Hence $$\frac{R_f o}{R_f} = 1 + \frac{k_q}{k_f}[M]$$

Now $1/k_f$ is the mean "lifetime" of Hg $(^3P_1)$, which can be designated τ

Hence $$\underline{\frac{R_f o}{R_f} = 1 + \tau k_q [M]}$$

This is the Stern-Volmer equation. By measuring the intensity of fluorescence in the absence and prescence of a quenching gas it is possible to evaluate the quenching rate constant, k_q, provided we have an estimate for the mean lifetime of $Hg(^3P_1)$ in the system. The quenching cross section, σ_q^2, is readily extracted from the quenching rate constant using the following equation;

$$k_q = \sigma_q^2 \left[8\pi RT \, (M_{Hg} + M_M \, / \, M_{Hg}M_M) \right]^{1/2}$$

One of the difficulties of this physical method is the uncertainity in the apparent lifetime of the $Hg(^3P_1)$ molecule. As ground state mercury absorbs 2537Å light very strongly, when a triplet mercury atom reverts to the ground state, a photon is emitted (2537Å), and is often recaptured by another ground state mercury atom. This process, usually known as "radiation imprisonment", can occur many times in a reaction cell and has the effect of prolonging the apparent lifetime of the species. Kang Yang[10] has eliminated the problem to a certain extent by noting the effect of increasing mercury vapour pressure on the value of τk_q. He found that τk_q varies roughly linearly with mercury vapour pressure and by extrapolating to zero vapour pressure the value of $\tau_0 k_q$ was obtained. Kang Yang estimated the quenching rate constant for ethylene by substituting the known τ_0 value (lifetime of an isolated $Hg(^3P_1)$ atom) into the extrapolated value obtained of $\tau_0 k_q$. k_q for the reaction $Hg(^3P_1) + C_2H_4 \rightarrow Hg(^1S_0) + C_2H_4^*$ was estimated to be $\underline{4.61 \times 10^{11} \text{ l.mol}^{-1} \text{ s}^{-1} \text{ at } 25^\circ\text{C}}$.

2. Chemical Method

Chemical methods of determining relative quenching cross sections have the following advantages;

1) They are independent of such effects as radiation imprisonment, mentioned above.

2) The experiments can be performed under conditions normally employed in mercury photosensitised studies.

The chemical method is competitive in character and will only yield the relative quenching cross section. The results may be placed on an absolute basis if the absolute cross section of the standard is known.

Cvetanović[3] studied the mercury photosensitised decomposition of nitrous oxide and mixtures of nitrous oxide with hydrocarbons. Briefly he found that triplet mercury atoms react with nitrous oxide to form nitrogen and oxygen atoms. This nitrogen can be readily measured quantitatively. If we consider the following competitive reaction scheme;-

a) $Hg + h\nu \longrightarrow Hg^*$ (Rate = R_i)

b) $Hg^* + N_2O \xrightarrow{k_{N_2O}} Hg + N_2 + O(^3P)$

c) $Hg^* + RH \xrightarrow{k_{RH}} Hg + \text{products}$

where Hg^* represents $Hg(6^3P_1)$.

If the rates of reactions b) and c) are R_b and R_c then

$$R_i = R_b + R_c$$

If there is no hydrocarbon present then

$$R_i = R_b^o = R_{N_2}^o \text{ (rate of formation of nitrogen)}$$

1) $R_i = [Hg^*][N_2O] k_{N_2O} + [Hg^*][RH] k_{RH} = R_{N_2}^o$

2) $R_{N_2} = k_{N_2O} [Hg^*][N_2O]$

Dividing 1) by 2):-

$$R_{N_2}o / R_{N_2} = 1 + k_{RH}[RH] / k_{N_2O}[N_2O]$$

A plot of $1/R_{N_2}$ vs $[RH] / [N_2O]$ should give a line of gradient k_{RH} / k_{N_2O} which is the required quenching rate constant of the hydrocarbon relative to nitrous oxide. This relationship holds well in practice as can be seen from Cvetanovic's results shown in Fig. 1.2 for ethane, ethylene and n-butane.

Both chemical and physical rate constants can be combined as the quenching cross section (and rate constant) of ethylene has been measured relative to nitrous oxide.[3,11] Some doubt has recently been cast on the results obtained by the nitrous oxide method. Rousseau[12] has observed that the quenching cross sections derived by the chemical method in some cases seem to be dependent upon incident light intensity. As much as a five-fold increase in the apparent cross section of n-butane relative to nitrous oxide is revealed by varying light intensity by a factor of 10^3. (σ_Q^2's increasing with decreasing light intensity.) He proposed that Cvetanović's basic mechanism is incomplete and that at high light intensity radical-radical reactions become important. Low light intensities are essential for meaningful results to be obtained. Further work is needed to clarify this problem.

1.2b The Mechanism of Mercury Photosensitised Reactions and the Electrophilic Nature of $Hg(6^3P_1)$.

It has been pointed out[13] that the triplet mercury atom exhibits electrophilic characteristics. In general, atomic reactants may show electrophilic,

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

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

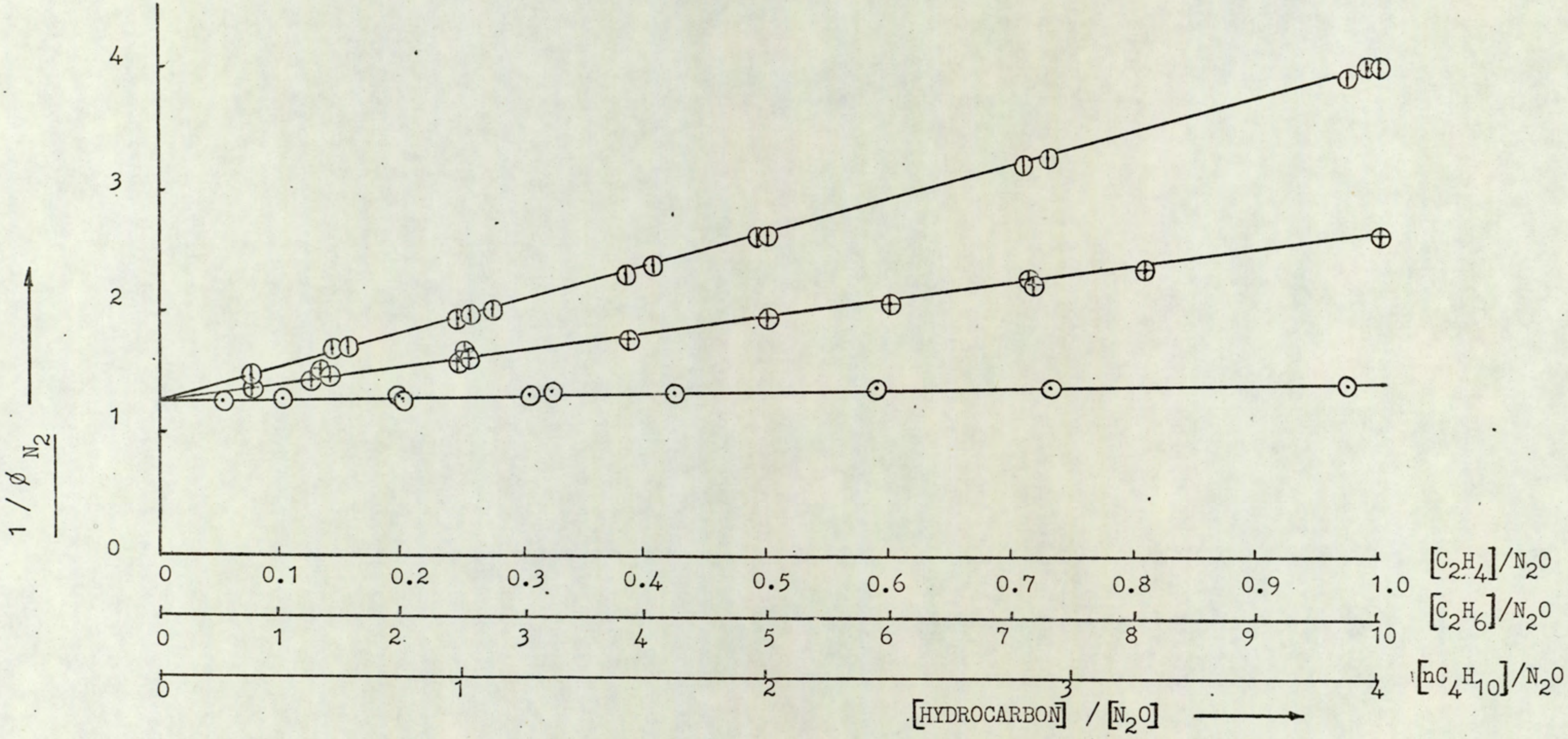
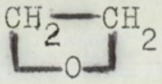


TABLE 1.1

CROSS SECTIONS AND RATE CONSTANTS FOR QUENCHING OF TRIPLET MERCURY (6^3P_1)

Compound	σ_Q^2	k_Q	Compound	σ_Q^2	k_Q
C_2H_6	0.22	0.20	$CH_2=CH_2$	48.2	46.1
C_3H_8	2.6	2.0	$CH_2=CHF$	46.1	36.3
$CH_3CD_2CH_3$	0.37	0.29	$CH_2=CF_2$	42.3	28.7
$CD_3CH_2CD_3$	2.2	1.7	$CHF=CF_2$	30.6	18.9
$CD_3CD_2CD_3$	0.19	0.15	$CF_2=CF_2$	16.5	9.5
n-C_4H_{10}	7.9	5.5			
i-C_4H_{10}	10.5	7.5	$(CH_3)_2CO$	79.5	58.5
$(CH_3)_3CD$	0.96	0.68			
C_2H_4	48.2	46.1	CH_3CHO	61.5	48.0
$CH_3CH=CH_2$	65.3	53.0			
$CD_3CD=CD_2$	62.9	48.2		5.9	4.7
C_4H_8 - 2	85.4	61.6			

Notes: units of k_Q are $l.mol.^{-1}s.^{-1} \times 10^{-10}$ at 25°C

units of σ_Q^2 are Å^2

References: 1) R.J.Cvetanović:

Progress in Reaction Kinetics, p.41,

vol.1, Pergammon Press, 1964.

2) A.R.Trobridge and K.R.Jennings

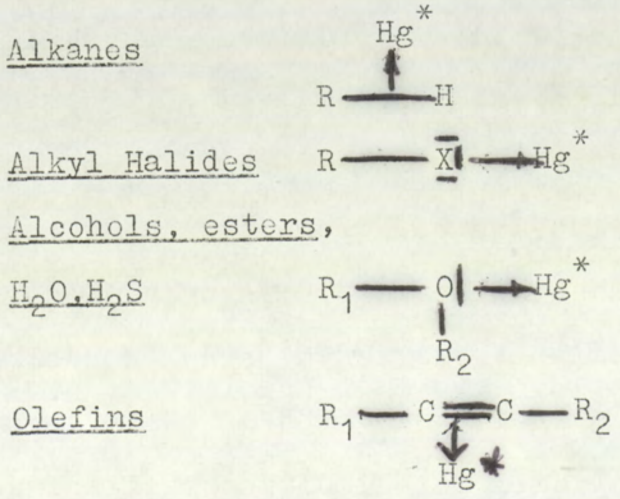
Proc.Chem.Soc., 335, (1964)

3) Kang Yang

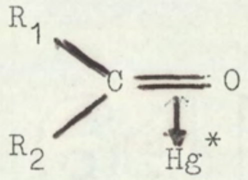
J.Amer.Chem.Soc., 88, 4575, (1966).

nucleophilic or radical reagent character. For example, it has been noted by Cvetanović[14] that oxygen atoms (O^3P) behave distinctly as electrophilic reagents in their reactions with olefins.

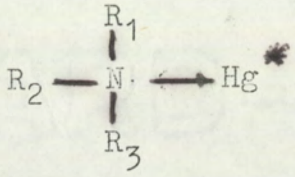
If $Hg(6^3P_1)$ is electrophilic in character this will be reflected in higher σ^2 values for the more nucleophilic reagents, even when account has been taken of differing molecular sizes. For example, it can be seen from Table 1.1 that the olefins exhibit a far larger cross sectional area than the saturated hydrocarbons of comparable molecular size. This is because of the high π electron density of the olefinic double bond which makes the olefins nucleophilic in nature. Also it has been noted by Rousseau that a progressive substitution of methyl groups in ammonia increases the σ_Q^2 values very much more than the sum of a methyl group and ammonia would indicate. Here, cross sections follow the increase in basicity of the methyl substituted ammonia. A proposed scheme of quemching interactions[13] can be written, based on the assumed electrophilic nature of Hg^3P_1: -



Carbonyl compounds



Amines, phosphines



In each case the triplet mercury atom quenches itself at the site of maximum electron density. Further evidence in support of this mechanism has been provided by deuteration experiments carried out by Rousseau, Gunning and Strausz.[13,15] The quenching rate constants of various deuterated compounds are compared with the undeuterated parent in the table below:-

TABLE 1.2

Effect of Deuteration upon the Relative Quenching Rate Constant of Various Molecules.

Compound	k_H/k_D
$CD_3CD_2CD_3$	13.3
$CH_3CD_2CH_3$	7.1
$CD_3CH_2CD_3$	1.2
$(CH_3)_3CD$	10.9
$CD_2{=}CD{-}CD_3$	1.04
cyclo C_6D_{10}	1.2
D_2O	2.2
ND_3	2.7
PD_3	0.9

The ratio k_H/k_D refers to the ratio of the quenching rate constant of undeuterated compound to the deuterated molecule shown in the 1st column of Table 1.2. If the quenching site is one of the C-D bonds then we would expect to see a considerable isotope effect for the quenching rate constant. It is evident from the ratio of rates for the deuterated hydrocarbons that the secondary C-H bonds must quench very much more effectively than the methyl (primary) C-H bonds. Similarly a tertiary C-H bond quenches more effectively than a secondary C-H bond. Deuterium substitution reduces quenching efficiency substantially. Rousseau has calculated the quenching efficiency of these secondary and tertiary C-H bonds and this is shown in the table below:-

TABLE 1.3

Compound	Minimum quenching on CH_2 or CH group
$CH_3CH_2CH_3$	87% (on CH_2)
$CH_3CD_2CH_3$	64% (on CD_2)
$CD_3CH_2CD_3$	96% (on CH_2)
$CD_3CD_2CD_3$	87% (on CD_2)
$(CH_3)_3CH$	91% (on CH)
$(CH_3)_3CD$	71% (on CD)

In contrast to the hydrocarbons, the olefins show very little isotope effect. With both $CD_2=CD-CD_3$ and cyclo C_6D_{10}, the decrease in quenching (relative to the undeuterated parent) is very small. This would suggest that the quenching site is not a C-H bond as with the hydrocarbons but is more likely to be the electron-rich C=C bond. As deuteration does not affect the electron density of the bond significantly, little effect would be expected.

Similarly, a smaller isotope effect is noted for D_2O, ND_3 and PD_3. This evidence points to the quenching site being the lone pair of the electronegative atom and not the bonds to hydrogen.

Thus the proposed schemes of interaction shown above are in accordance with observed results and suggest strongly that the triplet mercury atom behaves in an electrophilic manner.

1.2c Some Typical Primary Processes in Mercury Photsensitised Reactions.

a) Decomposition of Hydrogen

This reaction has been extensively investigated by a number of workers.[8,9,16,17] The latest indication put forward by Callear,[9] using resonance flash spectroscopy is that the primary process is

$$\underline{Hg^* + H_2 \longrightarrow HgH + H(^2S_{\frac{1}{2}})}$$

b) Decomposition of n-Butane

Cvetanović[18] has studied this reaction in detail. Experimental behaviour of the system could be explained without having to invoke the participation of metastable mercury atoms $Hg(^3P_0)$. Callear and Hedges[19] have not detected HgH in the quenching of $Hg(^3P_1)$ by saturated hydrocarbons. They suggest the primary process is either

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

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

c) Decomposition of Methyl Chloride and Hydrogen Chloride

Both reactions have been studied by Strausz and co-workers.[20,21] Flash resonance spectroscopy[9] has established the primary processes as:-

$Hg(^3P_1) + HCl \longrightarrow HgCl + H$

and $Hg(^3P_1) + CH_3Cl \longrightarrow HgCl + CH_3^{\cdot}$

d) Decomposition of Carbon Disulphide

Callear[9] has shown the reaction produces the CS molecule but only very slowly. The mechanism of quenching is probably electronic energy transfer

$Hg^* + CS_2 \longrightarrow Hg(^1S_o) + CS_2^*$

where CS_2^* is probably a triplet state of the molecule. CS is produced by secondary reactions of CS_2^*.

e) Decomposition of Nitrous Oxide

Early studies by Manning and Noyes[22] lead them to the conclusion that two processes were possible

(I) $N_2O + Hg(^3P_1) \longrightarrow NO(^2\Pi) + N(^4S) + Hg(^1S_o)$

or (II) $N_2O + Hg(^3P_1) \longrightarrow N_2(^1\Sigma) + O(^3P)$

Cvetanović[23] has shown that the experimental results can only be explained if (II) is the primary process. The quantum yield of (II) is unity. Callear[9] reported less than 1% metastable mercury atoms $Hg(^3P_o)$ are produced in the quenching process.

f) Decomposition of Carbonyl Sulphide

Gunning and Strausz[24] have investigated the decomposition of carbonyl sulphide as a potential source of sulphur atoms (^3P). They have proposed the scheme shown below

$Hg(^3P_1) + COS(^1\Sigma) \longrightarrow Hg(^1S_o) + CO(^1\Sigma) + S(^3P)$

1.3 PRODUCTION OF GROUND STATE OXYGEN ATOMS (^3P)

A number of different methods have been used to produce ground state oxygen atoms for investigation of their reactions. The more important methods are listed below :-

a) Electrical Discharge

Avramenko and Kolesnikova[25] generated oxygen atoms by passing molecular oxygen through an electrical discharge at pressures of about 1mm. The major disadvantage of this system is that undissociated molecular oxygen in ground and excited states participates in subsequent reactions and can influence the nature of the products.

b) Microwave Discharge

Westenberg and deHaas[26] have used the microwave discharge of a trace of oxygen in an inert gas (helium or argon). This method has been used as a source of ground state oxygen atoms by a number of other workers[27,28]. An alternative method of producing oxygen atoms in the absence of molecular oxygen is by the titration of discharged nitrogen with nitric oxide which yields ground state oxygen atoms by the following reaction:-

$$N + NO \longrightarrow N_2 + O(^3P)$$

Many investigators use both techniques to examine the effect of molecular oxygen. Discharge techniques in fast flow systems at low pressures are particularly useful for the determination of absolute rate constants of atomic reactions.

c) Thermal Production

Ozone, oxygen and nitrous oxide can be decomposed by a hot filament to give ground state oxygen atoms.[29] It has been pointed out by Lundell[29] that electrical discharge produces vibrationally and electronically excited molcules in addition to oxygen atoms. Lundell's basic source of oxygen atoms was nitrous oxide decomposed by cobalt oxide on a platinum filament. This has the following advantages:-

1) The other product is nitrogen which is inert.
2) The reaction of undecomposed N_2O with O atoms is very slow at room temperature.
3) A vibrationally excited N_2 or N_2O molecule produced thermally at the filament is rapidly quenched by the excess nitrous oxide.

Klein and Scheer[39,41,84] have found that a good source of oxygen atoms is the dissociation of molecular oxygen on either tungsten ribbon between 2400 and 2800 K, or rhenium filaments at 2300 K. The latter has the advantage that it lasts considerably longer than tungsten.

d) Photolysis of Nitrogen Dioxide

When mixtures of $^{18-18}O_2$ and NO_2 are irradiated at 3130Å, it has been shown[30] that the molecular oxygen becomes scrambled and ^{18}O transfer to NO_2 occurs. This evidence would appear to suggest complete dissociation at 3130Å and probably virtually complete dissociation at 3660Å. The proposed primary process was:-

$$NO_2 + h\nu \longrightarrow NO(^2\Pi) + O(^3P)$$

The scrambling mechanism is probably by the reaction below:-

$$O + O_2\ (+M) \longrightarrow O_3(+M)$$
$$NO + O_3 \longrightarrow NO_2 + O_2$$

Sato and Cvetanović[31] studied the photo-oxidation of butene-1 by NO_2 at wavelengths between 4047Å and 2288Å. They found that between 4047Å and 3261Å, the ratio of the two principal oxidation products α butene oxide and n-butanal, remained constant. It is pointed out that this would be difficult to explain if free oxygen atoms were not involved in the reaction.

Between 2537Å and 2288Å, a considerable increase in the amount of butene oxide formed was noted. Sato and Cvetanović[32] concluded that the primary reaction at these shorter wavelengths is

$$NO_2 + h\nu \longrightarrow NO(^2\Pi) + O(^1D)$$

It appears that NO_2 is a good source of triplet oxygen atoms between 4047Å and 2537Å and a convenient source of $O(^1D)$ at wavelengths shorter than 2288Å.

The disadvantage of using NO_2 as an oxygen atom source are

1) The parent molecule is very reactive.

2) NO_2 can react rapidly with oxygen atoms to yield molecular oxygen.

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

e) <u>The Mercury Photosensitised Decomposition of N_2O</u>

This reaction was studied by Manning and Noyes[22] in 1932. When the reaction was allowed to go to completion the products were nitrogen and mercuric oxide

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

It was noted that overall there was no pressure change although initially small pressure increases had been claimed. Two primary processes were considered possible

These were;-

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

or b) $N_2O + Hg(^3P_1) \longrightarrow N_2(^1\Sigma) + O(^3P \text{ or } ^1D) + Hg(^1S_0)$

After reinvestigation Cvetanović[3] found that the major products were nitrogen and oxygen in the ratio of 2:1, although a slight deficiency in the oxygen was noted, and attributed to the formation of mercuric oxide. The rate of formation of nitrogen in the system was found to be rather variable. This was due to depletion of the mercury vapour in the system and also formation of mercuric oxide which tends to reduce the transparency of the cell windows. Cvetanović also noted that in the presence of an oxygen consuming compound (olefin or hydrocarbon) no mercury depletion occurred and no mercuric oxide was formed. He also found that the rate of decomposition of nitrous oxide was identical to the rate of formation of nitrogen.

This result rules out reaction (a) above and reaction (b) appeared the more likely decomposition mechanism. Spin conservation rules predict that oxygen atoms formed should be in the triplet state.

Cvetanović[33] has also considered two further alternatives to the formation of free triplet oxygen atoms;

1) <u>Formation of an electronically excited N_2O molecule</u>

ie. $Hg(^3P_1) + N_2O \rightarrow Hg(^1S_0) + N_2O^*$

This was ruled out on spectroscopic grounds and also because the rate of decomposition is pressure-independent (the rate of decomposition would be expected to decrease at high pressure when the N_2O^* molecule could be collisionally deactivated.)

2) Formation of an energy rich HgO molecule

$$Hg(^3P_1) + N_2O \longrightarrow HgO^* + N_2$$

It is conceivable that HgO* could show the reactions **attributed** to triplet oxygen atoms in the Hg/N_2O system. Cvetanović has dismissed this for several reasons.

a) HgO formation is very pronounced in the absence of oxygen consuming substances, but not formed when oxygen consuming compounds are present.

b) When an N_2O/olefin mixture is irradiated, then the ratio of addition products to nitrogen formed is independent of the N_2O/olefin ratio. If the energy rich HgO molecule was involved, one would expect progressively more HgO to be deposited as the N_2O mole fraction is increased, which is contrary to observation.

c) Gunning[34] also found that no isotope enriched HgO was formed in the mono-isotopic photosensitised decomposition of N_2O. Enrichment would be expected if HgO was formed in the primary stage of the decomposition.

d) The addition product yields tend to increase with increasing total pressure. An energy rich HgO molecule would tend to be collisionally deactivated at these higher pressures leading to deposition of mercuric oxide within the reaction cell.

1.3a Advantages of the Hg/N_2O System as a Source of $O(^3P)$

1) The total pressure may be chosen from a wide range of values.

2) The rate of oxygen atom formation is easily monitored by measuring the rate of nitrogen formation.

3) The rate is easily altered by changing the lamp intensity.

4) Nitrous oxide is inert to radical attack under most conditions.

5) The absence of molecular oxygen can be ensured.

Quenching by nitrous oxide is only about half as efficient as by olefins (see quenching cross sections and rate constants in section 1.2). However by having a large excess of nitrous oxide it is possible to eliminate almost completely quenching of mercury atoms by the olefin.

1.4. THE REACTION OF GROUND STATE OXYGEN ATOMS WITH OLEFINS.

Previous to 1955, very little work had been done on these reactions. In 1955, Avramenko and Kolesnikova[25] and Cvetanović[35] carried out independent studies into the $O(^3P)$/olefin reactions.

The basic difference between the two lines of research was the source of ground state oxygen atoms, Avramenko and Kolnesnikova used the elctrical discharge technique whereas Cvetanović used the mercury photosensitised decomposition of nitrous oxide. The results obtained by the different workers were similar in some respects but showed appreciable differences in others. These differences have been attributed to the vastly dissimilar conditions in the two systems. Electrical discharge requires that the pressure is only a few millimetres and that molecular oxygen is present. As will be seen later these are two critical factors which can radically alter the nature of the products.

Cvetanović[35] studied the reaction of oxygen atoms with ethylene. The products of the reaction were carbon monoxide, hydrogen, several paraffins (to C_4), aldehydes (mainly CH_3CHO and some higher homologues) and a small amount of ethylene oxide.

These reaction products are best explained by a primary addition of $O(^3P)$ to ethylene and the split of the "hot" adduct into $CH_3\cdot$ and $\cdot CHO$. The following reactions then become clear

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

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

Stabilisation of the initial adduct could yield acetaldehyde. Cvetanović noted that the yields of CH_3CHO, and ethylene oxide increase with increasing pressure and that the CO yield decreased at higher pressures.

Cvetanović's studies of the higher olefins gave some very interesting results and enabled him to construct a more concrete picture of the "hot" adduct. He found that with propylene and 1,3 butadiene the amounts of addition products increase and fragmentation products decrease with increasing pressure (as had been observed previously with ethylene). In the case of propylene (see Fig.1.3), addition products included propylene oxide, propionaldehyde and acetone. Fragmentation products were mainly acetaldehyde and ethane.

This evidence points to the initial formation of a "hot" precursor of short lifetime. At high pressures, the precursor can be partially stabilised by collisional deactivation. This stabilised precursor then forms the observed addition products. At lower pressures, most of the energy remains with the adduct leading to a greater degree of fragmentation. This trend is immediately obvious from Fig.1.3.

1.4a) Mechanism of the Addition Process.

The main features evident from the reaction of oxygen atoms with propylene and the butenes noted by Cvetanović is that the major products are the epoxide and some isomeric carbonyl compounds. The products of a number of the reactions are shown in Table 1.4 overleaf.

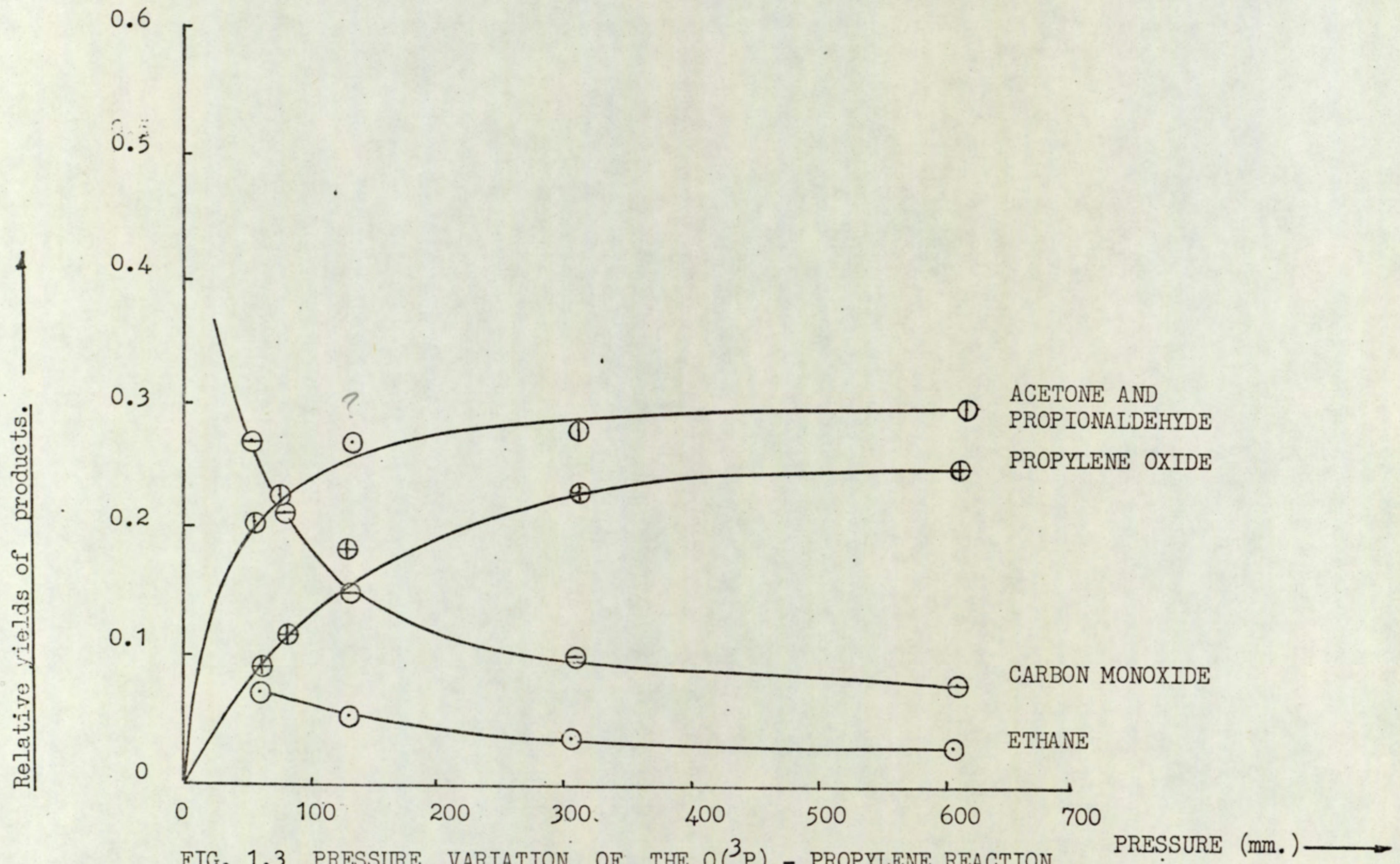
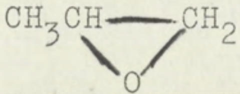
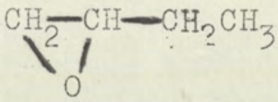
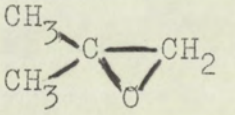
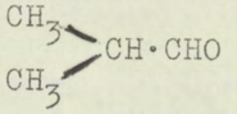
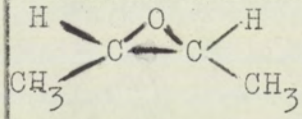
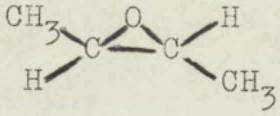
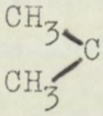
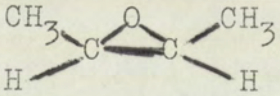
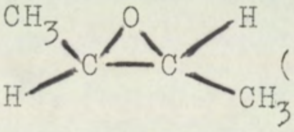
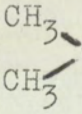


FIG. 1.3 PRESSURE VARIATION OF THE O(^{3}P) - PROPYLENE REACTION PRODUCT YIELDS.

(R.J. Cvetanovic Adv. in Photochem., 1 , 122 (1963))

TABLE 1.4

Types of Addition Products from O(^3P)/Olefin Reactions

Olefin	Addition products and their fractions	
	Epoxides	Carbonyls
Propylene	 (0.50)	C_2H_5CHO (0.50)
Butene-1	 (0.53)	C_3H_7CHO (0.43) $CH_3CO\cdot C_2H_5$ (0.04)
isobutene	 (0.54)	 $(CH_3)_2CH\cdot CHO$ (0.43) $CH_3COC_2H_5$ (0.03)
cis butene-2	 (0.25)  (0.26)	 $(CH_3)_2CH\cdot CHO$(0.23) $CH_3CO\cdot C_2H_5$(0.26)
trans butene-2	 (0.15)  (0.33)	 $(CH_3)_2CH\cdot CHO$ (0.21) $CH_3COC_2H_5$ (0.31)

Reference:- R.J.Cvetanović

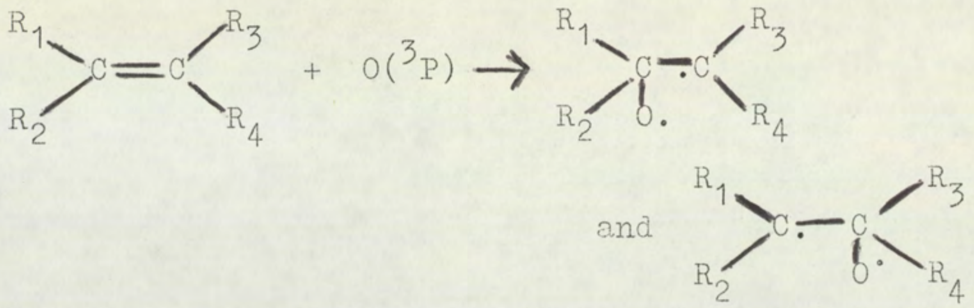
Advances in Photochemistry p.126.

The following points become clear if we study the types of products from each olefin.

a) <u>The addition products do not retain the stereo-specific character of the olefin.</u>

Starting with cis butene-2, we obtain a mixture of cis and trans butene-2 oxides as addition products . The same pattern is observed in the case of trans butene-2.

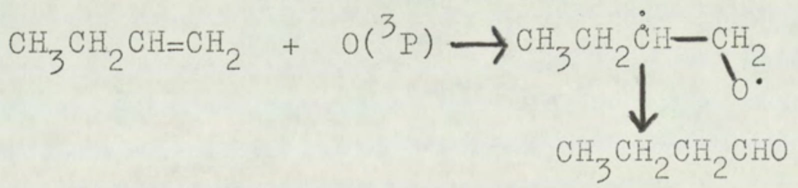
This perhaps best explained by the formation of a biradical intermediate.



This mechanism allows for possible rotation about the original C=C bond before ring closure to form the epoxide. Rotation will lead to loss of any stereospecific character of the original olefin. Another point in favour of the biradical intermediate is that the spin conservation rule is satisfied. These biradicals are probably short-lived. This is illustrated by the fact that different ratios of cis and trans butene-2 oxide is obtained from cis and trans butene-2.

b) Oxygen adds preferentially to the less substituted carbon of the double bond.

For example, with butene-1, the main carbonyl product is n-butyraldehyde and not methyl ethyl ketone.

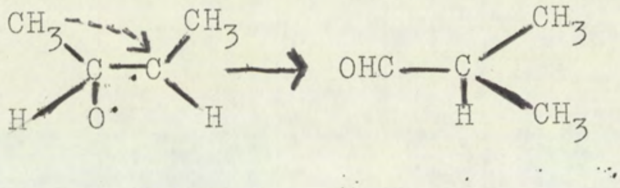


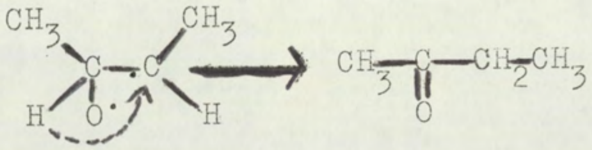
$$CH_3CH_2CH{=}CH_2 + O(^3P) \longrightarrow CH_3CH_2\dot{C}H{-}CH_2O^{\cdot} \longrightarrow CH_3CH_2CH_2CHO$$

Similar behaviour is observed with other olefins.

c) Internal rearrangements.

These generally occur in the formation of carbonyl compounds with the migration of a hydrogen or an alkyl group to the neighbouring carbon of the double bond. The migration is always from the carbon to which the oxygen is attached. The following example illustrates this point.


isobutyraldehyde

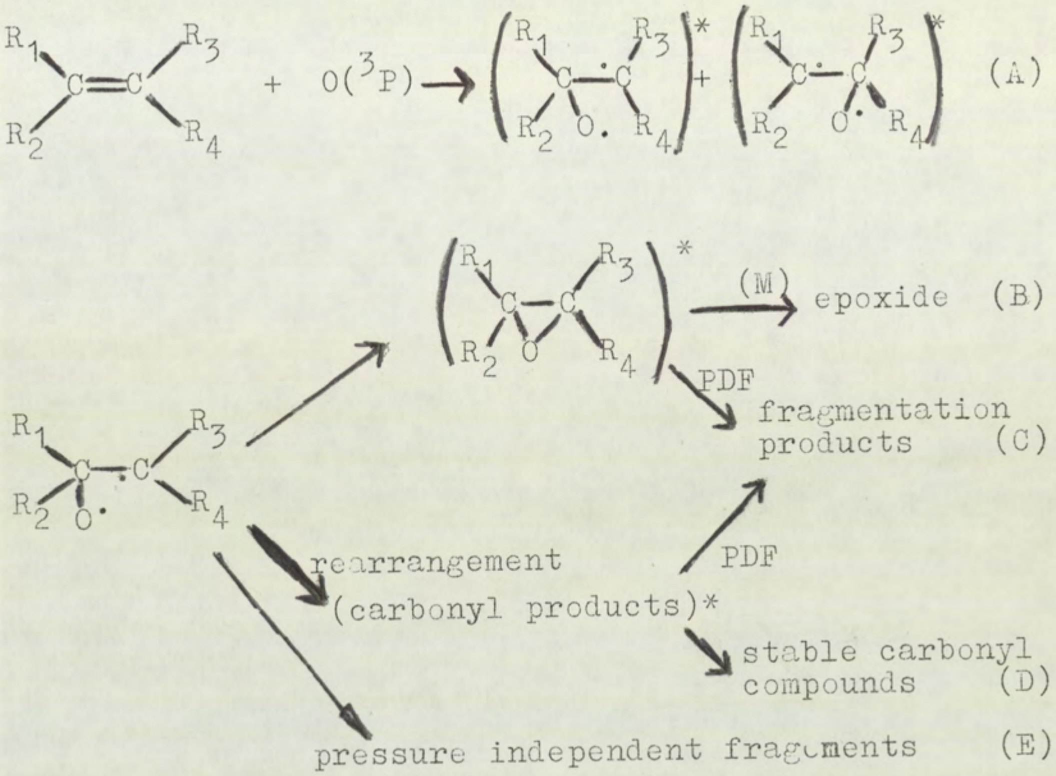
or 
methyl ethyl ketone

As shown in Table 1.4, approximately equal amounts of the aldehyde and ketone are formed. Cvetanović[33] suggested that H migration proceeds internally whereas migration of an alkyl group is only partly an internal process.

1.4b) Pressure Dependent and Pressure Independent Fragmentation.

If we consider the reaction of $O(^3P)$ with butene-1 the main products are α butene oxide, n-butanol, methyl ethyl ketone (small amount), and carbon monoxide. Butene oxide is clearly an addition product. The ketone and aldehyde have also been formed from the biradical intermediate (methyl ethyl ketone only in a small amount by addition of oxygen to the end of the double bond.) The carbon monoxide is a fragmentation product.

It is found that with increasing pressure all products except carbon monoxide show increasing yields per oxygen atom. Carbon monoxide yields, on the other hand decrease when the pressure increases. However, even at high pressures a certain amount of CO is still produced and this cannot be suppressed by any further increase in pressure. This portion of CO is caused by a pressure independent process, whereas the additional CO produced at lower pressure is formed from pressure dependent fragmentation. We can illustrate the scheme diagrammatically as shown below.



(PDF = pressure dependent fragmentation)

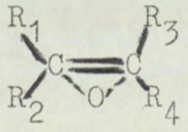
The pressure independent fragments are formed because the biradical is presumably very short lived and does not experience a collision before partially decomposing by the pressure independent route.

The biradical has a considerable amount of excess energy. If the energy is not removed by a collision, then it is carried over to the "hot" products of the reaction ("hot" carbonyls or epoxides.) These "hot" products can subsequently be stabilised by collision to yield normal epoxide and carbonyls. If the pressure is kept low, some of the products decompose by the pressure dependent pathway. If the reaction is carried out at a higher temperature or the oxygen atoms are given more kinetic energy (eg by NO_2 photolysis) then the excess energy of the biradical is increased. This energy increases the amount of pressure independent fragmentation. It also increases the amount of pressure dependent fragmentation when the excess energy is carried over to the carbonyl and epoxide stage, where it is increasingly more difficult to stabilise these products by collision (as their lifetime is shorter.)

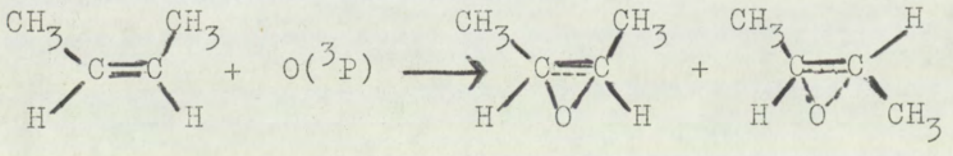
1.4c) Nature of the Transition State.

Klein and co-workers[39,40,41] studied the reactions of $O(^3P)$ with condensed simple olefins in the 77-90K temperature range. This has the advantage of suppressing the fragmentation processes observed in Cvetanović's system. Apart from this, the products obtained were the same as those at 300K.

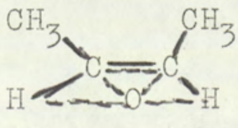
Klein has proposed a loose three-membered ring as the intermediate. The oxygen is bound in the plane of the olefinic structure.



This ring allows a certain amount of rotation about the very much weakened original carbon double bond, so that the initial reaction is, for instance, cis butene-2.

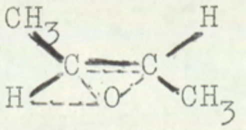


Klein also proposes that oxygen can form weak bonds with neighbouring hydrogens illustrated diagrammatically below



(A)

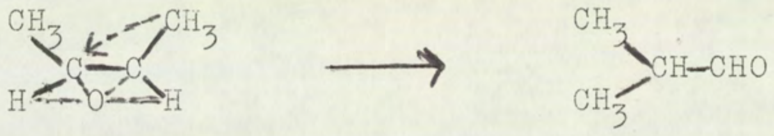
or



(B)

With form (A) both hydrogens are held by their proximity to oxygen. As a result, it is much more likely that there will be a migration of a methyl group

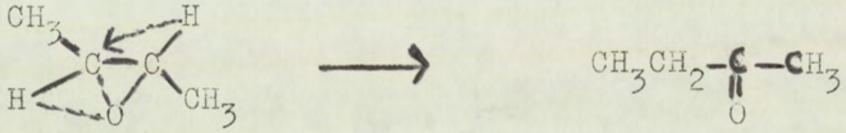
ie.



isobutyraldehyde

With form (B), only one of the hydrogens is held and the other is much more likely to migrate in preference to the two methyl groups.

ie.



2 butanone

This scheme can be generalised to predict that the cis form of olefin complex (A) will lead to aldehydic products, whereas form (B) gives rise to ketonic products.

Klein studied a series of reactions of olefins with oxygen atoms using both the cis and trans isomers of each olefin. The results are shown below.

TABLE 1.5

Fractional Product Yields for the $O(^3P)$ Addition to Internal Straight Chain Olefins at 90K [41]

Products	Olefin					
	2-butene		2-pentene		3-hexene	
	cis	trans	cis	trans	cis	trans
t.epoxide	0.30	0.50	0.26	0.59	0.17	0.65
c.epoxide	0.24	0.06	0.34	0.04	0.42	0.02
Aldehyde	0.21	0.06	0.20	0.04	0.28	0.03
Ketone	0.25	0.38	0.20	0.33	0.13	0.30
t.epoxide/ketone	1.2	1.3	1.3	1.8	1.3	2.2
c.epox./aldehyde	1.1	1.0	1.7	1.0	1.5	0.7
c.epoxide/ t.epoxide	0.8	0.12	1.3	0.07	2.5	0.03

As the aldehyde is derived from the cis intermediate then there should be a relationship between the two. This is obvious in Table 1.5. With all of the trans isomers of the olefins, only a small amount of cis epoxide and aldehyde is formed.

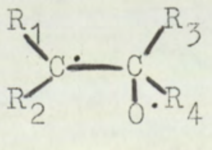
Klein also argued that if all the aldehydic products were derived from the cis intermediate then the ratio of cis epoxide to aldehyde should be the same as for the two isomers of each olefin. Using the same argument, the ratio of trans epoxide to ketone should also remain constant. The ratios in Table 1.5 are considered to demonstrate this point within the limits of the analytical uncertainities.

The general conclusions for the series of olefins were;

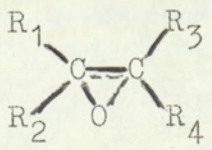
a) The retention of the configuration of products becomes more pronounced with increasing chain length of the olefin.

b) Reaction of $O(^3P)$ with olefins at low temperatures tends to be more stereospecific with trans than cis olefins.

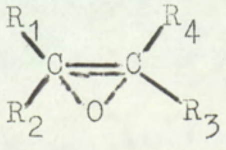
These ideas of the transition state do not conflict with those of Cvetanović if we imagine the initial adduct being the previously mentioned bi-radical



allowing rotation about the single bond and then formation of the two intermediates proposed by Klein.



and



1.4d) Relative Rates of Reaction of Oxygen Atoms with Olefins.

Cvetanović[33] has measured the relative rates of reaction of oxygen atoms with various olefins. The method used is competitive in nature, based on the theory discussed in detail in section 4.3. The standard olefin preferred in later experiments was cyclo-pentene which at 25°C, yields 27% ethylene for each oxygen atom produced. By measuring the ethylene yield in the presence of various amounts of other olefins, it is possible to calculate the reaction rate of that olefin relative to cyclopentene. Of course, the method will not be applicable to ethylene itself. This obstacle is surmounted by following the carbon monoxide yield from ethylene. Cvetanović's results are summarised in Table 1.6 below (rates calculated relative to cyclopentene).

TABLE 1.6

Relative Rate of Reaction of $O(^3P)$ at 25°C

Compound	Rel.rate constant	Compound	Rel.rate constant
Ethylene	0.034	trans butene-2	0.95
Propylene	0.19	cis 2-pentene	0.76
Butene-1	0.19	Cyclopentene	1.00
Hexene-1	0.22	trimethylethylene	2.67
Isobutene	0.84	tetramethylethylene	3.42
cis butene-2	0.80	1,3 butadiene	0.82

Taken from Advances in Photochemistry, vol.1, p.139 (1963)

Cvetanović[42] has also determined the Arrhenius parameters for some of the reactions in Table 1.6.

TABLE 1.7

Activation Energies and 'A' Factors of the Reaction of $O(^3P)$ with Olefins

Olefin	$^A/_{A_{CP}}$	$E-E_{TME}$ (kJmol.$^{-1}$)
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_{CP} is the pre-exponential factor for cyclopentene.

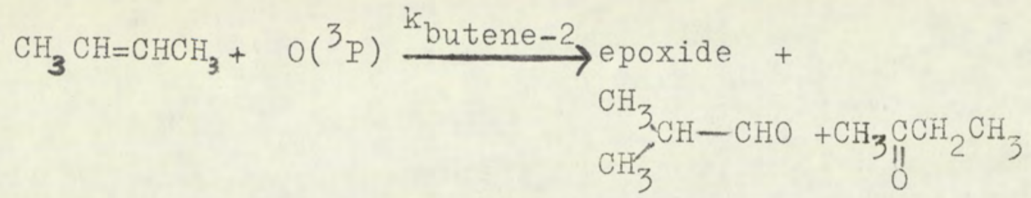
E_{TME} is activation energy for the tetramethylethylene reaction.

The results in Table 1.7 suggest that the difference in reactivity in the olefins is primarily due to a difference in activation energies and not controlled by the 'A' factor differences (which appear near to unity compared to cyclopentene).

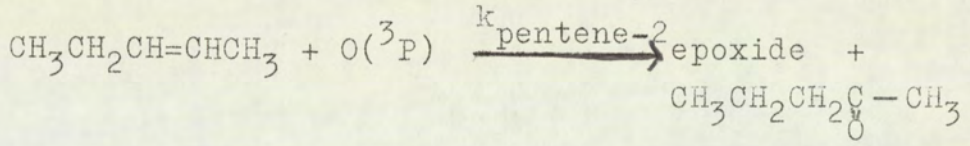
Cvetanović[14,43] has suggested that the initial interaction of the oxygen atom is with the double bond as a whole, and only at a later stage does the oxygen atom localise itself on one of two carbon atoms of the double bond. If we consider the rates and products of the following reactions:-

1) $CH_3CH{=}CH_2 + O(^3P) \xrightarrow{k_{propylene}}$ epoxide + CH_3CH_2CHO

2) $CH_3CH_2CH{=}CH_2 + O(^3P) \xrightarrow{k_{butene-1}}$ epoxide + $CH_3CH_2CH_2CHO$

3) 

$$CH_3CH{=}CHCH_3 + O(^3P) \xrightarrow{k_{butene-2}} \text{epoxide} + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH{-}CHO + CH_3\underset{\underset{O}{\|}}{C}CH_2CH_3$$

4) 

$$CH_3CH_2CH{=}CHCH_3 + O(^3P) \xrightarrow{k_{pentene-2}} \text{epoxide} + CH_3CH_2CH_2\underset{\underset{O}{\|}}{C}-CH_3$$

$k_{propylene} \hat{=} k_{butene-1}$ and $k_{butene-2} \hat{=} k_{pentene-2}$. It would appear that the contributions of methyl and ethyl groups to the reactivity of the olefin are about equal. Also, for these two olefins, the ethyl groups exert strong orientating effects as the addition is almost exclusively to the terminal carbon. If the orientating effect of the methyl and ethyl groups was related to their respective contributions to the reactivity of the olefin, we would expect, for pentene-2 almost equal addition to both carbons of the double bond (as the methyl and ethyl groups contribute equally to the reactivity). This is not the case as addition is almost exclusively to carbon attached to the methyl group (evident from the products obtained from pentene-2).

Cvetanović has suggested that the rate constants depend on the polarisability of the double bonds rather than the stability of the intermediates. The configuration of the activated complex should not therefore be identified with the configuration of the intermediates. In view of the electrophilic trend in the rates, it is probable that a π complex is formed with a partial charge transfer from the olefin to the attacking oxygen.

1.4e) The Electrophilic Character of Oxygen Atoms

Cvetanović[14,23,43] has pointed out that oxygen atoms exhibit electrophilic character, The reaction of $O(^3P)$ with olefins is closely related to the reaction of peracetic acid, bromine, dichloro- and dibromocarbene with the same olefins. This is best illustrated by a free energy plot of the logarithms of each of the above reagents' rate constants with the olefins, against the corresponding rate constant for oxygen atom reactions with the same olefins. This is shown in Fig. 1.4.

The significance of the straight line is established from the following theory.

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

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

where k is specific rate constant

k^1 is Boltzmann's constant

h is Planck's constant

T is absolute temperature

$\Delta G^{\neq}$ is the free energy of activation.

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

For a series of reactions at constant temperature the equation can be written as

$$\ln(k_i) = a_i + b_i\Delta G^{\neq}_i$$

where a and b are constants, and the subscripts i represent the reaction of the member of the series with <u>a particular reagent</u> (eg $O(^3P)$ atoms.)

If we write the same equation for the reactions of the same series with a different reagent, also at constant temperature; we obtain

$$\ln(k_j) = a_j + b_j \Delta G^{\neq}_j$$

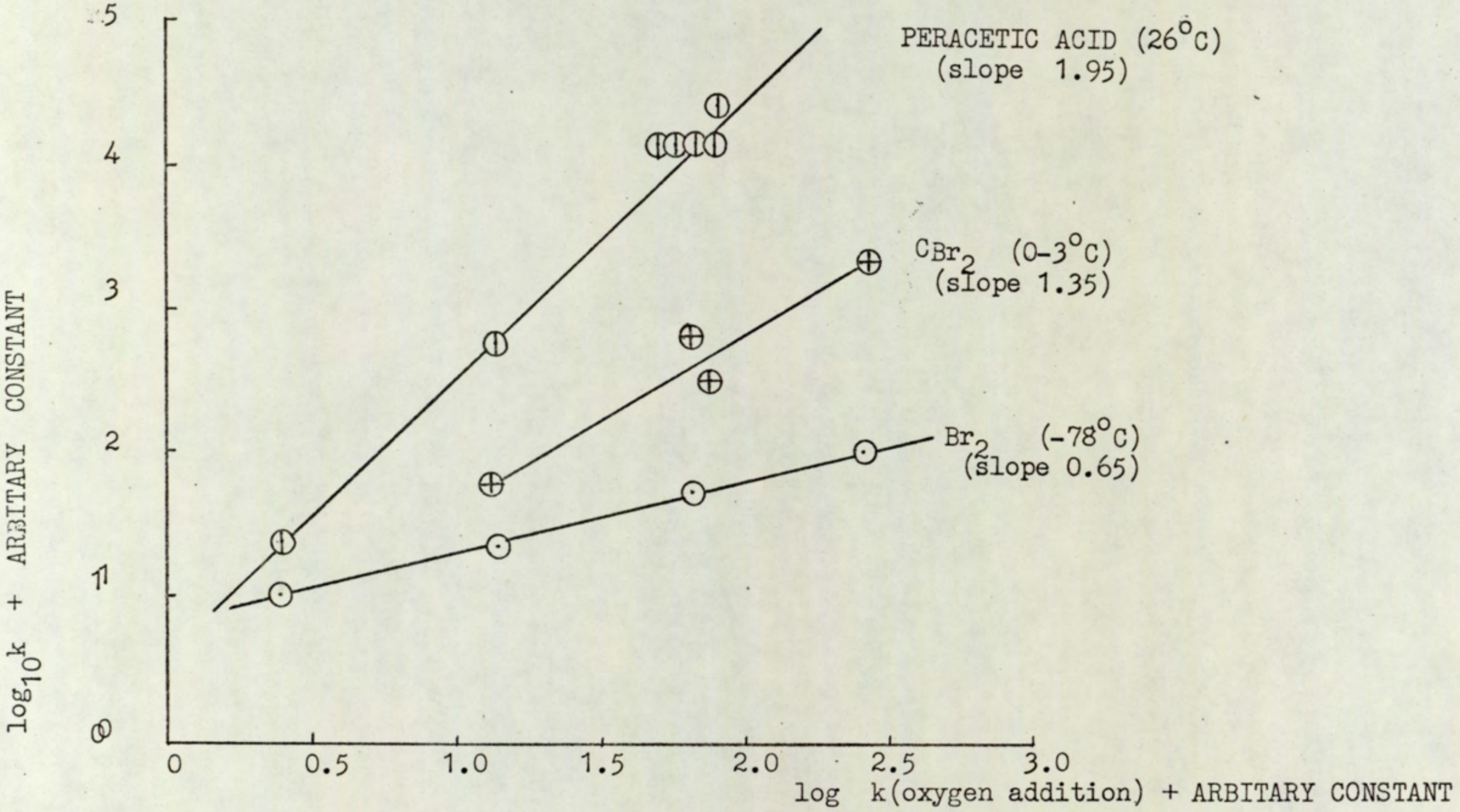


FIG. 1.4 FREE ENERGY PLOTS FOR BROMINE, PERACETIC ACID, CBr_2 AND OXYGEN ATOM REACTIONS WITH OLEFINS.

(R.J, Cvetanovic, J. Chem. Phys., 30, 19, (1959)) We can now see that if ln(k) for peracetic acid, bromine, dichloro- and dibromocarbene reactions with olefins are plotted against ln(k) for oxygen atom reactions, and a linear relationship is observed then the free energy of activation must be related by

$$\Delta G_j^{\neq} = n\Delta G_i^{\neq} + d \quad \text{(n and d constants)}$$

ie. there is a linear free energy relationship between the reactions of oxygen atoms with olefins and the other three reactants. This implies that the two series of reactions are related (usually the reactive species are related in character).

The gradient of the line obtained is significant as shown by the following argument:-

If we represent the rate of oxygen atom reaction by k_o and the rate of the other three reagents reactions by k_i and distinguish the various members (olefins) by superscripts a....n then the gradient of the line is

$$S = \frac{\ln(k_i^{\,n}) - \ln(k_i^{\,a})}{\ln(k_o^{\,n}) - \ln(k_o^{\,a})} \qquad (1)$$

Also the Arrhenius aquation gives

$$k^n = A^n \exp.(-E^n/RT) \qquad (2)$$

Substituting (2) into (1)

$$S = \frac{\left(\ln(A_i^{\,n}) - E_i^{\,n}/RT_i\right) - \left(\ln(A_i^{\,a}) - E_i^{\,a}/RT_i\right)}{\left(\ln(A_o^{\,n}) - E_o^{\,n}/RT_o\right) - \left(\ln(A_o^{\,a}) - E_o^{\,a}/RT_o\right)}$$

simplifying

$$\frac{\log\left(\frac{A_i^{\,n}}{A_i^{\,a}}\right) - \left(\frac{E_i^{\,n} - E_i^{\,a}}{RT_i}\right)}{\log\left(\frac{A_o^{\,n}}{A_o^{\,a}}\right) - \left(\frac{E_o^{\,n} - E_o^{\,a}}{RT_o}\right)} = S \qquad (3)$$

Cvetanović[42] has shown that for oxygen atom reactions with olefins, the 'A' factors are almost identical for the series.

ie $A_o^{\,n} = A_o^{\,a}$ (4)

Also Böeseken and Hanegraaff[44] have shown that the 'A' factors for peracetic acid oxidation of olefins are very nearly the same for the series.

ie $A_i^{\,n} = A_i^{\,a}$ (5)

Substituting (4) and (5) into (3) we obtain

$$S = \left(\frac{E_i^{\,n} - E_i^{\,a}}{T_i}\right)\left(\frac{T_o}{E_o^{\,n} - E_o^{\,a}}\right)$$

The graph indicates a gradient of 2 for the peracetic acid oxidation. As the two series of reactions were carried out at about the same temperature this would indicate $E_i^{\,n} - E_i^{\,a} = 2(E_o^{\,n} - E_o^{\,a})$ ie. the difference in activation energy for any two olefins' reactions is twice as large for epoxidation by peracetic acid as it is for addition of oxygen atoms.

Another argument in favour of the electrophilic character of oxygen atoms is the approximate correlation between the ionisation potential of an olefin and the rate of oxygen atom reaction with that olefin (ie. the lower the ionisation potential the faster the rate of attack). This trend is indeed observed.[43] In fact, other physical properties correlate well with the logarithm of the oxygen atom rate constant because of a relationship similar to that observed with the free energy plot. This relationship is

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

for spectroscopic excitation energies.

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

for ionisation potentials

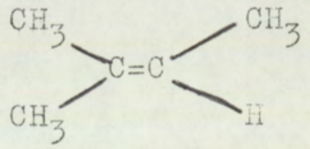
$$= RTS_h(\Delta H_h^{\,n} - \Delta H_h^{\,a})$$

for heats of hydrogenation.

where S represents the slope of the plots of $\log k_o$ against value of the measured physical property. $E_o^{\,n}$ and $E_o^{\,a}$ represent, as before, the activation energy of oxygen atom reaction with n th and a th olefin respectively. These linear relationships hold because of a constant 'A' factor for the series of olefin reactions.

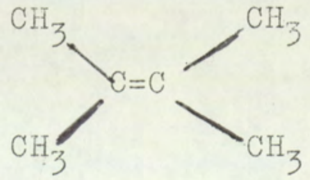
Yet another strong argument pointing to the electrophilic character of oxygen atoms is in the trend in the rates of reaction with various olefins shown in Table 1.6. The rates increase progressively as the number of alkyl groups attached to the double bond carbons increase. ie. the rates are in the order

$CH_2{=}CH_2 < CH_3CH{=}CH_2 < CH_3CH{=}CH{\cdot}CH_3 <$



$(CH_3)_2C{=}C(CH_3)H$

$<$



$(CH_3)_2C{=}C(CH_3)_2$

This is understandable when we consider that alkyl groups are electron donating, giving an electron rich double bond.

1.5 REACTION OF OXYGEN ATOMS WITH FLUORINATED OLEFINS

1.5a) Perfluoro-olefins.

Heicklen and co-workers have extensively investigated the reaction of oxygen atoms with perfluoro-olefins. Oxygen atoms were generated by nitrous oxide technique previously mentioned. Heicklen and Cohen[45] reinvestigated the mercury photosensitised decomposition of nitrous oxide and found that at least 99·9% of the oxygen atoms were $O(^3P)$.

Reaction of oxygen atoms with some perfluoro-olefins are discussed in detail below.

a) Tetrafluoroethylene (C_2F_4)

This reaction has been studied by Saunders and Heicklen[46] at temperatures of 23° and 125°C, over a wide range of pressures and lamp intensities (ie. oxygen atom concentrations). They found that the quantum yield of carbonyl fluoride, $\phi(CF_2O)$, was 1·0 for all conditions.

The only products formed in the absence of molecular oxygen were CF_2O and perfluoro-cyclopropane ($c\text{-}C_3F_6$). No tetrafluoroethylene oxide (C_2F_4O) or CF_3CFO was formed.

Cohen and Heicklen[47] re-examined the system at 22, 95, and 150°C. They proposed two possible mechanisms to explain the products.

Mechanism I

$$O(^3P) + C_2F_4 \longrightarrow CF_2O + CF_2 \qquad (1)$$

$$2CF_2 \longrightarrow C_2F_4 \qquad (2)$$

$$CF_2 + C_2F_4 \longrightarrow c\text{-}C_3F_6^* \qquad (3)$$

Mechanism II

$$O(^3P) + C_2F_4 \longrightarrow C_2F_4O^* \qquad (4)$$

$$C_2F_4O^* + C_2F_4 \longrightarrow CF_2O + c\text{-}C_3F_6 \qquad (5)$$

$$C_2F_4O^* \longrightarrow CF_2O\cdot + CF_2 \dashrightarrow \tfrac{1}{2}C_2F_4 \qquad (6)$$

CF_2 found in reaction (1) will probably be in the triplet state if the spin conservation rule holds. This has subsequently been verified.[48,49,50] Evidence of triplet CF_2 is that it can be scavenged by molecular oxygen, as was observed in the $O(^3P)/C_2F_4$ system. For the mercury photosensitised decomposition of C_2F_4, it is known that singlet CF_2 is produced,[51] which is not scavenged by molecular oxygen. This evidence points strongly to the CF_2 produced in reaction (1) being a triplet.

In the absence of O_2, the triplet CF_2 converts to the singlet state before removal.[47] In mechanism II $C_2F_4O^*$ is presumably a triplet which does not stabilise as C_2F_4O is not observed in the system.

Both mechanisms predict that $\phi\ CF_2O = 1\cdot0$ in accordance with observation. If we consider the quantum yield of cyclofluoropropane $\phi(c\text{-}C_3F_6)$ we find that mechanism II predicts

$$\phi(c\text{-}C_3F_6) = \frac{k_5[C_2F_4]}{k_5[C_2F_4] + k_6}$$

Mechanism II gives

$$\phi(c\text{-}C_3F_6) = 1\cdot0 \quad \text{if} \quad k_3 \gg k_2$$

$$\text{or} \quad \underline{\frac{(I_a)^{-\frac{1}{2}}k_3\,[C_2F_4]}{(2k_2)^{\frac{1}{2}}}} \quad \text{if} \quad k_2 \gg k_3$$

Heicklen found that by varying $[C_2F_4]$ and I_a that the behaviour of $\phi(c\text{-}C_3F_6)$ conformed to neither mechanism I nor II completely but all the data could be explained exactly if one assumed that both mechanisms operate simultaneously.

b) Reaction of Oxygen Atoms with Perfluoropropylene C_3F_6

Heicklen[46,52,53] found the products of the reaction to be CF_2O, CF_3CFO, C_5F_{10} and $CF_3\text{-}\underset{\diagdown CF_2 \diagup}{CF\text{--}CF}\text{-}CF_3$. C_2F_4 was probably formed but the analytical system could not detect its presence. Three primary schemes were proposed

a) $O(^3P) + C_3F_6 \longrightarrow CF_2O + CF_3CF:$

b) $O(^3P) + C_3F_6 \longrightarrow CF_3CFO + CF_2:$

c) $O(^3P) + C_3F_6 \longrightarrow C_3F_6O^*$

Proposed subsequent secondary reactions were

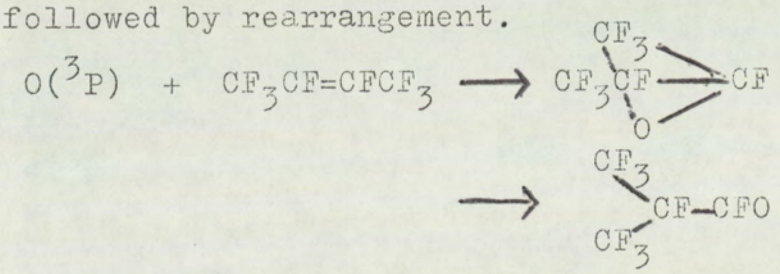
d) $C_3F_6O^* + C_3F_6 \longrightarrow C_5F_{10} + CF_2O$

e) $C_3F_6O^* + C_3F_6 \longrightarrow CF_3\text{-}\underset{\diagdown CF_2 \diagup}{CF - CF}\text{-}CF_3 + CF_3CFO$

f) $C_3F_6O^* \longrightarrow CF_2O + CF_3CF:$

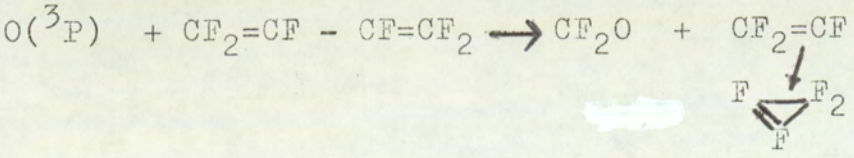
c) Perfluorobutene-2

The major product was $i\text{-}C_3F_7CFO$. Other products formed were CF_3CFO and CF_2O . In contrast to the previously mentioned reactions, the main route is not cleavage of the double bond but is probably addition followed by rearrangement.



d) Perfluoro 1,3 butadiene

The products are CF_2O and $c\text{-}C_3F_4$. The reaction is probably



$O(^3P) + CF_2{=}CF - CF{=}CF_2 \longrightarrow CF_2O + CF_2{=}CF - CF:$

One feature common to these reactions is evident.

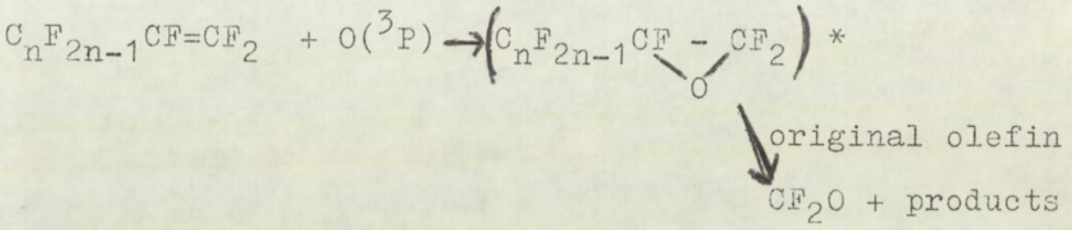
If the perfluoro-olefin has a terminal double bond then the major product is always carbonyl fluoride CF_2O.

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

The resulting biradical formed then can

1) add to the original olefin
2) Cyclise or rearrange
3) Dimerise with another biradical.

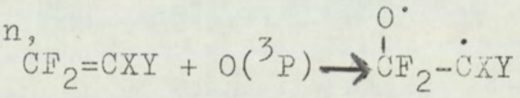
An alternative or complimentary scheme is



1.5b) Partially Fluorinated Olefins

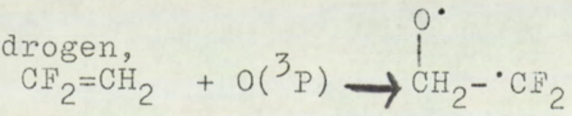
Although the relative rate constants for reactions of oxygen atoms with partially fluorinated olefins have been studied extensively,[54-57] little work has been undertaken to elucidate the products and mechanisms of the reactions. Mitchell and Simons[58] studied the reaction of $O(^3P)$ with halogenated 1,1 difluoroethylenes $CF_2{=}CXY$. They concluded that the oxygen adds to fluorinated carbon when X and Y are halogens, but to the other carbon if X and Y are hydrogen.

ie. if X,Y halogen,



$$CF_2{=}CXY + O(^3P) \rightarrow \overset{O\cdot}{\overset{|}{C}}F_2-\dot{C}XY \qquad (1)$$

If X,Y hydrogen,



$$CF_2{=}CH_2 + O(^3P) \rightarrow \overset{O\cdot}{\overset{|}{C}}H_2-{\cdot}CF_2 \qquad (2)$$

The main products observed from 1,1 difluoroethylene are carbon monoxide and hydrogen presumably by the scheme

$\cdot O{-}CH_2{-}\dot{C}F_2 \rightarrow CF_2 + CH_2O^* \rightarrow CO + H_2$

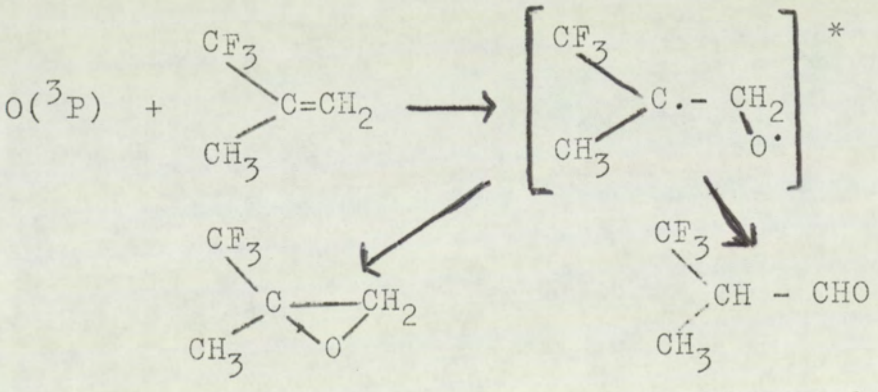
Halogenated 1,1 difluoroethylene gives carbonyl fluoride.

The reaction of oxygen atoms with 2 trifluoromethylpropene[54], suggests that with partly fluorinated propenes and butenes, the reaction is essentially the same as the unsubstituted compound ie. formation of an epoxide and isomeric carbonyl compound.

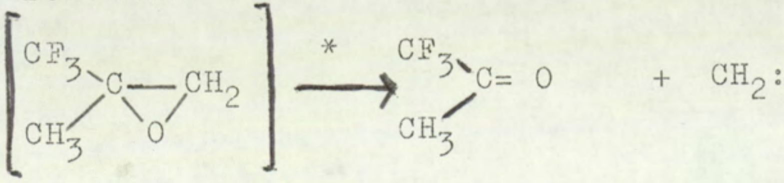
This generalisation can probably be extended to most partially fluorinated olefins, but excluding those with fluorine substitution at the double bond. One would expect olefins with a fully fluorinated double bond to behave similarly to the perfluoro-olefins.

a) Reaction of $O(^3P)$ with 2 trifluoromethyl propene

In a detailed study of this reaction Moss and Jennings[54] found that the products of the reaction were the expected epoxide (2 trifluoromethylpropylene oxide) and aldehyde (2 trifluoromethyl-propionaldehyde). A small amount of 1,1,1 trifluoroacetone (1%) was also formed. The products were explained by the scheme analogous to that proposed by Cvetanović for the reaction of $O(^3P)$ with hydrocarbon olefins.

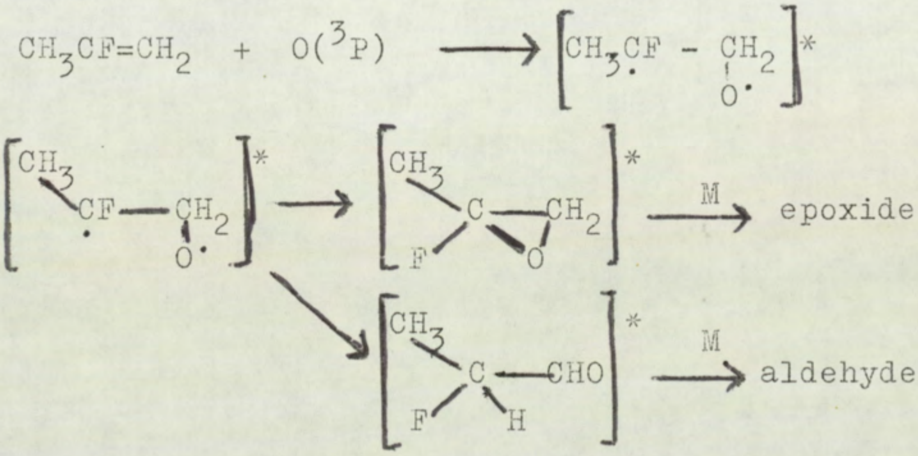


1,1,1 trifluoroacetone was probably formed by the reaction



b) Reaction of $O(^3P)$ with 2 fluoropropene

Morley[57] found the major products to be 2 fluoropropene epoxide and 2 fluoropropionaldehyde. These products accounted for 90% of the oxygen atoms produced at pressures greater than 500mm. Once more, Cvetanovic's mechanism can be used to explain product formation.



$$CH_3CF{=}CH_2 + O(^3P) \longrightarrow [CH_3\dot{C}F - \underset{O\cdot}{CH_2}]^*$$

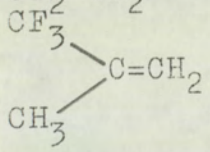
As with 2 trifluoromethylpropene, the oxygen appears to add to the less substituted carbon atom to form a biradical, which can then rearrange to form the aldehyde or cyclise to the epoxide.

1.5c) Relative Rate Constants of the Reaction of $O(^3P)$ with Fluorinated Olefins.

Using the nitrous oxide technique Moss and Jennings[55,56] have measured the relative rate constants of the reaction of oxygen atoms $O(^3P)$ with the fluorinated ethylenes and partly fluorinated propylenes and butenes. Their results are summarised in Table 1.8 overleaf.

TABLE 1.8

Relative Rate Constants for Reaction of $O(^3P)$ with some Fluorinated Olefins at 25°C

Olefin	$\frac{k(\text{olefin})}{k(\text{ethylene})}$	$\frac{k(\text{olefin})}{k(\text{hydrocarbon})}$	Ref.
$CH_2=CH_2$	(1.00)	(1.00)	
$CH_2=CHF$	0.38	0.38	56
$CH_2=CF_2$	0.22	0.22	56
cis $CHF=CHF$	0.32	0.32	56
trans $CHF=CHF$	0.54	0.54	56
$CF_2=CFH$	0.57	0.57	56
$CF_2=CF_2$	1.60	1.60	56
 $(CF_3)(CH_3)C=CH_2$	0.43	0.018	55
$CH_3CF=CH_2$	2.66	0.50	55
$CH_2F\cdot CH=CH_2$	1.12	0.21	55
$CF_3CH=CH_2$	0.057	0.011	55
$CH_2F.CH_2CH=CH_2$	3.30	0.58	55
$CH_3CH_2CF=CF_3$	5.30	0.93	55
$CH_3CH=CF_2$	2.4	0.45	55

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

1.5d) Relative Reactivity of the Fluoro-olefins

As mentioned previously in this section and shown in Tables 1.8 and 1.10 the rate of oxygen atom addition to fluorinated ethylenes is decreased progressively with increasing fluorination and reaches a minimum for 1,1 and 1,2 difluoroethylenes. Further substitution increases the reactivity and for tetrafluoroethylene, the rate constant is greater than ethylene itself. This has been explained by Moss and Jennings[55,56] in the following manner:- If a fluorine atom is introduced into a saturated system, fluorine is able to attract σ electrons by virtue of its high electronegativity ($-I_{\sigma}$ effect). The fluorine polarises the C-F bond, the resulting C-F dipole being capable of attracting other electrons in the molecule. On the other hand, if the fluorine is situated in an unsaturated (olefinic) molecule, the fully occupied 2p orbitals of fluorine have π symmetry and electrons in these orbitals will repel π electrons giving rise to a ($+I_{\pi}$) effect. Fluorine also exerts a strong electron donating mesomeric effect (+M) to π systems.

The combination of $-I_{\sigma}$, $+I_{\pi}$ and +M effects can lead to a reduction in electron density at the fluorinated carbon atom but an increased electron density of the double bond. A possible explanation of the minimum reactivity observed with the difluorinated ethylene is that the $-I_{\sigma}$ effect falls off with increasing substitution (ie. not additive) whereas the mesomeric and $+I_{\pi}$ persist producing an overall enrichment of the π electron system of the fully fluorinated ethylene. This could possibly explain why tetrafluoroethylene reacts faster with oxygen atoms than ethylene itself. This explanation can be used to account for the similar trend observed for the other fluoro-olefins.

1.6 ADDITION OF OTHER ATOMS AND RADICALS TO OLEFINS

A collection of relative rate constants [59] of radical species with olefins is shown in Table 1.9. Similarly, Table 1.10 shows the rate constants for the fluorinated ethylenes.[56] All the rate constants are expressed relative to ethylene for a particular attacking species. The uncertainity in absolute rate constant evaluation creates difficulty if one wishes to compare across the Table. However the relative rate constants can be placed on an absolute basis from information in Tabl 1.11, the rate constant for the reaction between some of the radical species and ethylene.

TABLE 1.9

Relative Rates of Addition of Atoms and Radicals with a Series of Olefins.

Olefin	O (^3P)	S (^3P)	Se (^3P)	Br	$^3CH_2$	$^1CH_2$	H	CF_3	CH_3	CH_3	NF_2
	25°	25°	25°	25°	25°	25°	25°	25°	65°	180°	78°
$CH_2=CH_2$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$CH_3CH=CH_2$	5.8	6.8	3.5	18	1.0	1.3	1.8	1.2	0.6	0.7	5.8
$C_2H_5CH=CH_2$	5.8	9.7	7.1	23	1.6	1.6	1.9	1.2	0.8	0.6	5.4
$(CH_3)_2C=CH_2$	25	51	45	384	2.9	2.0	4.4	3.7	1.1	1.1	28
cis $CH_3CH=CHCH_3$	24	16	24	95	0.94	1.4	0.8	0.9	0.10	0.23	14
trans $CH_3CH=CHCH_3$	28	19	56	99	0.89	1.4	1.1	1.0	0.20	0.33	16
$Me_2C=CHMe$	79	92			1.8	2.1			0.16	0.32	59
$Me_2C=CMe_2$	102	128			2.7	2.2	1.5	1.3		0.20	175
$CH_2=CHCH=CH_2$	24	93	98		19.0	3.9	8.7	8.7	59	12	
Reference	14,42, 43	24	60	61	62	62	63	64	65	59	83

TABLE 1.10

Relative Reactivities of Fluoroethylenes with Atoms and Radicals

Olefin	O(^{3}P)	S(^{3}P)	CCl$_3$		H		CF$_3$	CH$_2$	Hg (^{3}P)	I.P.
	25°	20°	25°	164°	25°	25°	164°	25°	25°	(eV)
$CH_2=CH_2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	10.66
$CH_2=CHF$	0.38	0.42	0.68	0.71	0.51	0.79	0.47	0.60	0.79	10.45
$CH_2=CF_2$	0.22	0.10	0.12	0.25	0.42	1.45	.47	0.33	0.62	10.45
c.CHF=CHF	0.32				0.07	0.70				
t.CHF=CHF	0.54				0.10	1.15				
$CHF=CF_2$	0.57	0.07	0.05	0.27	0.07	1.65		0.16	0.41	10.33
$CF_2=CF_2$	1.60	0.09	0.23	1.21	0.09	1.70	0.12	0.10	0.21	10.12
Reference	56	66	67	67	68	69	70	71	72	73

TABLE 1.11

Absolute Rate Constants and Arrhenius Parameters for Atom and Radical Addition to Ethylene at 25°C

Atom or Radical	$\log_{10}k$	k/k(O^{3}P addition)	$\log_{10}A$	E (kJmol^{-1})	Reference
O(^{3}P)	8.6	1.0	9.7	6.3	28,74
S(^{3}P)	Not known				
Se(^{3}P)	8.0	0.27	10.0	11.7	60
H	8.3	0.5	11.2	16.8	75
Br	7.6	0.1			61
Cl	10.2	40	10.2	0.0	76
CH_3	3.2	4×10^{-6}	8.1	28.5	77
CF_3	6.7	1×10^{-2}	8.6	10.1	78
CH_2F	4.5	8×10^{-5}	7.6	18.0	79
NF_2	-3.6	1×10^{-12}	7.6	65.0	80
CCl_3	4.5	8×10^{-5}	6.8	13.4	67
C_2H_5	3.3	5×10^{-6}	7.3	23.0	81
C_3H_7	3.7	1×10^{-5}	7.4	21.3	77

Activation energies for radical additions range between 14 and 65 kJmol.$^{-1}$, and A factors between 10^4 and 10^9 l.mol.$^{-1}$sec.$^{-1}$. [82] Depending on the species we often find that either activation energies are responsible for reactivity differences (A factors being constant) or that these reactivity differences are due to both E and A variations within a given series. The atom and radical species can be divided roughly into three classes.

a) Electrophilic species - these include $O(^3P)$, $S(^3P)$, $Se(^3P)$ and CF_3.

b) Electroneutral species - CH_3 and alkyl radicals.

c) Intermediate species : fall between those classed as a) or b) above. These include hydrogen atoms, triplet and singlet methylene.

Stefani[82] has also included cyclopropyl radicals as exhibiting very slight nucleophilic characteristics Table 1.9 shows well the different behaviour of these species. It is helpful if we discuss each class in turn.

a) Electrophilic species.

Oxygen, sulphur and selenium show the same reactivity trends with the various olefins, namely very susceptible to methyl and alkyl substitution at the double bond. The rates of addition increase dramatically as the number of alkyl groups increase (due to the electron donating power of alkyl groups to π electron systems.) For instance, oxygen atoms react more than 100 timesas fast with tetramethylethylene as with ethylene :

Trifluoromethyl radicals (in contrast to alkyl radicals)are also selective in the same respect as other electrophilic species discussed above. This suggests CF_3 behaves basically in an electrophilic fashion.

b) Electroneutral species

Methyl radicals show a very different trend to that of oxygen and sulphur. Substituting alkyl groups at the double bond decreases the reactivity of the olefin. Cvetanović[59] has suggested that reaction rates seem to be dictated primarily by the stability of the radicals formed in the addition process. Steric effects also appear to play a considerable part in the reactivities of the olefins. It can be seen from Table 1.9 that methyl radicals react (at 65°C) almost 60 times as fast with 1,3 butadiene as with ethylene, which is best explained by resonance stabilisation of the allylic radical which is formed by addition.

c) Intermediate species.

Cvetanović[62] points out that triplet methylene radicals exhibit electrophilic properties but much weaker than oxygen atoms. It is also suggested that the transition complex is similar to that formed in oxygen atom reactions. Activation energy and entropy effects are important in these radical reactions and in this respect resembled the addition reactions of CF_3.

As discussed earlier the nature of the attacking radical species is often easily assessed from logk-ionisation potential plots. Stefani[82] has shown that good linear correlations exist for NF_2 and CF_3 radicals with various hydrocarbon olefins (rates increasing with lower ionisation potential). Cyclopropyl radicals show the opposite trend suggesting slightly nucleophilic character. The rates of methyl radical addition appear not to be influeneced by the ionisation potentials of the hydrocarbon olefins.

1.6a) Nature of the Transition Complex

Stefani[82] has suggested a method of tentatively assigning a π or σ character to the intermediate complex formed in the addition process, by examining the Arrhenius parameters for the reaction. He suggests that for a set of reactions, each of which proceeds through a σ transition state (this being the rate determining step), structural rearrangements during the activation process may be essentially similar for each member of the set. In support of this assumption he uses the example of small molecules in which the rearrangement is largely the rehybridisation of carbon from a trigonal (double bond hybridisation) to a tetrahedral state. Activation energy differences should then mainly govern the rate process of addition. Stefani also added that the activation energies should correlate with the atom localisation energy of the carbon atom with which the attacking radical associates itself.

In contrast, if the reactions proceed through a π transition state, varying the number of substituents at the carbon double bond causes constraint on the movement of both trigonal carbon atoms and attacking radical, as the environment of the double bond is altered by changing the substituents. It is anticipated that

E and A factors will be important variables in determining the rate of addition.

It is accepted that the reaction of the species listed below, with olefins, proceed with the formation of the corresponding complex:-

O(^{3}P)	π complex
S(^{3}P)	π complex
Se(^{3}P)	π complex
CF_3	σ complex
CH_3	σ complex
H	σ complex
CH_2(triplet and singlet)	probably πcomplex

It should be understood that when a radical attacks an olefin, the transition state can assume anything from from a nature resembling the olefin(π complex) to a resembling the products (σ complex). Generally it is not possible to explain the reaction on the assumption that the complex is pure 'π' or pure 'σ'. More often than not, the complex is of intermediate character.

1.6b)Comparitive Rates of Atom and Radical Reaction

Table 1.11 usefully illustrates that atoms react faster than radicals with ethylene. In column 3, the rate of each species is compared to the rate of oxygen addition. With the exception of CF_3 radicals, radical reactions are 10^5 to 10^6 times slower than atom reactions. This is predominantly due to the much smaller 'A' factors of the radical reaction (related to steric hinderence imposed by the size of the attacking radical.)

CHAPTER TWO

EXPERIMENTAL

2.1 APPARATUS

The description of the apparatus can be conveniently dealt with by considering each of the functional units.

a) Main line (Fig.2.1)

Evacuation of the main line was by mercury diffusion pumps backed by single stage rotary pumps.

Pressures of better than 10^{-5} mm. of mercury (as measured by an Edwards Vacustat) were possible with both mercury and rotary pumps working and better than 5×10^{-3} mm. with only the rotary pump. Pressures higher than 1 mm. were measured by a mercury manometer. To prevent the pumps operating with too little water flowing through the jackets, a safety device was fitted to the outlet water pipe, consisting of a trap filled partly with mercury which could monitor the water pressure. When the pressure fell below the necessary value, a mercury contact was broken which switched off the relay controlled power to the diffusion pump.

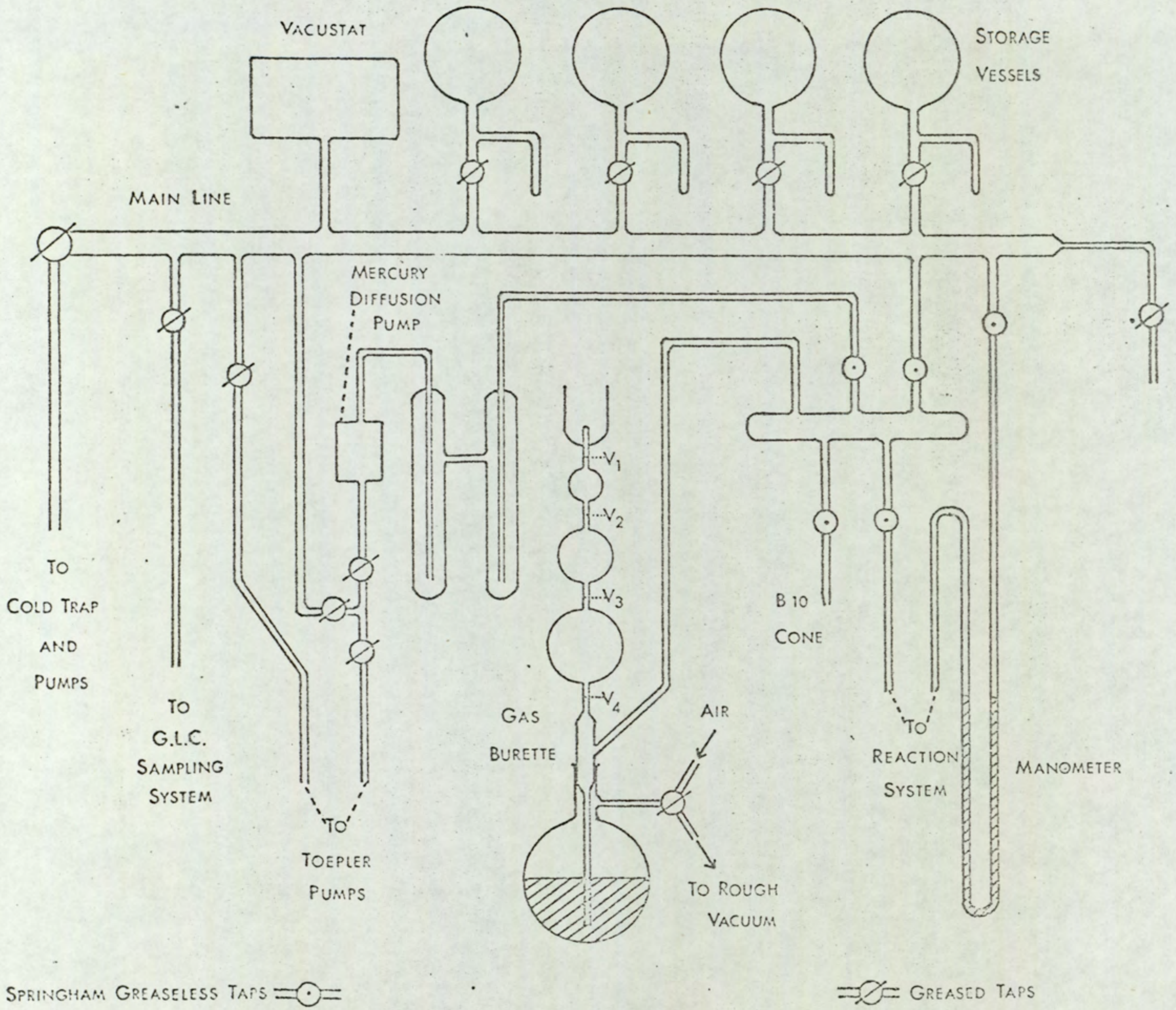
The reactant gases were stored in 2 litre bulbs (nitrous oxide in a 5 litre bulb) attached to the main line via greased taps. The volume of the main line was 570 ml.

b) Gas burette (Fig.2.1)

The gas burette enabled the transfer of small amounts of gas at an accurately known pressure to the reaction system.

The volumes of the calibrated gas burette were

V_1 5.30 ± 0.03 ml.



MAIN VACUUM LINE

FIGURE 2.1.

V_2	17.35 ± 0.15 ml.
V_3	56.6 ± 0.2 ml.
V_4	176.6 ± 0.6 ml.

c) Reaction system (Fig.2.2)

The greaseless reaction system is essentially a closed loop in which gas can be circulated continuously through a reaction cell. The reaction cell was a cylindrical quatz vessel 10cm. long and 5cm. in diameter. This was connected by graded seals to pyrex glass at both inlet and outlet. Within the closed system was a pool of clean mercury to ensure that the reaction mixture remains saturated with mercury vapour at room temperature. All pressures in the reaction system were measured by a mercury manometer.

Two sampling systems were incorporated into the loop. The first was a precision-made stainless steel valve of the type devised by Pratt and Purnell[85] (sec.2.3a), which could be used to inject directly into the G.L.C. This valve was used for all quantitative work. The alternative method of sampling was a closed greaseless sample volume which enabled removal of samples by a gas-tight syringe. This was found to be occasionally useful.

A trap was included in the reaction system to enable the transfer of gases from other parts of the apparatus. It also made possible the freezing of mixtures after irradiation and allowed the removal of non-condensible gases(section 2.1(d)).

An important part of the reaction system was the all-glass circulating pump. The piston was a sealed

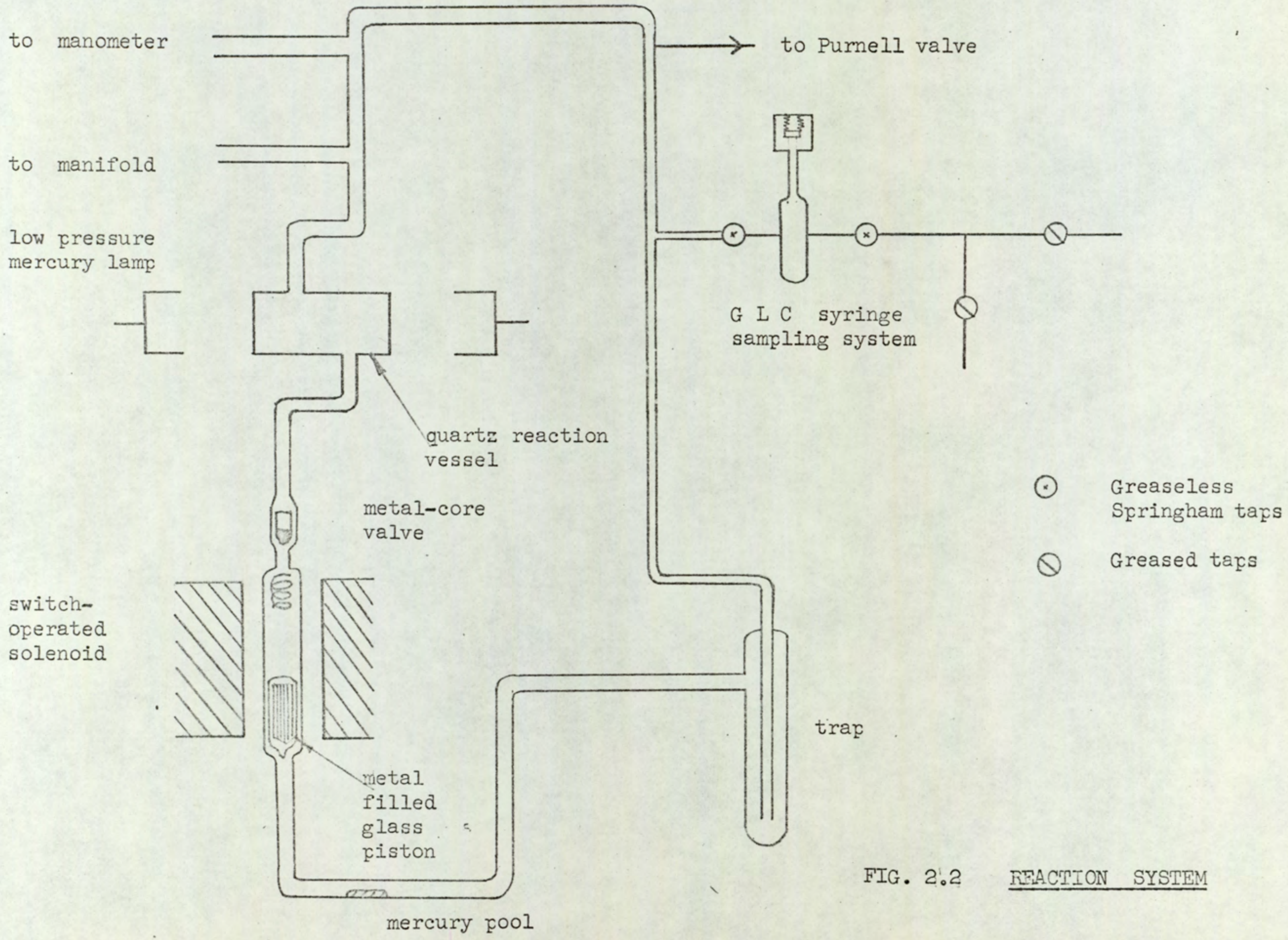


FIG. 2.2 <u>REACTION SYSTEM</u>

Pyrex tube containing a number of mild steel rods held rigidly inside the glass envelope with 'Telcothene! The piston was enclosed within another close fitting tube, enough clearance being allowed to enable the free movement of the piston. Cushioning between piston and extremities of the outer glass casing was by 'Telcothene' coated springs. The whole piston and casing was surrounded by a solenoid wound on a water-cooled brass former (approx. 6000 turns, 40 ohms resistance). When the coil was energised, the piston rose into the field and when switched off the piston returned to its original position. This series of operations was automated by connecting the power to the solenoid through a microswitch, opened and closed once a second by an eccentric cam on the spindle of a motor.

A ground glass metal cored valve located above the circulating pump ensured a unidirectional flow of gas within the reaction system. By this method, secondary reaction products were kept to a minimum and ensured evenness of reaction within the mixture being irradiated.

Irradiation was by two Hanovia (type 1641/s) low pressure mercury lamps (double lamp arrangement for the reason explained in section 2.1(e)) to give mostly unreversed radiation at 2537 Å. The lamps were fed by a constant voltage 150watt transformer to ensure a steady output. The lamps were housed in a cylindrical can which acted both as a support for the quartz spiral and as a collimator of the light produced. The lid was conveniently used as a shutter.

For variable temperature work, an oven was constructed to heat the reaction cell. The oven was an aluminium block furnace of the type described by Calvert and Pitts,[86] consisting of two aluminium cylindrical shells which key together to form a tight but non binding joint. Each cylinder is heated by 30ft. of resistance wire (1ohm/foot). Quartz windows cover the open end of the oven. Power was supplied by a Variac and temperatures within the cell were measured by two copper-constantan thermocouples, one positioned at the top of the cell and the other at the bottom. Subsequent checks of the temperature variation revealed that the oven could maintain temperatures within ± 2°C Variations across the cell itself were generally less than 1°C.

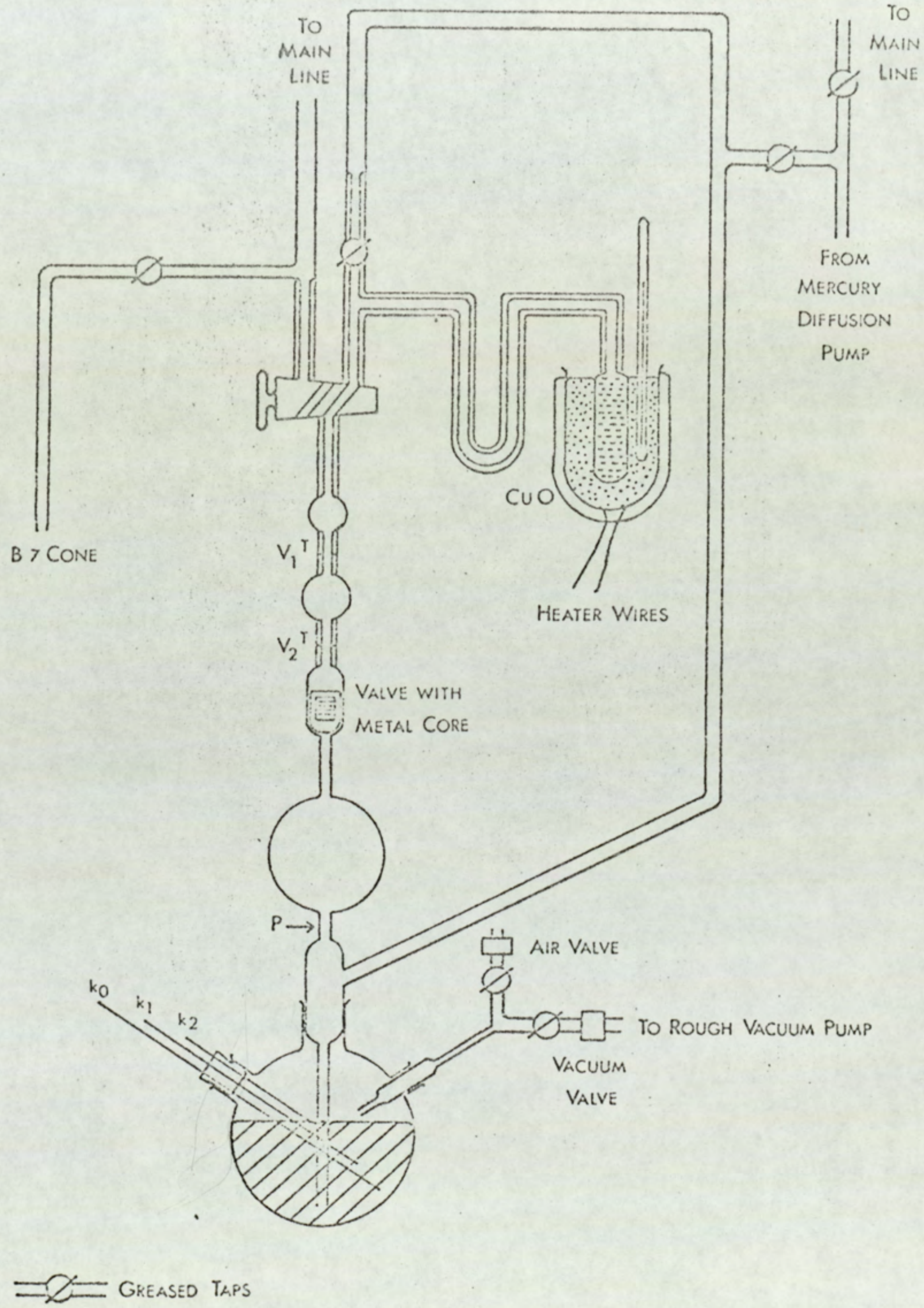
Gases were preheated just before they entered the cell. This preheating was achieved by winding heating tape around the section located just before the inlet to the cell. Power to the tape was supplied through a rheostat and temperature of the preheat section measured also with a copper constantan thermocouple. It was generally thought advisable to set the preheat about 5° above the cell temperature.

d) <u>Toepler pump</u> (Fig.2.4)

After reaction, any products not condensible by liquid nitrogen (eg. N_2,CO and CH_4) were collected and measured in the analysis line. This consisted of two fixed traps cooled in liquid nitrogen and a mercury diffusion pump which pumped the small amount of non-condensible products to the Toepler pump. The

FIGURE 2.3.

TOEPLER PUMP AND COPPER OXIDE FURNACE



Toepler pump concentrated the products in a small gas burette where the pressure of the sample in a known volume could be measured. The sample was retained in the gas burette by a ground glass valve with a metal core, sealed by a pool of mercury. Manipulation of the valve was possible using a permanent magnet. To automate the collection of the gases by the Toepler pump, three platinum contacts inserted into the mercury reservoir, controlled a simple relay circuit governing both air and vacuum valves.

Any carbon monoxide in the non-condensible gases was estimated by transferring the gases to a copper oxide furnace heated to 240°C, for not less than one hour. Gases were cooled in liquid nitrogen and retoeplered to the gas burette. Any carbon monoxide in the mixture is oxidised to carbon dioxide which condenses at 77°K and hence is not recovered.

Calibration of the gas burette of the Toepler pump was by transference of a measured amount of gas from the calibrated reactant gas burette (described previously) to volumes V_1^T and V_2^T (Fig.2.3). These volumes were found to be

V_1^T 2.22 ± 0.01 ml.
V_2^T 7.48 ± 0.01 ml.

e) Mercury double lamp arrangement

The lamps used for irradiation were Hanovia (type 1641/S) low-pressure mercury lamps, mounted approximately 6cm. from each of the wall faces.

Two lamps were used to achieve more uniform reaction throughout the whole of the cell and not just in the vicinity of the cell windows. The advantage of two lamps over a single lamp can be seen from Fig. 2.4. The graph of available relative light intensity v.s. distance from the cell face has been drawn using two values of the extinction of $Hg(^1S_o)$, quoted in the literature. These values have been estimated in systems closely resembling that used in this work. The two values chosen were

$1{\cdot}5 \times 10^{-14} cm^2 atom^{-1}$ Pinder and Le Roy[87]

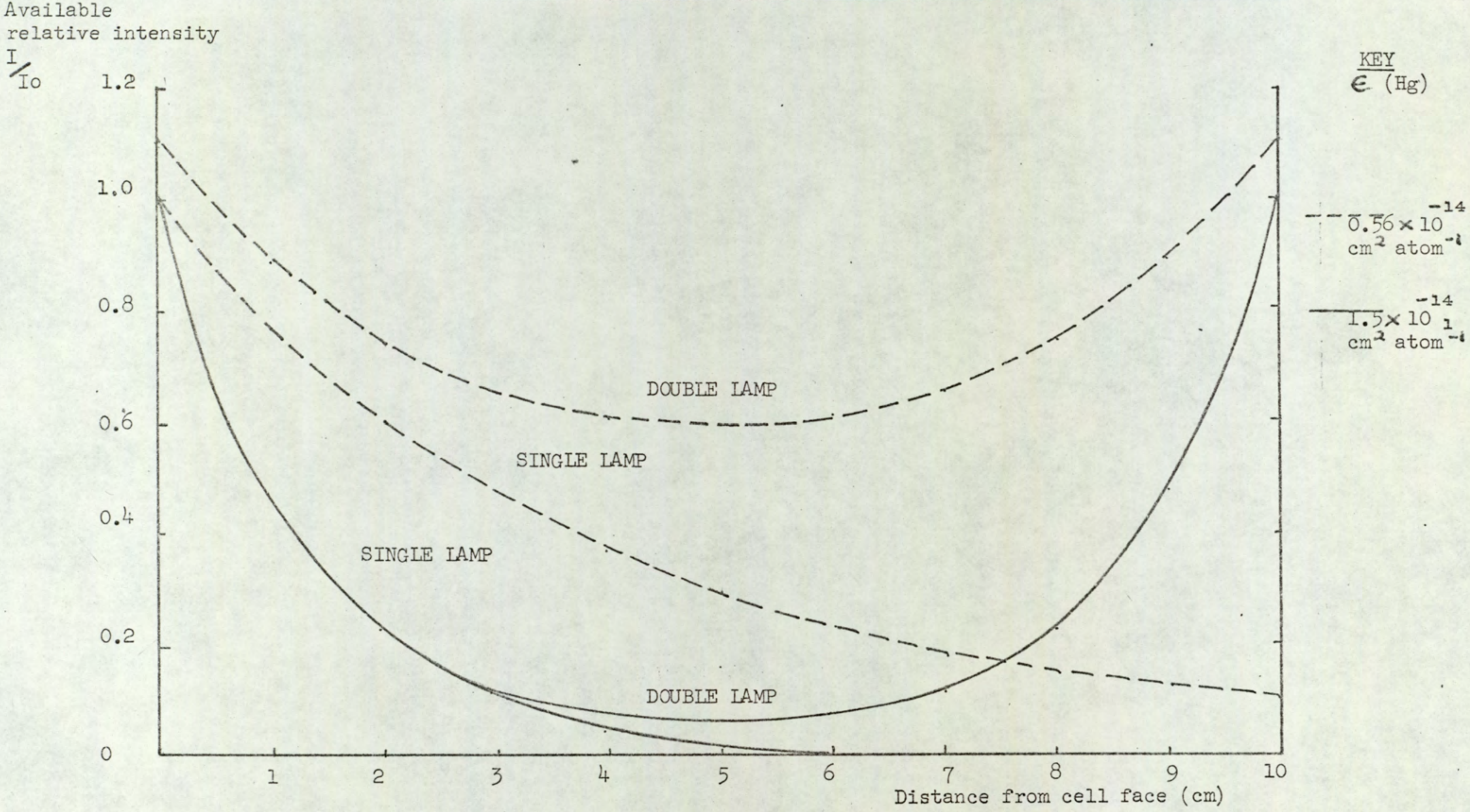
and $0{\cdot}56 \times 10^{-14} cm^2 atom^{-1}$ McAlduff and Le Roy[88]

These values can be expected to enclose the value appropriate to the present system. The graph is drawn using both these values for single and double lamp arrangements and assuming the vapour pressure of mercury at 20°C to be $1{\cdot}5 \times 10^{-3}$mm.

As the concentration of the activated species, $Hg(^3P_1)$, is proportional to the available light intensity at any part in the cell, the local rate of reaction is similarly proportional to available light intensity at that point. Hence if the intensity profile across the cell is relatively uniform, the reaction will be distributed throughout the cell.

It can be seen from Fig.2.4 that if the high value of extinction coefficient is operative in the cell, then a double lamp arrangement will have little effect in alleviating the problem. However, the lower value shows that the profile is considerably improved with two lamps.

FIG.2.4 LIGHT ABSORPTION BY Hg(^{1}So) IN REACTION CELL WITH DOUBLE AND SINGLE LAMPS.



2.2. PROCEDURE

a) Irradiation of an olefin-nitrous oxide mixture

The following description covers the procedure during a normal run.

A portion of the olefin was transferred from one of the storage bulbs to the main line, the pressure was noted, and then either transferred to the gas burette (if the amount of olefin needed to be known accurately) or the reaction vessel with liquid nitrogen. The olefin was degassed at this stage. Nitrous oxide was then similarly measured and transferred to the reaction system, with subsequent degassing. The reaction system was closed, the mixture allowed to warm up to room temperature and circulated for at least 30 minutes. Before irradiation, the shuttered lamp was allowed to stabilise for about 15 minutes. Pressure and temperature of the mixture were noted and irradiation started by removing the shutter. Typical irradiation time for a standard run was 45 minutes.

After irradiation, the mixture was frozen with liquid nitrogen for at least 10 minutes. The one-way valve above the circulating pump was raised by a permanent magnet to allow efficient freezing of condensible products. At this stage, the reaction system was opened to the Toepler pump and the pump set into operation for at least 15 minutes, when it was generally found that the pressure of non-condensibles collected in the small gas burette was essentially constant. The reaction vessel was then warmed to room temperature and cooled once more in liquid nitrogen to degas the reaction mixture. Any residual gas was again collected by the Toepler pump. The pressure in either V_1^T or V_2^T was noted at measured temperature. The non-condensible gases were then transferred to the copper oxide furnace for at least an hour, with the U-bend to the furnace (Fig.2.3) immersed in liquid nitrogen, then returned to the gas burette and the new pressure noted. On appropriate occasions, the non-condensible gases were analysed for CH_4 by mass spectrometry.

Condensible gases in the reaction system were allowed to warm up and circulate for another 45 minutes. Chromatograms were obtained by introducing samples of this mixture into the G.L.C. with the valve, at least three G.L.C. samples being taken from each run.

For competitive runs, the procedure is essentially the same, except that both olefins are measured in the gas burette (pressures being corrected for room temperature variations) before being transferred to the reaction system. Nitrous oxide was added to make the total pressure about 600mm, irradiation times were 40 minutes and a minimum of three consistent chromatograms were taken of the products.

b) Isolation of reaction products.

Generally, reaction products were isolated using the apparatus described in section 2.3(iv). It was occasionally found convenient to separate some of the excess nitrous oxide from the reaction mixture. This could be achieved with a certain amount of success by either cooling in acetone/dry ice or a slush bath of 50/50 chloroform and carbon tetrachloride with liquid nitrogen coolant. This had the effect of condensing most of the products and leaving the nitrous oxide gaseous. Most of the nitrous oxide was then transferred to another part of the apparatus, leaving an enriched mixture of nitrous oxide, reactants and products, which could be separated relatively quickly by G.L.C.

For product analysis, it was also found convenient to carry out irradiations to high conversions, which resulted in a mixture rich in reaction products.

c) Calibration of the detector

When most of the products of the 1,1,2 trifluorobutene-1 and $O(^3P_1)$ reaction had been identified it was necessary to calibrate the detector to determine the absolute amounts of these products present. This was achieved by preparing a synthetic mixture containing a measured amount of each of the products. These products were purified synthetic samples or C.P. grade commercial samples. The products were measured in the gas burette and each transferred to the reaction system. Nitrous oxide was added to make a total pressure of about 600mm. After mixing a number of samples were introduced into the G.L.C., the areas of the peaks from each product being measured by the disc integrator. To confirm detector linearity smaller samples were analysed by expanding the mixture into the manifold and analysis line, and re-analysing the residual gas.

d) Calibration of the I.R. spectrometer for carbonyl fluoride

A synthetic mixture was made of carbonyl fluoride (about 17mm) and nitrous oxide (about 700mm.) in the reaction vessel using the method previously described. Pressure of each component was accurately noted. After effecient mixing, this mixture was allowed to expand into an I.R. gas cell, (volume about 120ml. path length 100mm. with KBr windows) which had previously been evacuated. The new pressure was noted and the gas cell closed. From the total pressure in the cell, the partial pressure of carbonyl fluoride was calculated. The cell was then transferred to the sample compartment of a Perkin-Elmer 225 spectrometer. When the spectrometer began to scan the 2000cm^{-1} region, the instrument was set to zero transmittence and allowed to scan slowly down to 1800cm.$^{-1}$ This region contains the principal stretching frequency of C=O. The transmittence at 1955,1942 and1926cm.$^{-1}$ was noted. After evacuating the cell, the pressure in the reaction vessel was reduced as described before, by the allowing the contents to expand into a larger volume and the cell refilled at this lower pressure (and hence lower partial pressure of carbonyl fluoride). The I.R. was measured and the procedure repeated.

Another mixture was made up with less carbonyl fluoride but about the same total pressure. In this way, most of the spectra obtained were for carbonyl fluoride pressures of below 2mm. This was the partial pressure anticipated for a standard run, in the reaction vessel. The effect of any pressure broadening on the absorbance of the C=O band was examinedby repeating the calibration with much reduced initial pressure

The results of this calibration are shown and discussed in section 3.2.

2.3 ANALYSIS INSTRUMENTATION

a) G.L.C. equipment

The essential units of the G.L.C. are as follows

i) sampling system

ii) columns and temperature control units.

iii) detector, amplifier and recorder

iv) product isolation equipment

v) reaction chromotography columns

A description of each section follows

i) Sampling system

As previously mentioned, two sampling systems were used at various stages of this work. All quantitative sampling was done with a precision stainless steel valve as described by Pratt and Purnell[85]. To this valve was attached a copper sampling loop of approximately 10ml.volume. For product isolation, relatively large samples need to be injected into the G.L.C. and in this respect the copper sampling loop was useful as itcould be cooled in liquid nitrogen. When warmed up as much as two atmospheres of gas in this loop could be introduced into the G.L.C. without significant deterioration of column performance. The six connections to the valve consisted of two to the sampling loop, one to incoming carrier gas, one to the outgoing carrier gas, one to the main line (for evacuation of the sample loop) and one to the reaction system (for filling of the sample loop). The sample loop could be pumped down to 5 x 10^{-3}mm. and it was found that this sampling system used only 3% of the reaction mixture. Hence correction factors were 1.03 for the first sample, 1.06 for the second sample etc.

The alternative sampling system was the sample volume , used for sampling by gas-tight syringe. This was used only for qualitative work such as peak enrichment, when suspected products of a reaction could be added to a small portion of the reaction mixture.

ii) Columns and temperature control.units.

A variety of columns were used for both analysis and preparative work.

For analysis work, $^{1}/8$" O.D. stainless steel columns were usually employed, using nitrogen carrier gas.

For most preparative and isolation work, $^{1}/4$" O.D. copper columns were found to be most useful as they could handle larger samples without overloading. Helium carrier gas was necessary as nitrogen tends to condense in the liquid nitrogen-cooled collection traps.

For sub-ambient temperatures a dewar was filled with the coolant, and the column placed in the dewar. This could be used only for isothermal operation.

Temperatures of higher than 30°C were obtained using a precision temperature controlled oven. This could be operated isothermally or temperature programmed at most practical heating rates. This was found to be very useful for analysis of the products from the $O(^3P_1)$/1,1,2 trifluorobutene-1 reaction.

iii) Detector, amplifier and recorder.

Detector and amplifier were those as supplied as the F11 Perkin Elmer G.L.C. unit. The detector was a flame-ionisation detector, the flame being fed by hydrogen (17½lb./sq.in.) and air (25lb./sq.in.). The detector unit was maintained at 300 volts relative to earth.

Output from the detector was fed into the ionisation amplifier and output from this into a Kent recorder (1 millivolt input). The recorder was equipped with a disc chart integrator for the measurement of peak areas (144 counts/sq.cm.) Carrier gas, hydrogen and air all passed through molecular sieves$^{(13X)}$ to remove water, carrier gas being regulated by a constant flow valve. The flowmeter attached to this valve had been previously calibrated for different carrier gases.

iv) Product isolation equipment.

At various stages in this work, it was necessary to collect products from a reaction. This was achieved by injecting the reaction mixture and noting the position of the peaks on the chromatogram. A larger sample of the mixture was then injected and when the peak to be identified was due to appear, the stream of carrier gas was diverted through a T piece inserted between the exit from the column and the inlet to the detector The diverted gas passed through a collection tube immersed in liquid nitrogen. The exit from this collection tube was connected to a similar tube also cooled in liquid nitrogen to prevent back diffusion and subsequent condensation of air in the collection trap. After collection of the peak in question, the carrier gas was recirculated through the detector . This operation was repeated until sufficient product was collected for identification by standard physical methods. It was found necessary to insert a restrictor tube (stainless steel capillary bore) between the T piece and detector to ensure that the carrier gas was prefernetially diverted into the collection tubes.

v) Reaction chromatography columns

These columns are for determining the type of compound each peak represents. By inserting short columns, which remove certain types of compounds, between the inlet of the G.L.C. and the inlet to the column, information can be obtained of the types of compounds comprising the mixture. For example, by using a short tube filled with silica gel, coated with concentrated sulphuric acid and silver sulphate, olefinic compounds can be removed from the mixture. By comparing chromatographs obtained with and without the tube in place, those peaks which are affected can be attributed to olefinic compounds.[89,90,91] Similarly a 5 Å molecular sieve will remove n paraffins of greater than C_3, whereas 4 Å molecular sieve will remove CH_4 and C_2H_6 (but not propane). The molecular sieves will not remove branched paraffins. For the sake of convenience, a four-way greaseless valve was incorporated into the G.L.C. inlet system. The sample entering the G.L.C. could be

i) diverted through the silica gel/sulphuric acid tube
ii) injected directly into the G.L.C.
iii) diverted through a molecular sieve (5Å or 4Å)

It was necessary to heat the molecular sieve reactor to 100°C with a heating tape to prevent the retention times of unadsorbed compounds altering appreciably. The sulphuric acid / silica gel mixture had to be enclosed in a thick walled PTFE tube to prevent corrosion of the tube.

b) I.R. cell

In order to obtain a reasonable infra red spectrum from small quantities of gaseous material, a miniature infra-red cell was constructed.

The cell consisted of a piece of rectangular brass microwave tubing, 69mm.x 17mm. x 3mm., closed at both ends by sodium chloride cell windows. The cell was chosen to be of minimum VOLUME yet of maximum path length. Gases were introduced into the cell through a ground microtap attached to the cell by a metal-to-glass seal. A cold finger was incorporated into the glass section of the cell, so that small amounts of gas could be condensed into the cell.

This cell was found to give very satisfactory results on both Perkin Elmer 225 and 457. I.R. spectrometers with only 10 micromoles of sample. Path length of the cell was 60 mm. and the volume was 7ml.

c) Mass spectrometry

Samples for mass spectrometric analysis could be transferred directly to tubes with greased taps, from the apparatus via the manifold.(Fig.2.1) Non-condensible gas could also be analysed by being transferred to the mass spectrometry tube using the two--way greased tap on the Toepler pump.(Fig.2.3) Mass spectra were obtained from an A.E.I. MS9 spectrometer, using a direct entry to the MS 9 source through a Varian leak valve in place of the normal solid-sample probe.

2.4 MATERIALS- PREPARATION AND PURIFICATION

a) 1,1,2 Trifluorobutene-1 (1,1,2 TFB)

was prepared by the following method. Tetrahydrofuran was dried by sodium wire for one day. Further drying was by adding 10g. of lithium aluminium hydride and distilling the mixture, the fraction between 66-67°C being collected. Fresh sodium wire was added to the distillate and the mixture allowed to stand overnight in a stoppered flask.

Magnesium turnings(2.4g.) were washed in sodium dried ether and allowed to dry at 80°C for one hour. The magnesium was then added to 30ml. of the dried T.H.F. and the mixture cooled in ice. At this stage 19g. of $CF_2= CFCH_2CH_2Br$ (Peninsular Chemical Co.) was added dropwise and the mixture stirred magnetically. When the magnesium had fully dissolved the resulting solution of Grignard reagent was hydrolysed with 5-10% sulphuric acid (ice cool). The 1,1,2 TFB evolved was carried through to a pair of traps cooled in liquid nitrogen using a slow stream of helium until the reaction had reached completion. It should be noted that the whole apparatus had to be dried over night in an oven as the Grignard preparation is severely inhibited by even slight traces of water. A crystal of iodine was found useful for iniation of the reaction.

Yield was approximately 50%.

Purification:

The collected 1,1,2 TFB was transferred to a vacuum line and degassed thoroughly. The gas was then condensed onto active charcoal and allowed to warm up slowly to room temperature. Residual gas was purified twice by gas chromotography, once on an 8m. dibutyl phthalate and then on a 4m. column of Porapak Q (temperature programmed).

Finally, the purified gas was condensed onto 1g. of Porapak Q in a small glass bulb. cooled in liquid nitrogen. The gas after warm up was found to contain approximately 0.25% of a diene (identified by mass spectrometry to be $CF_2=CFCH_2=CH_2$, presumably formed from an elimination reaction) and less than 0.15% of THF. This was considered to be of sufficient purity for quantitative work.

b) <u>Allyl Fluoride</u> ($CH_2=CH-CH_2F$)

To 80g. of finely powdered and dried potassium fluoride was added 80ml. of ethylene glycol in a three-necked flask (500ml.). The mixture was agitated with an oil-sealed stirrer and heated to 140-150°C. Allyl bromide(25ml.) was added dropwiseover a period of three hours and the product gas passed through $CaCl_2$ and $CaSO_4$ drying tubes to remove traces of water. The yield of the mixture was good (80%) with little contamination of the gas by allyl bromide or ethylene glycol.

The identity of the allyl fluoride was confirmed by mass spectrometry and I.R.

c) <u>Propioyl Fluoride</u> [93]

To 1 mole(74ml.) of water free proprionic acid (dried with $CaCl_2$ overnight) was added 60g. of potassium hydrogen fluoride. No warming up was observed. Benzoyl chloride(116ml.) was slowly added and the mixture heated to 60°C in a water bath. After one hour, the mixture was distilled with collection of the fraction between 42-44°C.

The propionyl fluoride was subsequently identified by mass spectrometry and I.R.

d) Cis and trans 1 Fluoropropene.

A two stage synthesis was required

1) preparation of 1,1,difluoropropane $CH_3CH_2CHF_2$

2) Pyrolysis of the difluoropropane to cis and trans 1 fluoropropene.

Stage 1

Onto 5ml. of propionaldehyde in a 50ml. autoclave was condensed 1 atmosphere of sulphur tetrafluoride (in 2½l.) This gave a maximum calculated pressure (assuming propionaldehyde vapourised at reaction temperature,) of 120 atmospheres in the autoclave. After heating to 45°C overnight in a thermostated oven, the yield of gaseous products was found to be 15%, assumed to be mostly 1,1 difluoropropane. The sulphur tetrafluoride for the reaction was synthesised in this laboratory.[95]

Stage 2

The unpurified 1,1,difluoropropane (from stage 1) was pyrolysed by passing through a quartz spiral heated to 690°C in a cylindrical oven. Helium carrier gas was used. Any hydrogen fluoride formed by the elimination reaction was removed by passing through two wash bottles containing 40% potassium hydroxide. Before collecting in liquid nitrogen, the gas was dried by calcium chloride and calcium sulphate.

Purification:

Gas chromotography indicated approximately 20%

conversion of 1,1 difluoropropane to cis and trans 1 fluoropropene. The main contaminant was removed by preparative G.C. and found by mass spectrometry to be allene, presumably formed by the elimination of two molecules of hydrogen fluoride from 1,1 difluoropropane.

Cis and trans 1 fluoropropene were purified by gas chromotography using an 8m. dibutyl phthalate column (helium carrier gas).

e) Formyl fluoride (CHFO)[93]

The preparation was essentially the same as that used for propionyl fluoride, but using formic acid (46g.), potassium hydrogen fluoride (60g.) and benzoyl chloride (116ml.) as the starting materials. Gaseous formyl fluoride (B.P. -29°C) was collected on formation in liquid nitrogen traps and purified by degassing. Identification was by the characteristic carbonyl stretching frequency at 1834cm^{-1}(Q branch), 1849cm^{-1} (R branch) and 1819cm^{-1}(P branch).[96]

f) 2 trifluoromethylpropene

The source was cylinder (K and K Labs.). Purification was by G.C. on 4m.(1/4" O.D. copper column) of 25% squalane and 1% carbowax 1000 on chromosorb W-AW-dcms(60-80 mesh). The column was cooled to 0°C in an ice-filled dewer.

g) Nitrous oxide (BDH)

Purified by degassing twice and fractionating from activated charcoal.

h) Propane,ethane

(BDH CP grade) From cylinder, used without further purification.

i) Oxygen (British Oxygen)

Fractionated from activated charcoal.

j) Carbonyl fluoride (Pierce Chemical Co.)

stated 95% purity. Supplied in cylinder.

k) Ethylene, Vinyl fluoride, 1,1 Difluoroethylene and Trifluoroethylene. (Cambrian Chemical Co.)

All purified by fractionation from activated charcoal. Residual impurities totalled less than 0.2% in each case (by G.L.C.)

l) Tetrafluoroethylene (Cambrian Chemicals)

was purified by fractionation from activated charcoal. Although G.L.C. analysis indicated that impurities were less than 0.2% M.S. examination showed approximately 3% of C_3F_6 (perfluoropropene or perfluorocyclopropane) which could not be removed. Both compounds are known to be less reactive than C_2F_4.[46]

m) 1,2 difluoroethylene (Pierce Chemical Co.)

was supplied as an approximately equimolar mixture of cis and trans isomers. These were separated by G.L.C. on 4m. of dimethoxyethyl adipate (13½%) and diethylhexyl sebacate (6½%) at 0°C (helium carrier).

The cis isomer was contaminated by approximately 1.5% of trans isomer and the trans isomer contained approximately 0.5% of the cis.

Isomers were distinguished and identified by their I.R. spectra[97]. Compounds in sections (k) and (l) were purified by Dr.S.J.Moss in this laboratory.

CHAPTER THREE

RESULTS OF THE REACTION OF OXYGEN ATOMS WITH 1,1,2 TRIFLUOROBUTENE-1

3.1 PRODUCT ANALYSIS

Using the methods of analysis described in section 2.3, the following products were identified:-
cis and trans 1 fluoropropene, carbonyl fluoride, fluorocyclopropane, ethane, ethylene, propane, propionyl fluoride.

In the **presence** of molecular oxygen, the additional products identified were ethanol and acetaldehyde. A summary of the techniques used to identify individual compounds is shown in Table 3.1.

The products were isolated by G.L.C. from standard high conversion runs. Those products not isolable were confirmed by as many alternative techniques as possible.

Explanatory notes are given below for the individual compounds.

cis and trans 1 fluoropropene

It was found that the Ag_2SO_4/silica gel/H_2SO_4 reactor was only partially successful in the removal of these olefins. Possibly this is due to the difficulty of protonating fluorinated olefins with sulphuric acid (ethylene protonates very easily to give ethyl hydrogen sulphate). Although the I.R. spectra of cis and trans isomers were very similar (both C=C stretch at 1690cm^{-1}) trans has a characteristic peak 901cm^{-1} which is absent in the cis spectrum. This was in

TABLE 3.1 IDENTIFICATION OF PRODUCTS

COMPOUND	METHOD OF IDENTIFICATION			
	COL.RET. TIME (a)	REACTION GAS CHROMATOGRAPHY (b)	INFRA RED (c)	MASS SPECT. (c)
cis 1 fluoropropene	A,B,C,	-	(1s)	(s)
trans 1 fluoropropene	A,B,C	-	(1s)	(s)
carbonyl fluoride	-	-	(2)	-
fluorocyclopropane	A,B	D	-	(s)
propionyl fluoride	A,B	-	-	-
ethylene	A,B,C	D,E	-	-
ethane	A,B,C	D,E	-	-
propane	A,B,C	D,E	(3s)	(s)
ADDITIONAL PRODUCTS WITH ADDED OXYGEN				
ethanol	B	-	-	-
acetaldehyde	B	-	-	-
propionyl fluoride	A,B	-	(4s)	-

Notes:

a) letter indicates the compound was identified by its retention time (compared with authentic sample) on one of the following columns:

A- 8m. 20% di-n-butylphthalate (23°C)

B- 4m. Porapak Q (temperature programmed)

C- 4m. dimethoxyethyl adipate (13.5%) + diethylhexyl sebacate (6½%) at 23°C

b) letter indicates type of reactor column employed. An entry in this column indicates behaviour on this column was as expected.

D -Ag_2SO_4/silica gel / H_2SO_4

E -molecular sieve (5") heated to 100°C

c) A bracket in this column gives reference(given below) to a comparison spectrum."S" indicates comparison to a synthetic sample.

References

(1) KILCOYNE,J.P. Ph.D. University of Sheffield,134,(1969)

(2) WOLTZ,P.J.H. and JONES,E.A.,J.Chem.Phys.,17,502,(1949)

(3) CATALOGUE OF IR SPECTRAL DATA - Project 44 -Cards 529 and 188

(4) OLAH,G.A.,TOLGYESI,W.S.,KUHN,S.J.,MOFFATT,M.E.,BASTIEN,I.J. and BAKER,E.B., J.Amer.Chem.Soc.,85,1328,(1963)

accordance with reported observations.[68]

Mass spectral data was of little use for distinguishing between the different isomers. It has been found that the mass spectra of cis and trans 1 fluoropropene, allyl fluoride, fluorocyclopropane and 2 fluoropropene (ie. C_3H_5F compounds) are closely similar.[98]

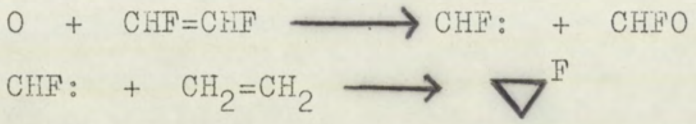
Carbonyl fluoride

The presence of carbonyl fluoride could not be ascertained by G.L.C. as it does not give a response on a flame ionisation detector. However, the I.R. spectrum was examined under high resolution and compared with an authentic sample. Matching was so unambiguous, as to a make identification positive.

Fluorocyclopropane

This compound was collected on a Poropak Q column and found, by mass spectrometric peak matching, to have the empirical formula C_3H_5F. However, insufficient was collected for a reasonable I.R. spectrum to be obtained. As for cis and trans 1 fluoropropene, mass spectral data yielded no unique information of the structure. A sample of allyl fluoride was prepared (section 2.4(b)) and although it had a very similar mass spectrum, its retention time on a dibutyl phthalate column differed from that of the product collected. Also, as the product had a different retention time from cis and trans 1 fluoropropene, the only alternatives were2 fluoropropene and fluorocyclopropane. Previous work[98] has shown that the retention time of 2 fluoropropene on a dibutyl phthalate column differed from the product and the evidence pointed strongly towards the product being fluorocyclopropane.

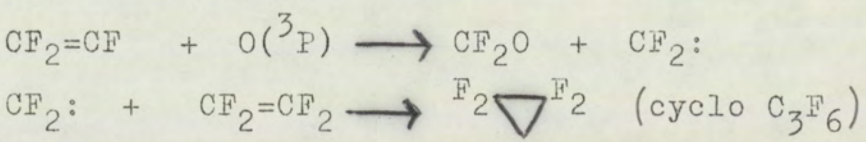
A sample of suspected fluorocyclopropane had previously been prepared in this laboratory by a completely different route. The reaction of oxygen atoms with cis and trans 1,2 difluoroethylene yields mostly fluoroethylene radicals(CHF:).[99] A mixture of 1,2 difluoroethylene and ethylene when reacted with oxygen atoms, would reasonably be expected to yield fluorocyclopropane by the following mechanism.



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

$$CHF: + CH_2=CH_2 \longrightarrow$$

This is the analogous route to the formation of perfluorocyclopropane in the reaction of oxygen atoms with tetrafluoroethylene.[49,100]



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

$$CF_2: + CF_2=CF_2 \longrightarrow$$

The fluorocyclopropane, prepared by the above method, was found to have identical retention times on the three columns and the same mass spectrum as the product collected from 1,1,2 TFB and $O(^3P)$ reaction. It appears therefore that this product must be fluorocyclopropane.

Propionyl fluoride

The reaction of oxygen atoms with 1,1,2 TFB yields only small amounts of propionyl fluoride, and makes collection difficult. However, a sample of propionyl fluoride was synthesised (section 2.4c) and was found to have the same retention time as the product in question on two completely different columns (dibutyl phthalate and Poropak Q). When molecular oxygen was added to the system, the product peak size increased very significantly and an I.R. spectrum obtained of the product mixture after irradiation, revealed a very characteristic new peak at 1845cm^{-1} identical in position to the C=O stretch frequency of the prepared propionyl fluoride. This frequency is also in accordance with reported work.[57,101]

Ethylene, ethane and propane

Ethylene and ethane were difficult to collect from the reaction mixture because on all three columns (see Fig 3.1), they were eluted very near to nitrous oxide. Hence, these compounds were identified by alternative techniques.

The ethylene peak matches the retention time of an authentic sample injected onto the three columns used. Also, a silica gel/Ag_2SO_4/H_2SO_4 reactor column removed this peak completely, indicating that the compound was probably an olefin. A 4Å molecular sieve also removed this peak as it would ethylene.[90]

The ethane peak similarly matched that of an authentic sample on all three columns and was not affected by the silica gel reactor (indicating product was saturated). The peak was also removed by a 4Å sieve indicating it was an n-paraffin.

A sample of propane was collected with difficulty on a Poropak Q column, and identified by all the techniques indicated in Table 3.1. A 5Å molecular sieve was used to remove this compound from the column. (4Å sieve will not remove compounds above C_2)[90]

Ethanol and acetaldehyde

These products were formed in the $O(^3P)$/1,1,2TFB reaction in the presence of molecular oxygen. They were identified by retention time on only one column, Poropak Q. However, it was anticipated that these compounds might be found when molecular oxygen was added to the irradiation mixture as they are the known main products from the reaction of ethyl radicals with oxygen[102]. For this reason the identification procedure was thought sufficient.

Unidentified products

Two unidentified products with long elution times were evident in the reaction mixture (see chromatogram shown as Fig.3.1). All attempts to identify these compounds failed, because the small quantities formed made collection of a sufficient amount for analysis very difficult.

The quantum yield of these products was estimated to be less than 0.001.

Carbon monoxide

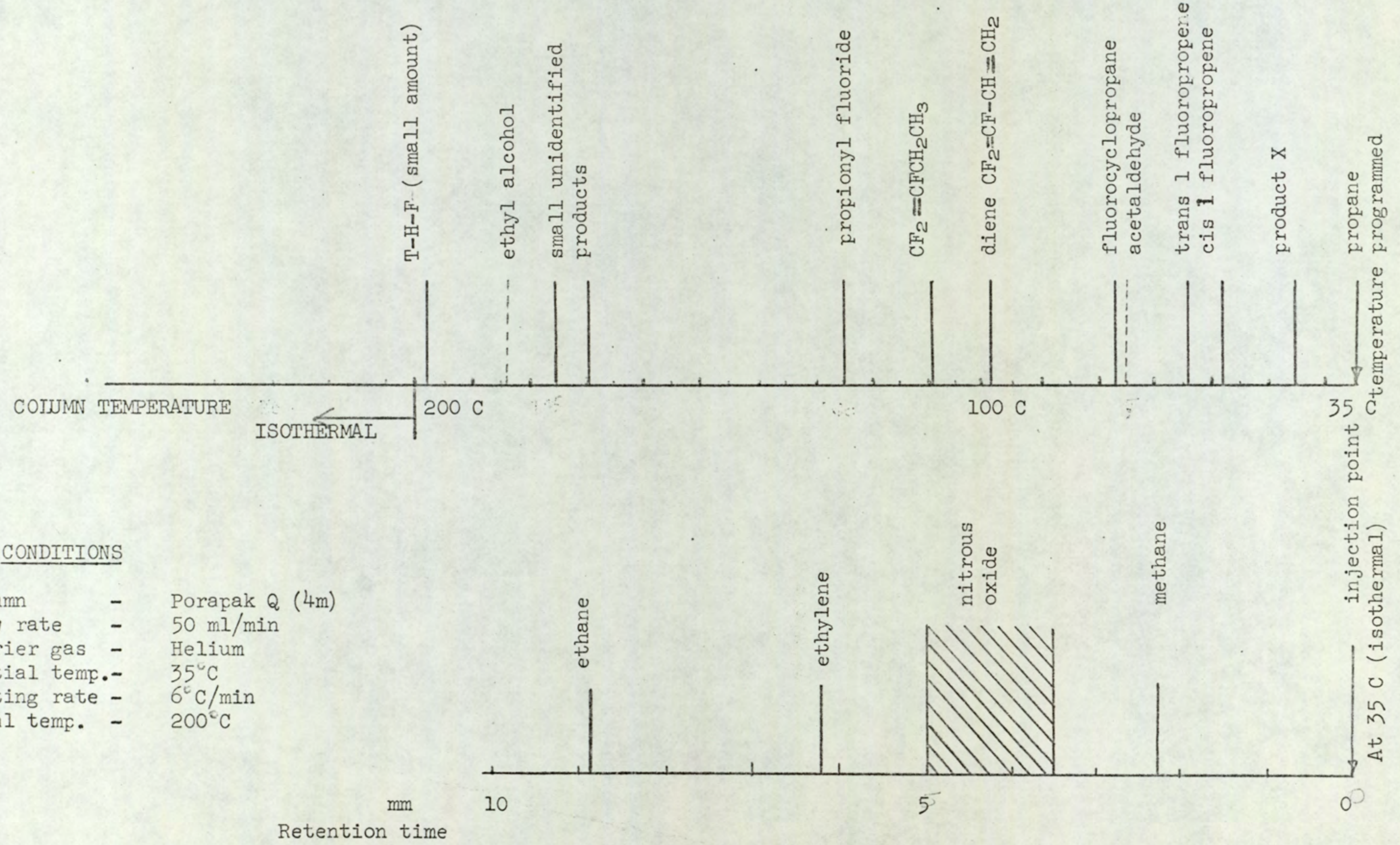
Using the copper oxide furnace incorporated into the Toepler pumping system(section 2.1d), it was found that at no time did the amount of carbon monoxide in the nitrogen collected exceed 1%.

Choice of columns

A number of columns were used for the analysis, two were found occasionally useful. These were am 8m. 20% dibutyl phthalate column and a 4m. mixed ester column (dimethoxyethyl adipate ($13\frac{1}{2}$%) + diethylhexyl sebacate ($6\frac{1}{2}$%)).

However, far superior results were obtained with a 4m. Poropak Q (1/8"O.D.) column, temperature

FIG- 3.1 GLC SEPARATION OF PRODUCTS FROM THE REACTION OF O($^3P_1$) WITH 1,1,2TFB



CONDITIONS

column - Poropak Q (4m)
flow rate - 50 ml/min
carrier gas - Helium
initial temp.- 35°C
heating rate - 6°C/min
final temp. - 200°C

programmed from room temperature to 200°C at 6°C/min. This column had the advantage that it gave good separationof very volatile products (eg. ethane, ethylene etc.) by isothermal operation at room temperature and could be programmed to give similar separation of less volatile compounds. Good peak shape can be maintained for at least 20 minutes after the sample had been injected, if the column is operated under temperature programmed conditions.

A chromatogram representing a typical run is shown in Fig.3.1.

3.2 CALIBRATION RESULTS

Detector

The detector was calibrated for 1,1,2 TFB, propane, allyl fluoride, cis and trans 1 fluoropropene, ethylene, and ethane, by the method discussed in 2.2c. Each of the compounds exhibited good linearity in the entire pressure region investigated (0 - 2mm.) During a run none of the products exceeded this partial pressure.

The results are shown in Fig.3.2 and are summarised in Table 3.2 below.

TABLE 3.2

Calibration Results

Compound	Conversion factor mm/100 counts at 1×10^4	micro moles/100 counts at 1×10^4
1,1,2 TFB	0.32_0	14.5
propane	0.37_5	17.0
ethane	0.58_3	26.5
ethylene	0.58_3	26.5
cis and trans 1 fluoropropene	0.50_2	22.8
allyl fluoride	0.41_2	18.7
propionyl fluoride	0.58	26.5(calculated)
acetaldehyde	0.29	13.3 "
ethanol	0.68	31.0 "

note: 1 mm. of gas inreaction vessel (773ml.) is equivalent to 45.4 micro moles.

Unfortunately it was not possible to obtain a sample of fluorocyclopropane for calibrating the detector. It has been assumed for subsequent work that it has the same response factor as cis and trans 1 fluoropropene.

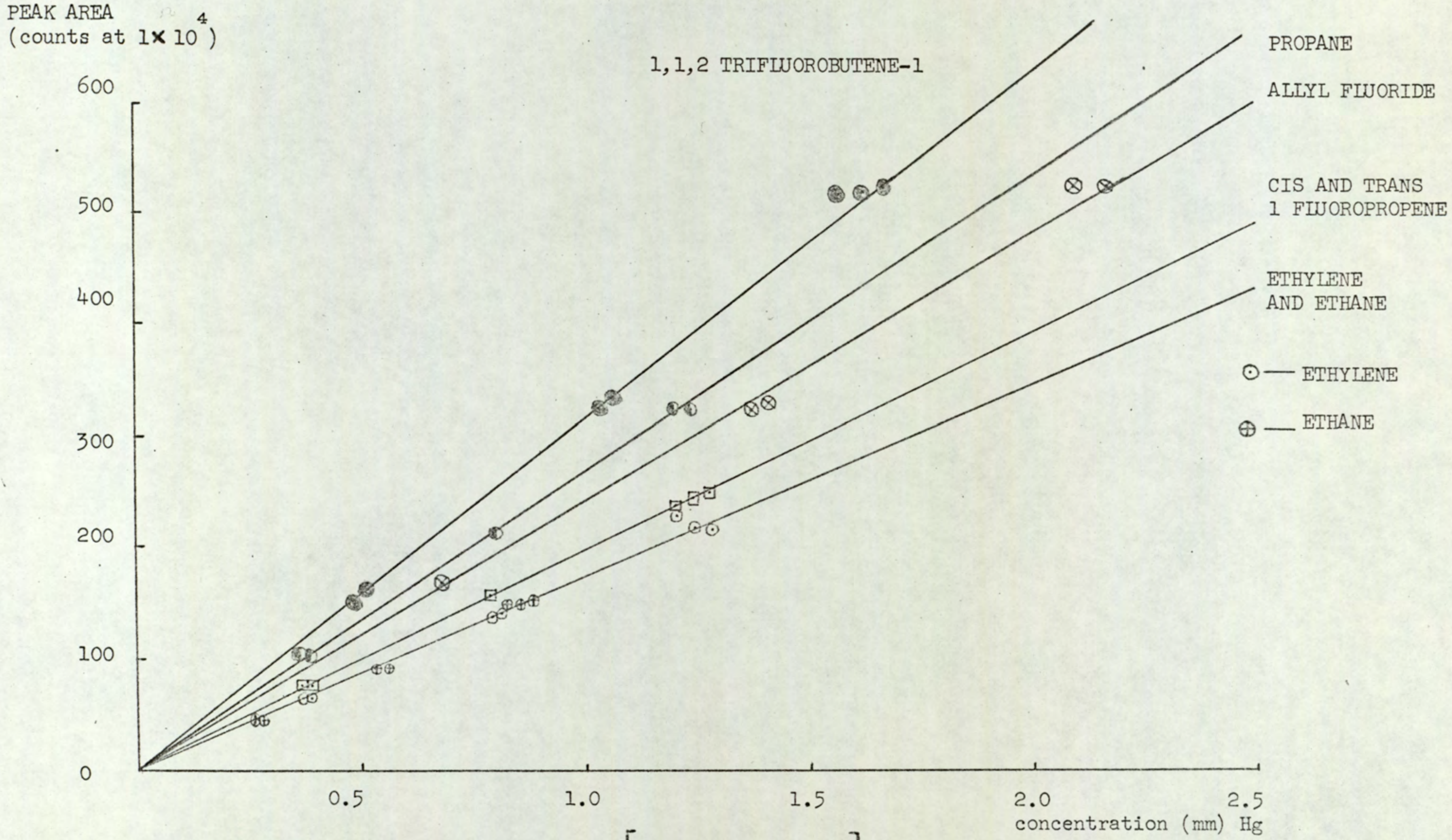


FIG. 3.2 GLC CALIBRATION OF PRODUCTS $[O(^3P) + 1,1,2\ TFB]$ -Peak area vs. concentration.

This approximation is justified to some extent as the yield of fluorocyclopropane was always much less than the yield of the 1 fluoropropenes.

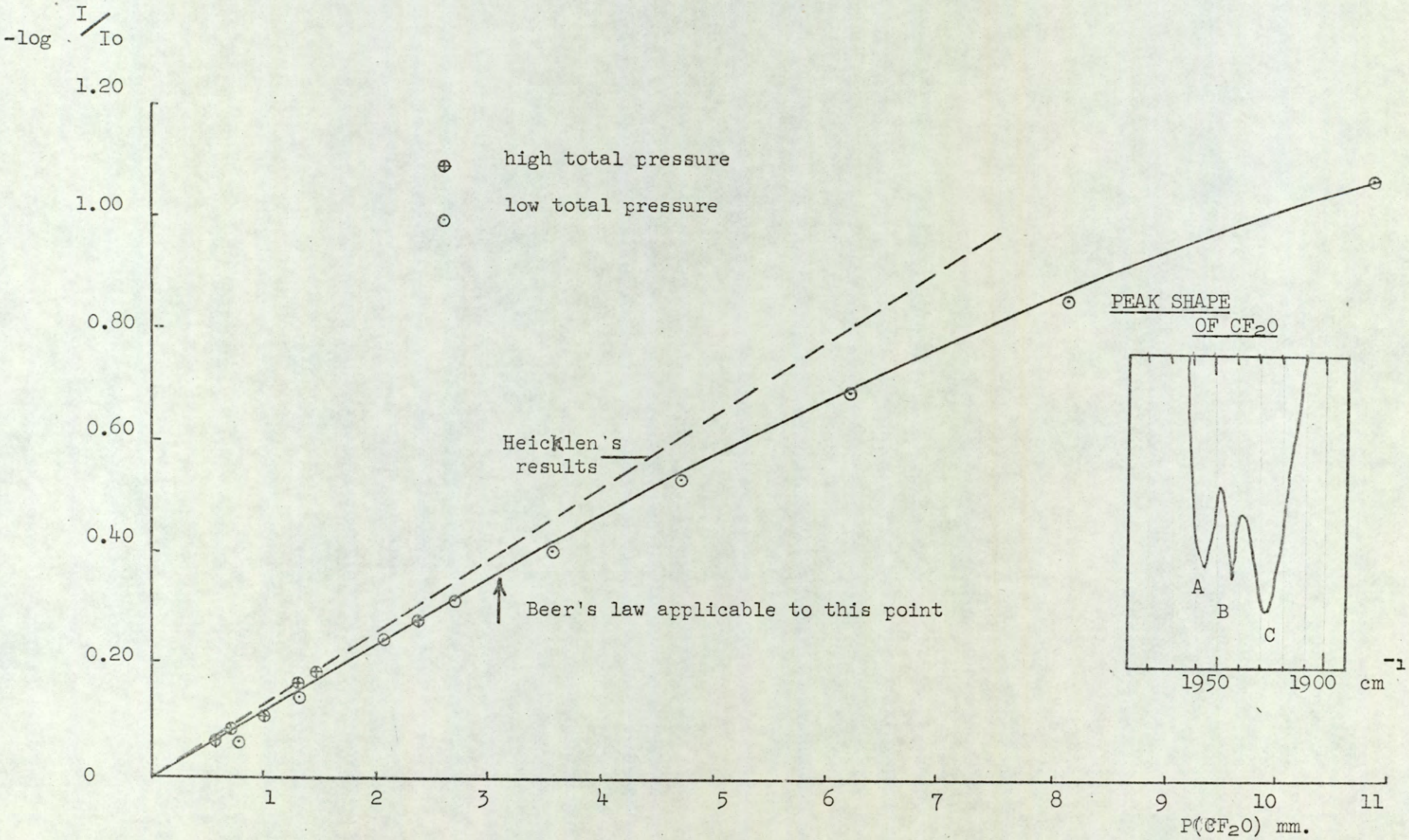
The calibration factor for ethanol was calculated from the value relative to ethane, given in a paper by Galloway, Sternberg and Jones.[103] It has been noticed that a carbonyl group effectively reduces the reponse factor approximately to that of the corresponding n hydrocarbon containing one less carbon (ie.=O effectively deactivates that carbon to which it is attached.) For example[103] acetone $(CH_3)_2CO$ has an effective carbon number of 2,06 (nearly the same as ethane) and isobutyraldehyde $(CH_3)_2CH_2CHO$ a carbon number of 2.83 (very nearly that of propane). For this reason the calibration factor of acetaldehyde CH_3CHO is assumed to be the same as methane and propionyl fluoride, CH_3CH_2CHFO to be that of ethane.

Carbonyl fluoride calibration

This was carried out in the manner described in section 2.2d. The results are shown on Fig.3.3 It is of interest to note that Heicklens' results[46] agree well with the calibration. Heicklen obtained a value for the extinction coefficient of 0.013 $(\text{mm.Hgcm.})^{-1}$ for the 5.12 micron peak of carbonyl fluoride. The value for the calibration was 0.012$(\text{mm.Hgcm.})^{-1}$ in the 0 - 3 mm. carbonyl fluoride pressure region.

It can be seen from Fig.3.3 that Beer's law is obeyed up to pressures of 3mm., but deviations appear at higher pressures. Also it can be seen that total pressure of the carbonyl fluoride/nitrous oxide mixture

FIG- 3.3 BEER'S LAW PLOT FOR CARBONYL FLUORIDE



has very little effect on the measured extinction coeffiecient, indicating no significant pressure broadening in the range examined.

The carbonyl fluoride was measured during a run by the following method: The mixture was irradiated, allowed to circulate thoroughly and then allowed to expand into the evacuated I.R. cell and manifold. The I.R. cell was then closed, and transferred to the I.R. spectrometer. From the calibration graph it was possible to determine the concentration of carbonyl fluoride in the gas cell and hence calculate the pressure of carbonyl fluoride in the reaction cell.

3.3 TIME DEPENDENCE STUDIES

Variations in yields of major and minor products with irradiation time are shown in Fig.3.4and 3.5

a)Major Products

Nitrogen

The yield of nitrogen from the reaction $Hg(^3P_1) + N_2O \longrightarrow N_2 + O(^3P) + Hg(^1S_o)$ was found to be virtually linear with time throughout a reaction up to at least 60% conversion.

cis and trans 1 fluoropropene

Yields of these compounds are linear with time up to approximately 25 minutes irradiation (corresponding to 10% conversion of the trifluorobutene.) At higher conversions, the rate of formation falls. This had been attributed to,the competition of 1 fluoropropenes with 1,1,2 TFB for the oxygen atoms. If the reaction is continued to high conversion (85%), in the latter stages the fluoropropenes reach a maximum concentration and then diminish as the oxygen atoms remove these products from the syatem. The results of a high conversion run can be seen in Fig.3.6. It is possible to calculate from this graph the rate constants of cis and trans 1 fluoropropene relative to 1,1,2 TFB from the following reasoning

Suppose the following reaction scheme is in operation

3.1 $O(^3P) + 1,1,2TFB \xrightarrow{k_1} \alpha_c c\text{-}1FP + \alpha_t t.1FP + CF_2O...$

3.2 $c\text{-}1FP + O(^3P) \xrightarrow{k_2}$ products

3.3 $t.1FP + O(^3P) \xrightarrow{k_3}$ products

$$d\left(\frac{c\text{-}1FP}{dt}\right) = k_1 \alpha_c [O] [1,1,2TFB] - k_2 [O] [c\text{-}1FP]$$

At the maximum in the curve of c-1FP vs.t., $d\left(\frac{c\text{-}1FP}{dt}\right) = 0$

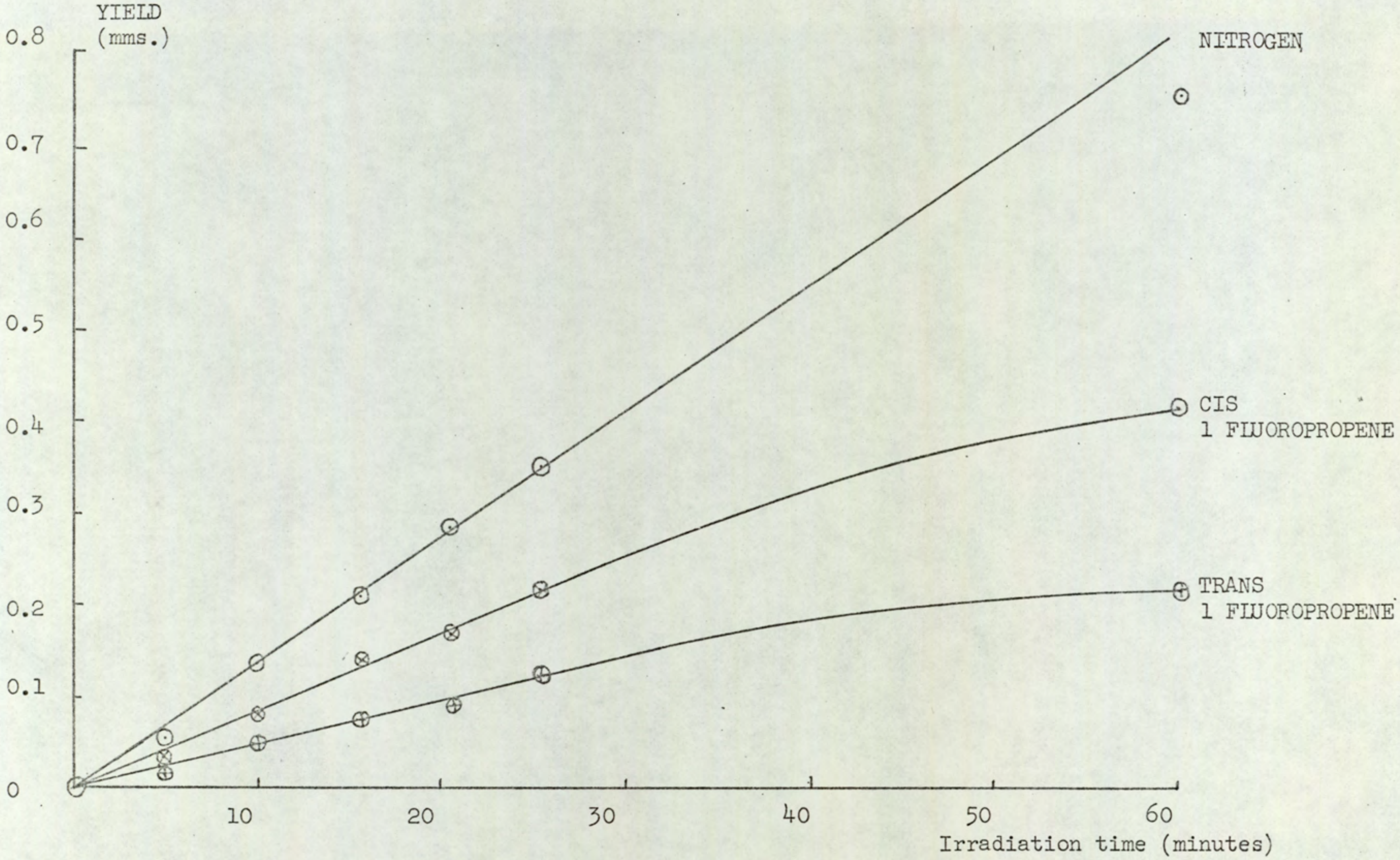


FIG. 3.4 MAJOR PRODUCTS IN REACTION OF $O(^3P)$ WITH 1,1,2 TRIFLUOROBUTENE-1

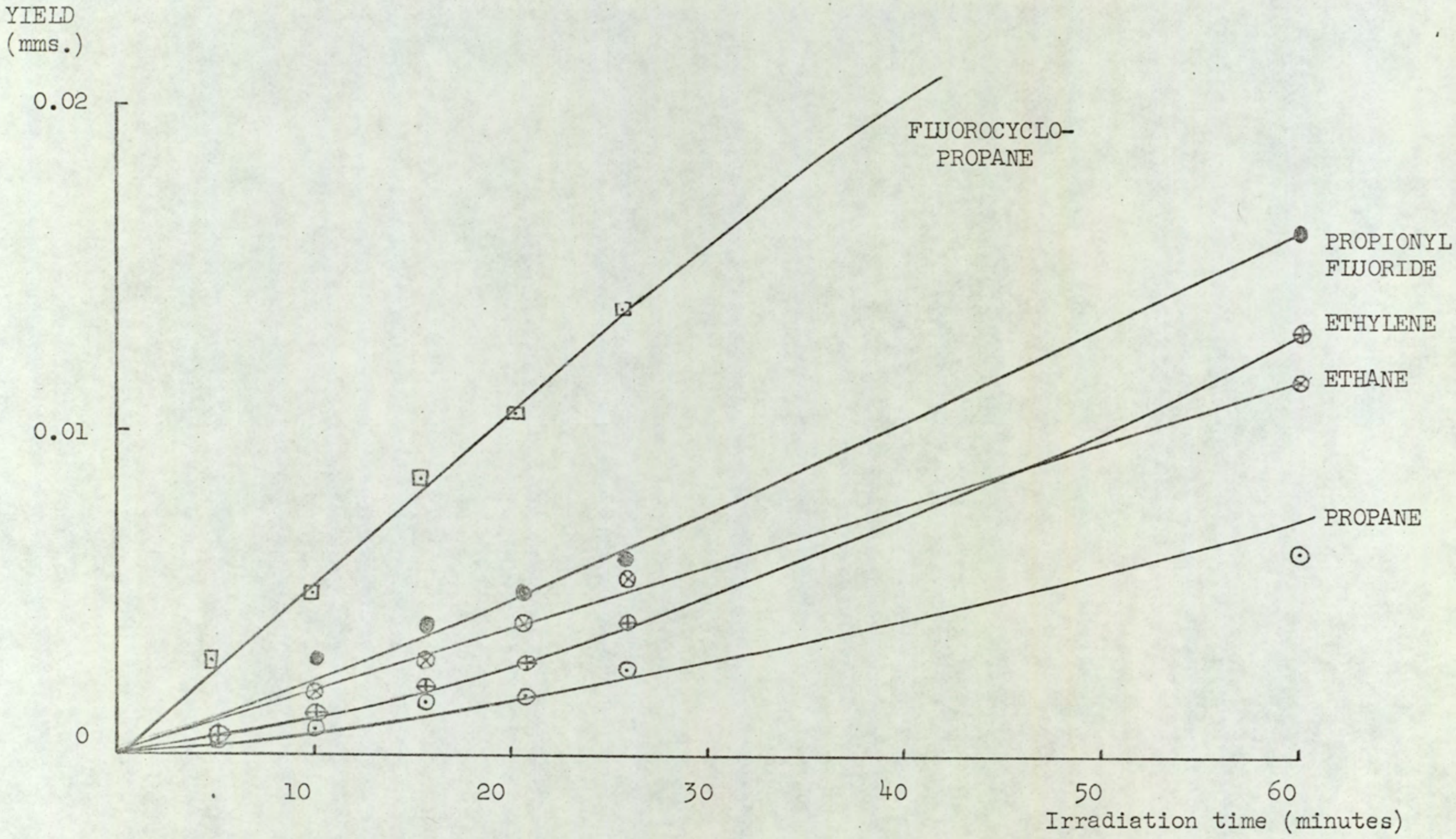


FIG. 3.5 MINOR PRODUCTS IN REACTION OF O(^{3}P) WITH 1,1,2 TRIFLUOROBUTENE-1

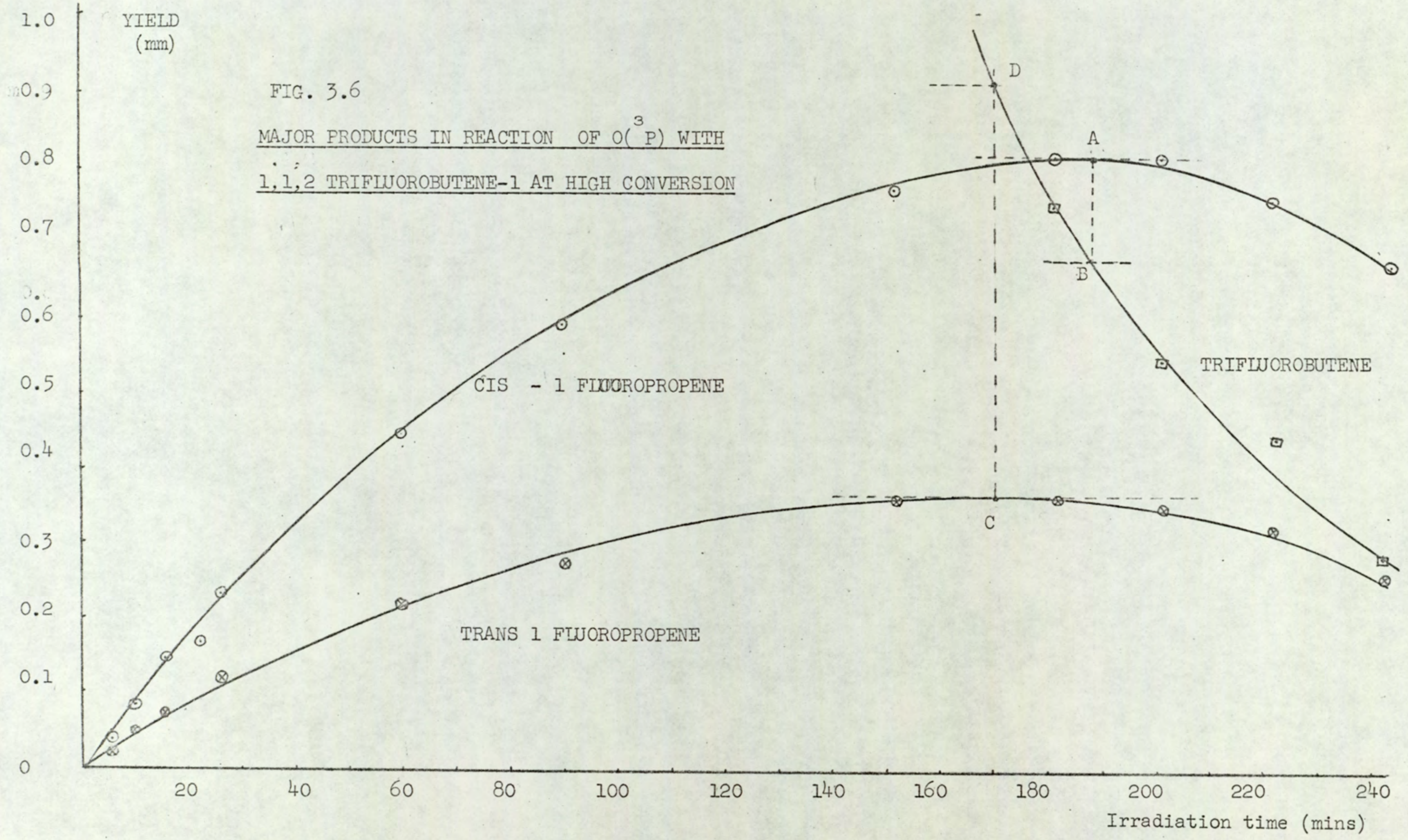


FIG. 3.6

MAJOR PRODUCTS IN REACTION OF O(^{3}P) WITH 1,1,2 TRIFLUOROBUTENE-1 AT HIGH CONVERSION

3.4 ie. $$\frac{k_2}{k_1} = \frac{\alpha_c \left[1,1,2\ TFB\right]_1}{\left[c\text{-}1FP\right]_{max.}}$$

where $\left[c\text{-}1FP\right]_{max.}$ is maximum concentration of cis 1 fluoropropene (point A on the graph 3.6).

and $\left[1,1,2\ TFB\right]_1$ is concentration of 1,1,2 TFB when the concentration of cis reaches a maximum(point B.)

Now, α_c is the proportion of cis isomer formed per oxygen atom in the main reaction 3.1 and is $0,65_5$ (see following section).

$\left[1,1,2\ TFB\right]_1$ is 0.67_3 mm. and

$\left[c\text{-}1\ FP\right]_{max.}$ is 0.82_2 mm.

Substituting these values into equation 3.4

$$\frac{k_2}{k_1} = \frac{0.65_5 \times 0.67_3}{0.82_2} = \underline{0.53_6}$$

similarly, $$\frac{k_3}{k_1} = \frac{0.34_5 \times 0.90_7}{0.37_0} = \underline{0.84_6}$$

ie. the rate constant of cis 1 fluoropropene relative to 1,1,2TFB, is $\underline{0.53_6}$ and for the trans isomer is $\underline{0.84_6}$

From this $$\frac{k_{cis}}{k_{trans}} = 0.63_4$$

These ratios have been measured previously and are compared with those above in Table 3.3(overleaf).

As trans 1 fluoropropene reacts with oxygen atoms faster than the cis isomer, the ratio of cis to trans should increase with conversion, as is shown in Fig.3.6A.

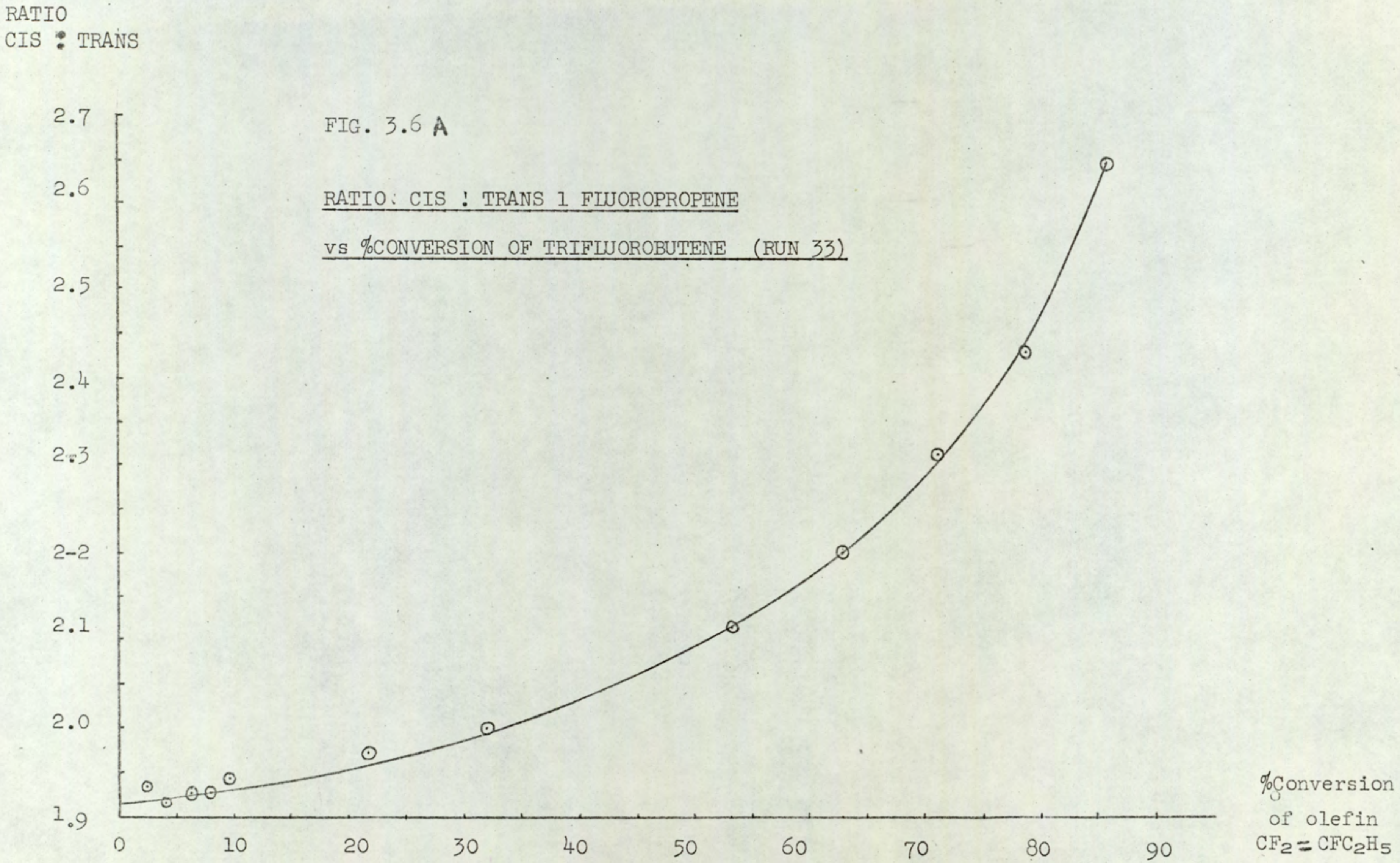


FIG. 3.6 A

RATIO: CIS : TRANS 1 FLUOROPROPENE vs %CONVERSION OF TRIFLUOROBUTENE (RUN 33)

TABLE 3.3

olefin	$k_{ol} / k_{CF_2=CFEt}$	
cis 1 fluoropropene	0.53_6	0.35_5
trans 1 fluoropropene	0.84_6	0.61_2
ratio k_{cis}/k_{trans}	0.63_4	0.58_0
Reference	this work	57,99

Carbonyl fluoride

The yield of carbonyl fluoride was not followed as a function of time. We anticipate that the carbonyl fluoride time dependence would closely ressemble that of total 1 fluoropropene. However, as carbonyl fluoride cannot react with oxygen atoms, the only deviation from linearity should be due to the competition of cis and trans 1 fluoropropene with 1,1,2 TFB for O(^{3}P). This is the analogous argument to the deviation of fluorocyclopropane formation from linearity explained in greater detail below.

b) Minor Products

Fluorocyclopropane

The yield of this compound also appears to fall with time, in a similar manner to the fall of the cis and trans 1 fluoropropene yields, (Fig.3.5). This is explained from the competitive scheme proposed in dealing with 1 fluoropropene yields. If the fluorocyclopropane is formed from the reaction of O(^{3}P) with 1,1,2 TFB then as the reaction proceeds and cis and trans 1 fluoropropene compete for the available oxygen atoms then the yield of fluorocyclopropane must decrease.

Propionyl fluoride, ethane and propane.

These products appear to increase linearily with time It is difficult from the scatter of the points, to ascertain if there is any significant fall off at high conversion.

Ethylene

This shows a definite increase with irradiation time although in the initial stages a linear production rate is indicated. As shown in the discussion section, C_2H_4 is believed to be derived from the reaction of oxygen atoms with 1-fluoropropene as well as the reaction with 1,1,2 TFB.

3.4 PRESSURE DEPENDENCE STUDIES

Variations of quantum yields with total pressure for major and minor products are shown in Fig.3.7 and 3.8 respectively. Pressures were varied between 100mm. and 800mm. Ratios of olefin to nitrous oxide were always in excess of 1:20, ensuring reactions involving mercury photosensitised decompositions of the olefin are kept to a minimum. All reactions were at room temperature 23°C(± 2°) and carried to 2% conversion. It was necessary to work at constant conversion as cis and trans 1 fluoropropene quantum yields are dependent upon this factor (due to the competition with 1,1,2 TFB for oxygen atoms).

a) Major Products

Nitrogen

Cvetanović[23] has noted that the quantum yields of the reaction $Hg(^3P) + N_2O \longrightarrow N_2 + O(^3P) + Hg(^1S_0)$ proceeds with a quantum yield of unity. It has been assumed that this is true for the range of pressures investigated.

cis 1 fluoropropene

The apparent trend is for a slight increase in the quantum yield with increasing pressure. The quantum yield varies between 0.6(at low pressures) to 0.7 at 800mm.

trans 1 fluoropropene

There appears to be no effect of pressure on the quantum yield of the trans isomer, which remains essentially constant at about 0.3. The variation of the ratio of cis to trans quantum yield with pressure is illustrated in Fig.3.9.

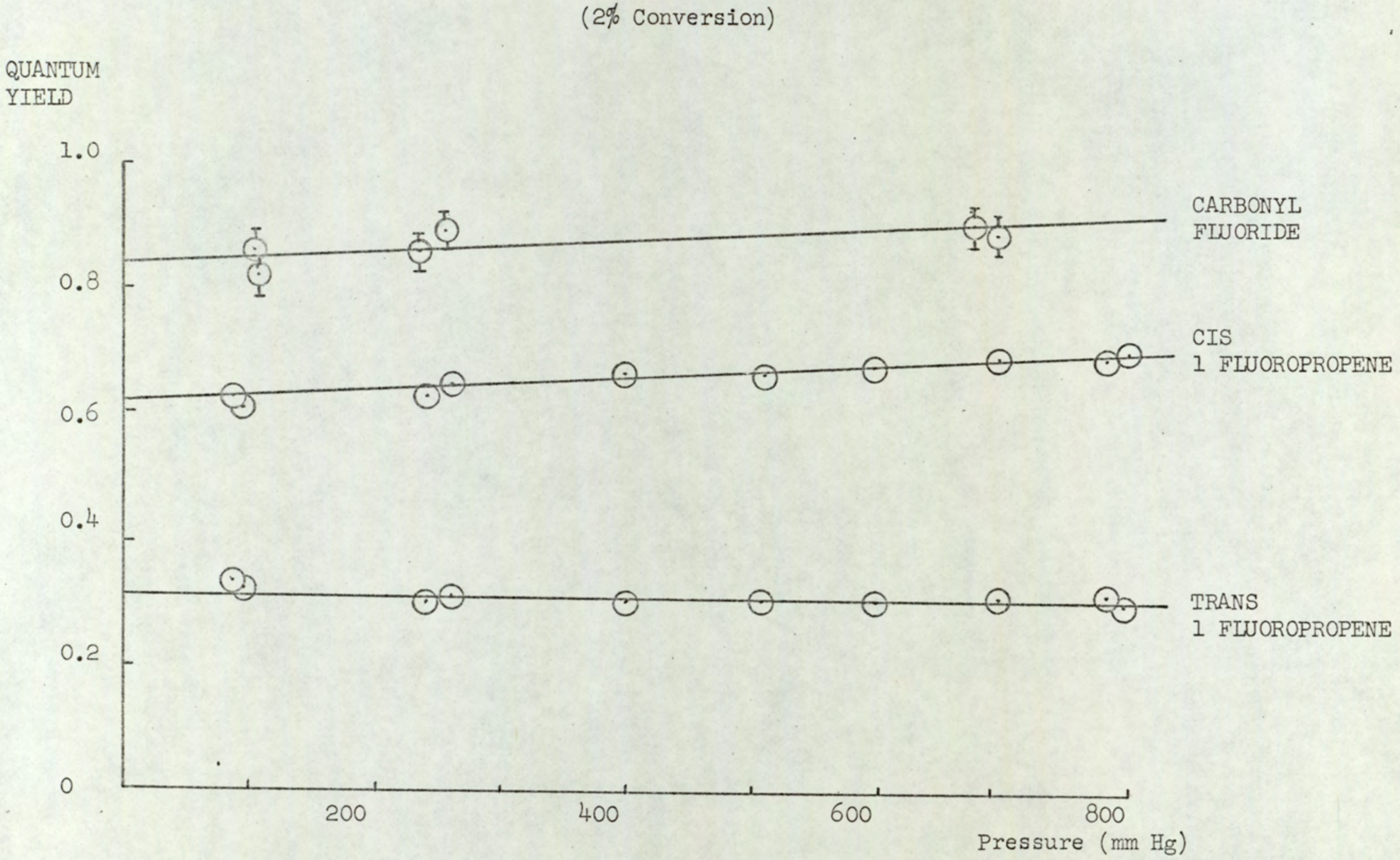


FIG. 3.7 PRESSURE DEPENDENCE OF MAJOR PRODUCTS O(^{3}P) WITH 1,1,2 TRIFLUOROBUTENE-1

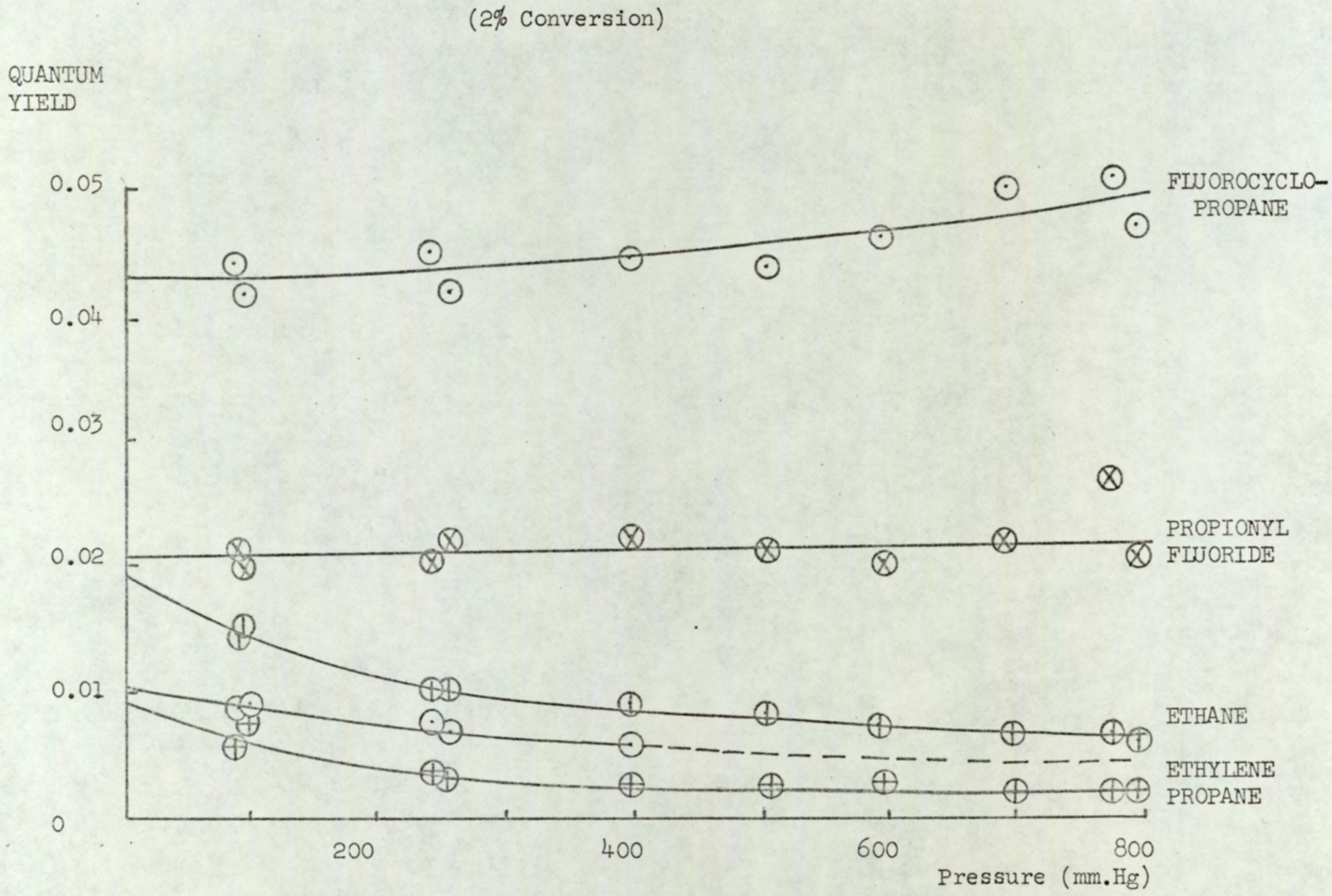


FIG. 3.8 PRESSURE DEPENDENCE OF MINOR PRODUCTS O(^{3}P) WITH 1,1,2 TRIFLUOROBUTENE-1

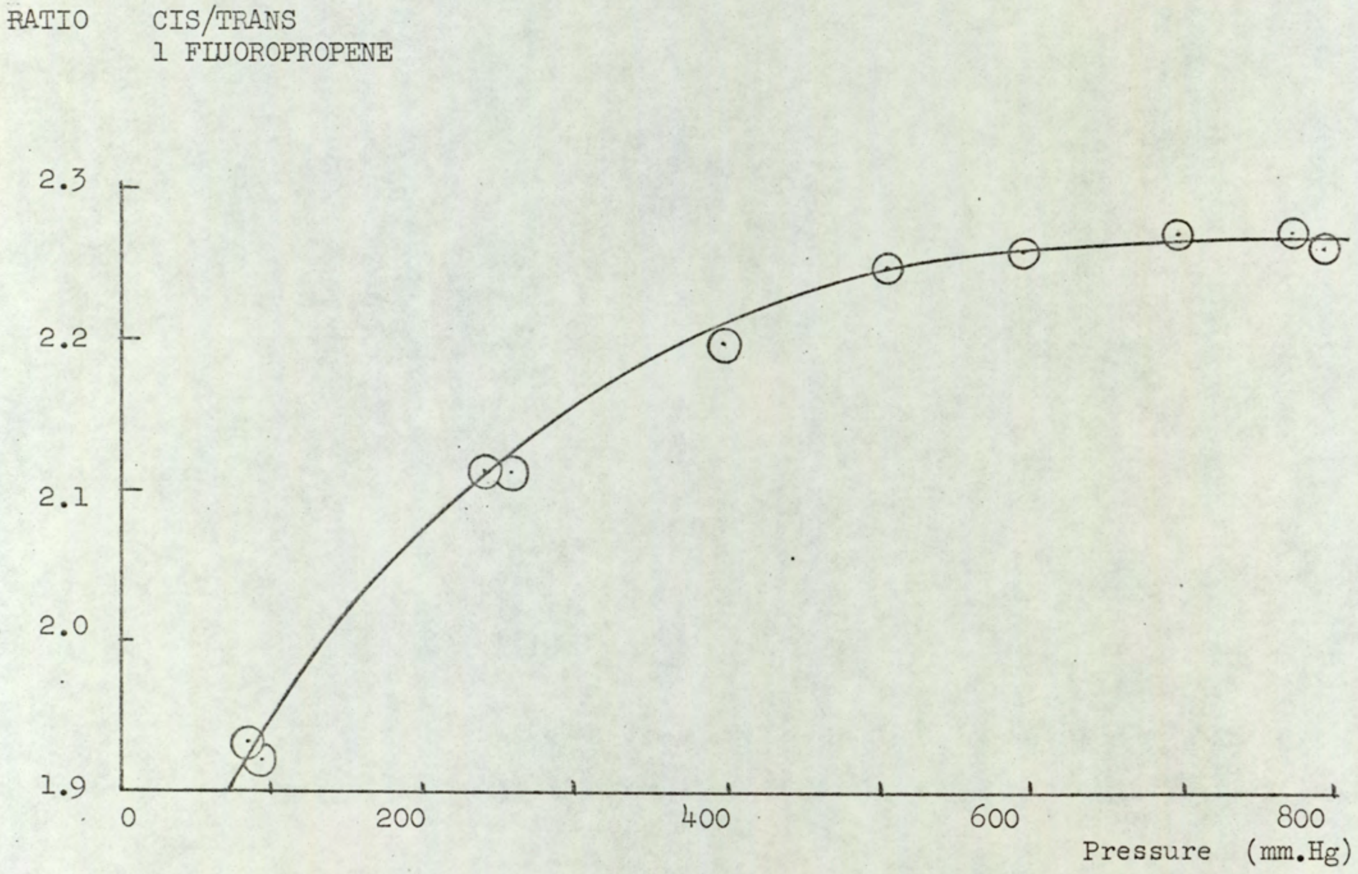


FIG. 3.9 PRESSURE DEPENDENCE OF CIS: TRANS RATIO OF 1 FLUOROPROPENE

The behaviour of the two isomers has been considered in more detail in the discussion section.

Carbonyl fluoride

The carbonyl fluoride quantum yields were measured by the infra-red technique described in section 3.2. It was inconvenient to measure carbonyl fluoride at the same time as following the other products by G.L.C. hence a series of six runs were carried out exclusively to investigate the effect of pressure on the quantum yield of carbonyl fluoride. The results are shown in Fig.3.7.

It is difficult from the graph to distinguish a definite trend. This is because of inherant inaccuracy in the method of measurement compared to measurement by G.L.C. The limits of error are indicated in Fig.3.7. by vertical lines. However it can be said that the results indicate a constant or slightly increasing quantum yield with pressure, of about $0.8_8 \pm 0.04$.

It should also be noted that the six runs were carried out to between 6 and 8% conversion. It was necessary to work at these relatively high conversions because of the insensivity of the I.R. spectrometer compared to the G.L.C.

b) Minor Products

Fluorocyclopropane and propionyl fluoride

Both show little dependence on pressure. It is possible that fluorocyclopropane quantum yields increase slightly above 500mm.pressure, but this is uncertain due to the scatter of the points.

Average quantum yields are:-

propionyl fluoride 0.02_2 (± 0.002)

fluorocyclopropane 0.04_6 (± 0.004)

Ethane, ethylene and propane

Quantum yields of these products show a definite decrease with increasing pressure. They vary over the range of about 0.02 and 0.002.

The quantum yields of all the products at various pressures is shown in Table 3.4 and 3.5.

TABLE 3.4

Variation of Quantum Yields with Pressure

Pressure (mm.)	Ethylene	Ethane	Propane	cis 1FP	trans 1FP	Fluorocyclopropane	Propionyl fluoride
88	0.0087	0.0148	0.0057	0.621	0.330	0.044	0.022
93	0.0088	0.0155	0.0078	0.610	0.321	0.042	0.020
240	0.0076	0.0105	0.0037	0.632	0.304	0.045	0.021
253	0.0068	0.0107	0.0036	0.649	0.309	0.042	0.023
396	0.0057	0.0094	0.0024	0.668	0.300	0.045	0.022
509	*	0.0084	0.0023	0.670	0.302	0.044	0.022
596	*	0.0071	0.0022	0.681	0.304	0.047	0.020
692	*	0.0068	0.0019	0.692	0.310	0.051	0.002
773	*	0.0071	0.0017	0.685	0.307	0.051	0.027
794	*	0.0068	0.0017	0.700	0.302	0.047	0.021

Note: * It has been found that in high pressure runs, the great excess of nitrous oxide causes overlap of the N_2O peak with ethylene on a Poropak Q column. For this reason no quantum yields have been given for ethylene in Table 3.4 above 500mm. pressure.

TABLE 3.5

Variation of Carbonyl Fluoride Quantum Yields with Pressure

pressure(mm.)	Quantum yield
107	0.86
107	0.82
234	0.86
251	0,89
679	0.90
695	0.89

3.5 EFFECT OF REDUCED LIGHT INTENSITY

The reaction mixture, total pressure 296mm., was irradiated at a lower light intensity, but under otherwise identical conditions to those used for the pressure dependence runs. Light intensity was reduced by using only a single lamp. Also a double-layered fine copper gauze was inserted between lamp and cell window to further reduce the intensity of radiation incident upon the cell. The transmission of the gauze at 2537 Å had previously been measured using an SP700 UV spectrometer and was found to be 12.5%. The reduction in the incident radiation intensity could be measured by the reduction in the nitrogen yield measured by the Toepler pump. For the run quoted below, the total irradiation time was 400 minutes the pressure of nitrogen produced in the reaction vessel was 0.45_2mm. **This corresponds to a reduction of light intensity to 8.5% of that operative in a standard run.**

The results in Table 3.6 are compared to a run of a normal light intensity, at the same pressure (approximately 300mm.) and carried out to the same conversion (2%).

TABLE 3.6

Effect of Reduced Light Intensity on Quantum Yields

Compound	Quantum Yield	
	(reduced light intensity)	(normal intensity)
ethane	0.012	0.011
ethylene	0.008	0.007
propane	0.004	0.003
fluorocyclopropane	0.044	0.044
cis1 fluoropropene	0.66	0.64
trans 1fluoropropene	0.32	0.31
propionyl fluoride	0.020	0.022

It can be seen that reducing the light intensity has very little effect on the quantum yields of the products. The effect of reduced light intensity on the quantum yield of carbonyl fluoride was not measured. However, as cis and trans 1 fluoropropebe yields are not affected, there is reason to suppose that the carbonyl fluoride quantum yield is similarly not affected.

3.6 TEMPERATURE DEPENDENCE STUDIES

The reaction cell was heated by the oven previously described in section 2.1(e). Temperatures were measured with a copper constantan thermocouple and were constant to better than ± 2°C.

Runs shown in Table 3.7 were carried out at a pressure of 300mm.,(± 10mm.) and all conversions were kept within 2 to 3%.

TABLE 3.7

Variation Of Product Quantum Yields with Temperature

Product	Temperature			
	23°C	89°C	118°C	193°C
ethane	0.010	0.016	0.019	0.024
ethylene	0.007	0.010	0.013	0.016
propane	0.003	0.005	0.005	0.003
cis 1fluoropropene	0.66	0.69	0.66	0.60
trans 1 fluoropropene	0.30	0.33	0.32	0.30
total 1 fluoropropene	0.96	1.02	0.98	0.90
propionyl fluoride	0.022	0.020	0.017	0.014
fluorocyclopropane	0.043	0.040	0.042	0.035

cis and trans 1 fluoropropene

The relationship between the quantum yields of these two products and temperature is not clear, as the variation does not follow any clearly defined trend. It would appear, however, that the quantum yield of the cis isomer falls at high temperatures by about 10%. Also, the ratio of cis and trans isomers shows a steady decrease with increasing temperatures. This is illustrated in Fig. 3.10.

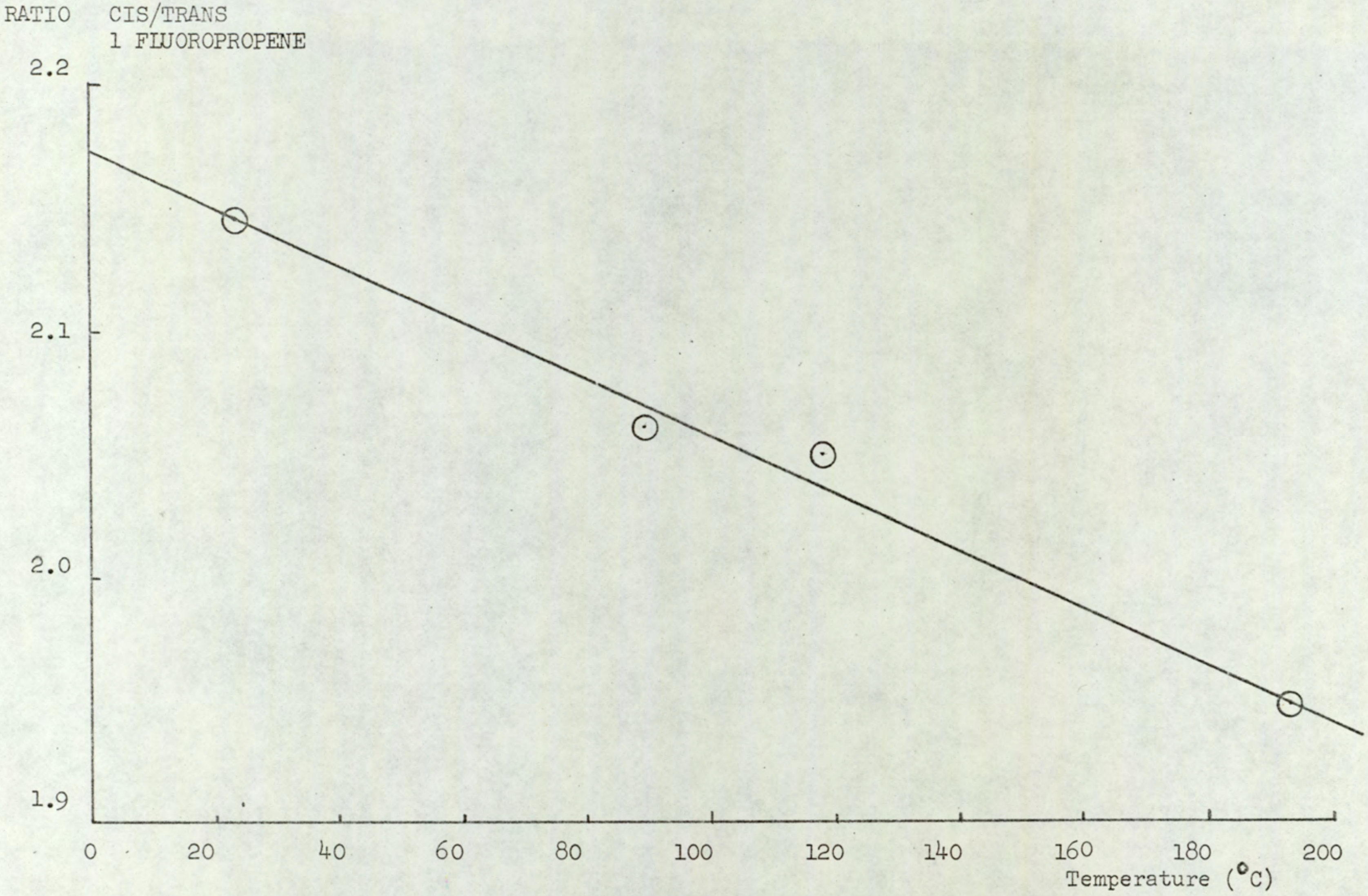


FIG. 3.10 1 FLUOROPROPENE FORMATION : VARIATION OF CIS/TRANS RATIO WITH TEMPERATURE

Ethylene and ethane

The quantum yields of these products show a definite increase with increasing temperature.

Propane

This seems to, show a slight increase at moderate temperatures but falls again at higher temperatures.

Propionyl fluoride and fluorocyclopropane

A definite decrease of quantum yield is indicated with increasing temperatures for both these products.

Carbon monoxide

A check was made of the carbon monoxide yield in the reaction carried out at 193°C. It was found that even at this high temperature carbon monoxide constituted less than 1% of the nitrogen yield (ie quantum yield was less than 0.01).

Carbonyl fluoride

No measurements were made of the quantum yield of carbonyl fluoride. It has been assumed that the variation with temperatures is similar to that shown by the total 1 fluoropropene (shown in the Table) ie. falling by about 10% at about 200°C.

3.7 THE EFFECT OF ADDED MOLECULAR OXYGEN UPON THE REACTION OF O(^{3}P) AND 1,1,2 TFB

Molecular oxygen (British Oxygen) was admitted to an evacuated trap filled with activated charcoal. The trap was cooled in liquid nitrogen, which had the effect of condensing most of the oxygen onto the charcoal. The trap was allowed to warm slowly and the first few centimetres of oxygen was pumped away. A few millimetres of oxygen was then admitted to the reaction vessel via the manifold. The reaction vessel contained a previously measured amount of trifluorobutene and nitrous oxide frozen with liquid nitrogen. The reaction vessel was closed and the gases thoroughly circulated at room temperature for about half an hour prior to irradiation. At the end of a reaction, oxygen and nitrogen were collected by the Toepler pump and the pressure measured. Knowing the normal production rate of nitrogen in a run containing no oxygen it was possible to estimate accurately the pressure of oxygen initially admitted to the reaction vessel.

Carbonyl fluoride quantum yields were measured by I.R. spectrometry and all other products by G.L.C.

a) Effect of added oxygen on the rates of formation of products

Two runs were carried out for the investigation. In the first, 5mm. of oxygen was admitted to the reaction vessel after 15 minutes irradiation. The irradiation was then continued for a further 60 minuted. Yields were measured just previous to oxygen addition and

and after 15, 30 and 60 minutes further irradiation. The results are shown in Fig. 3.11 and 3.12 (major and minor products respectively.)

In the other run, 5mm. of oxygen was admitted at the start of the reaction, and samples analysed after 16,31,46 and 61 minutes irradiation. The yields of major and minor products as a function of nitrogen produced are illustrated in Figs. 3.13 and 3.14. Both runs were carried out at 300mm. pressure. conversion was kept to below 5%.

Note:- Nitrogen production rate was 0.87 mm.(in reaction vessel) per hour for both runs. ie.0.1 mm. of nitrogen represents 6,9 minutes irradiation.

Cis and trans 1 fluoropropene

In the table below(Table 3,8) the quantum yields of the two isomers are compared to a run carried out at the same temperature and pressure but in the absence of molecular oxygen.

TABLE 3.8

Effect of Oxygen on Quantum Yield of Cis and Trans 1 Fluoropropene

	oxygen added initially	oxygen added during reaction	no oxygen added
cis 1 fluoropropene	0.64(±0.04)	0.61(±0.04)	0.66(±0.02)
trans 1fluoropropene	0.29(±0.02)	0.27(±0.02)	0.31(±0.01)
Ratio cis:trans	2.20	2.26	2.15

It can be seen that within experimental error that the addition of oxygen has no effect on the observed quantum yields of the cis and trans isomers. Also the ratio of cis : trans remains unaltered. For all

FIG. 3.11 EFFECT OF ADDED OXYGEN ON MAJOR PRODUCT YIELDS (O + 1,1,2 TFB)

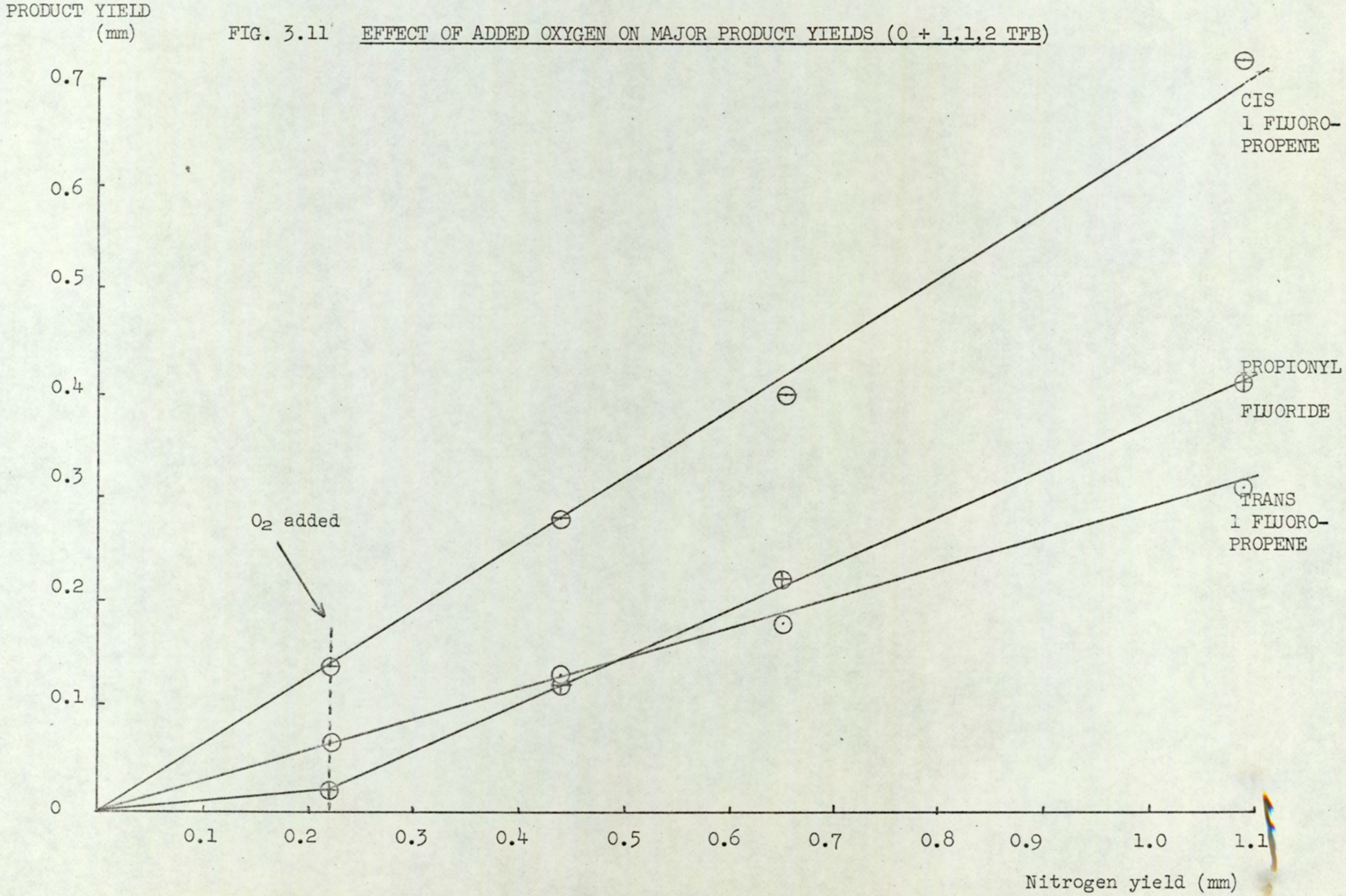


FIG.3.12 EFFECT OF ADDED OXYGEN ON MINOR PRODUCT YIELDS (O + 1,1,2 TFB)

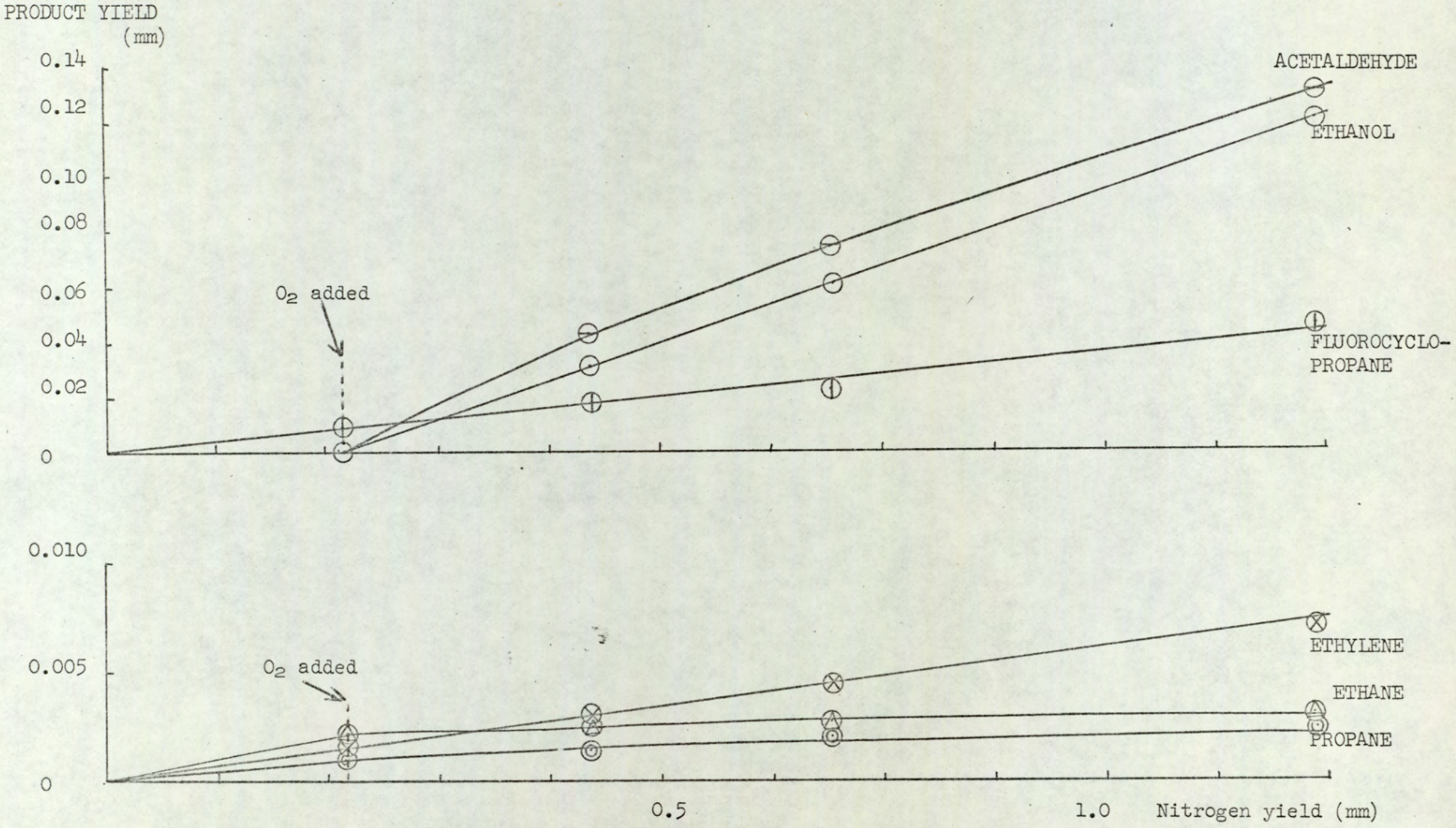


FIG. 3.13 EFFECT OF ADDED OXYGEN ON MAJOR PRODUCT YIELDS (O + 1,1,2 TFB)
(oxygen added initially)

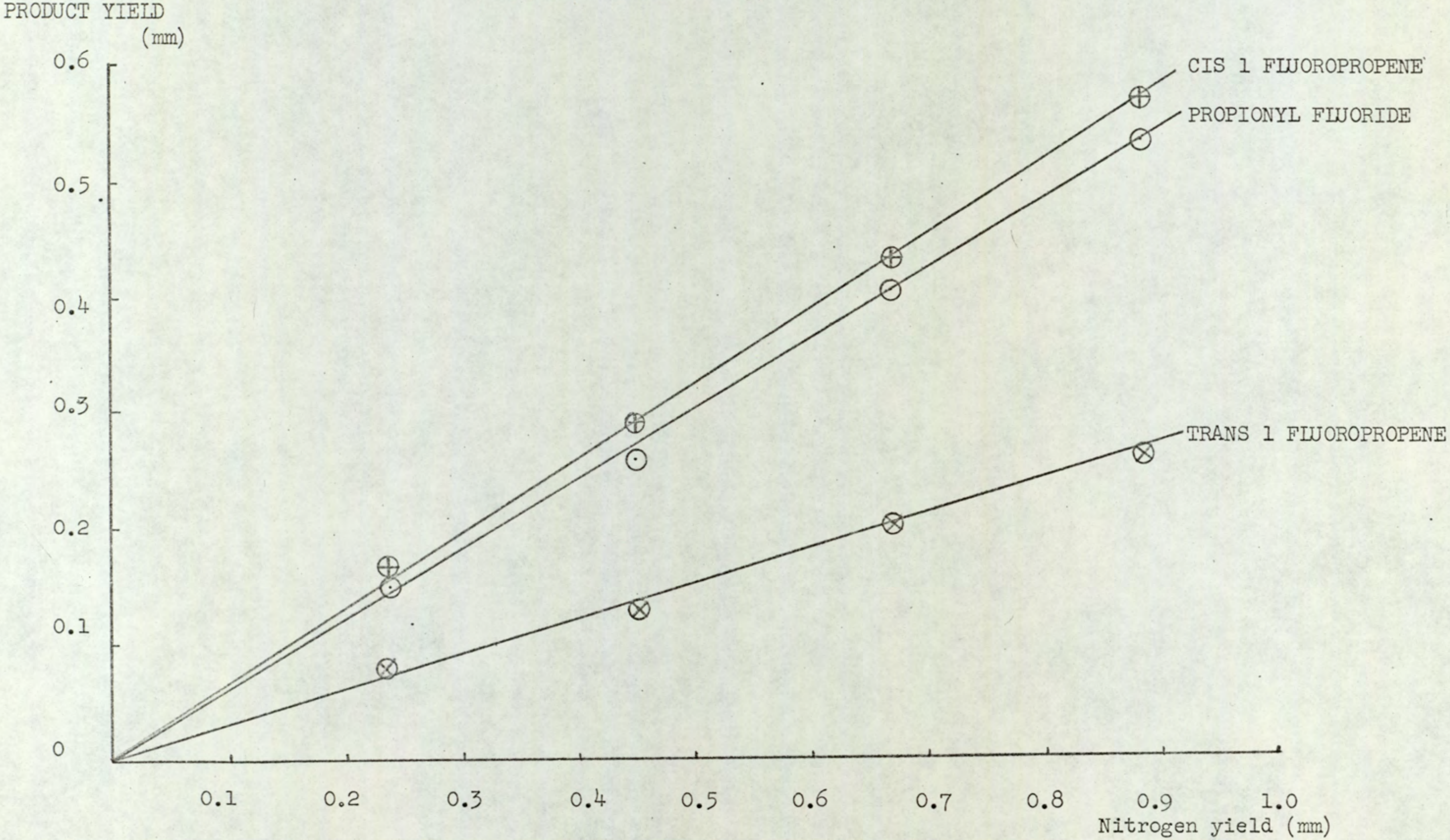
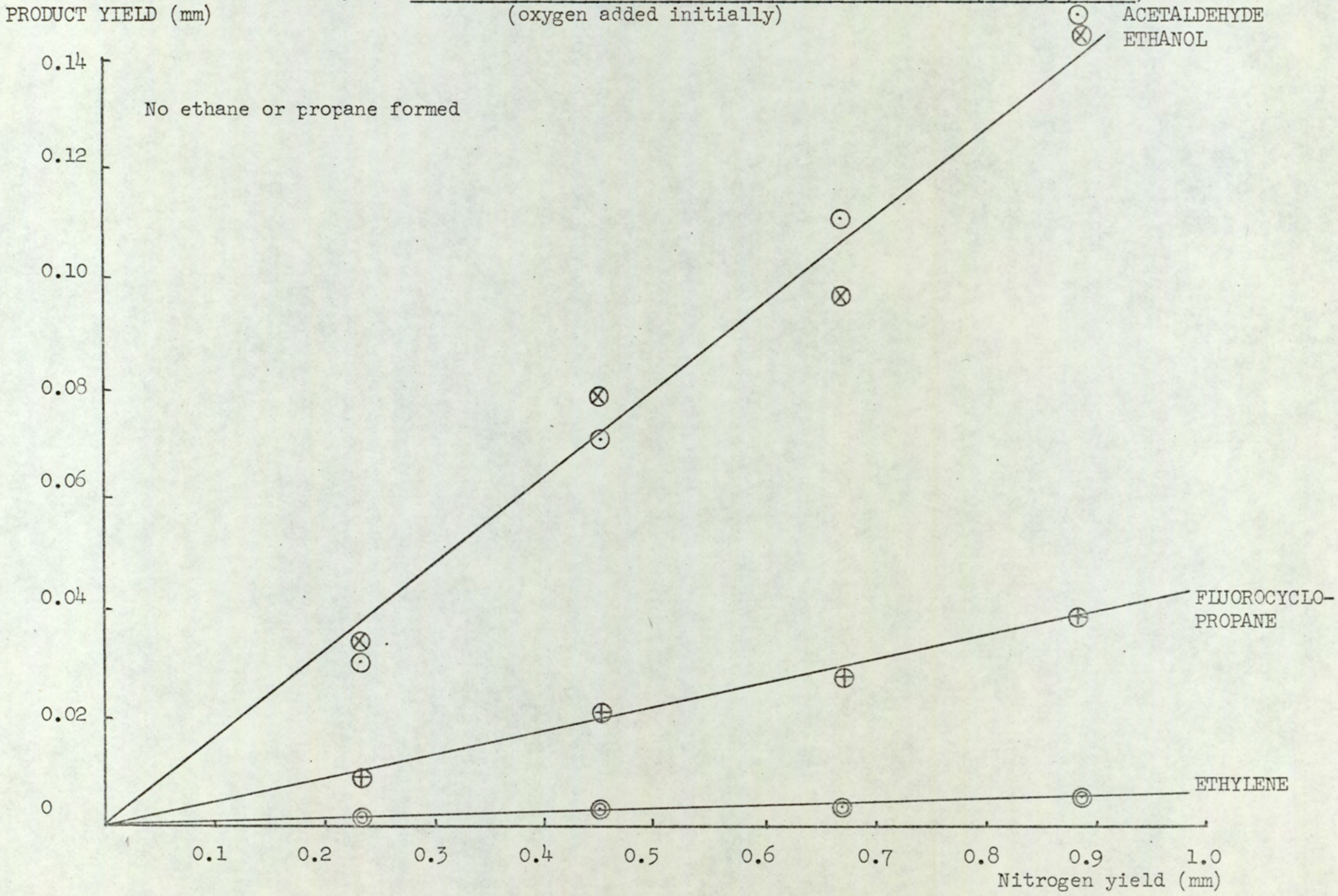


FIG.3.14 EFFECT OF ADDED OXYGEN ON MINOR PRODUCT YIELDS (O + 1,1,2 TFB)
(oxygen added initially)



runs involving addition of oxygen, it should be noted that the experimental error involved in estimating quantum yields is correspondingly greater than normal. This is because nitrogen yields cannot be measured directly, but are estimated assuming a constant output from the mercury lamps. As day to day variations of up to 5% have been noted previously it should be borne in mind that additional experimental errors of the same magnitude will be included in the calculated quantum yields.

Propionyl fluoride

It is very evident from Fig.3.11 that addition of oxygen greatly increases the quantum yield of propionyl fluoride. In the absence of oxygen, the quantum yield of this product is 0.02. With oxygen present, a quantum yield of as high as 0.6 has been observed. (It was later found that the quantum yield of propionyl fluoride was dependent upon the oxygen concentration. For this reason, no exact quantum yield is quoted above.)

Ethane and propane

From the run involving oxygen addition during the reaction (Fig.3.12), it was noted that the oxygen markedly reduced the ethane and propane production rates. However, because of sampling inaccuracies it was difficult to ascertain whether the rate was reduced dramatically or formation ceased completely. It became obvious from the second run, in which oxygen was added initially, that no ethane or propane was formed.

Fluorocyclopropane

Oxygen was found to have no effect upon the rate of formation of this product. The quantum yield in the presence of oxygen was 0.04_2 (expected quantum yield in absence of oxygen was 0.04_4)

Ethylene

Similarly, oxygen had no effect on the quantum yield of ethylene.

quantum yield ethylene in presence of oxygen = 0.007
" " " " absence " " = 0.006

Acetaldehyde and ethanol

These products were formed only in the presence of molecular oxygen and in approximately equal amounts. Average quantum yields in the runs shown in Figs. 3.12 and 3.14 were 0.14 for each product.

Carbonyl fluoride

Quantum yields were not measured during the two runs considered above. However, yields were measured in the experiments described in the following section.

b) Effect of olefin/oxygen ratio upon quantum yield of the products

The following runs were carried out at room temperature. Quantum yields of all products except ethanol and acetaldehyde were measured. The ratio of oxygen to trifluorobutene was varied (olefin concentration being kept constant) and results of this variation summarised in Table 3.9 overleaf.

TABLE 3.9

Effect of Oxygen/Olefin Ratio Upon the Quantum Yield of Products

Run No.	O_2 (mm)	TFB (mm)	QUANTUM YIELDS						
			ethylene	ethane	propane	CIS 1FP	TRANS 1FP	Propionyl fluoride	CF_2O
50	0	12	0.0085	0.0106	0.0043	0.72	0.34	0.02	0.98
51	0	13	0.0080	0.0110	0.0042	0.65	0.31	0.02	1.00
52	0	6.2	0.0086	0.0103	0.0037	0.65	0.31	0.02	0.98
53	4.5	13	0.0065	0o	0	0.66	0.31	0.38	1.84
54	9.1	13.2	0.0067	0	0	0.65	0.31	0.34	1.71
55	0	13.8	0.0092	0.0099	0.004	0.63	0.29	0.02	1.00
56	0.4	13.2	0.0068	0.0027	0.001	0.66	0.32	0.32	1.55

All conversions were about 3% except Run55 which was carried to 6%. This explains the low cis and trans 1 fluoropropene quantum yields of this run.

The main points evident from the table are

1) The quantum yield of carbonyl fluoride is greater than unity in the presence of oxygen.

2) Propionyl fluoride and carbonyl fluoride quantum yields are dependent upon oxygen concentration.

3) Cis and trans 1 fluoropropene yields are unchanged in the presence of oxygen.

CHAPTER FOUR

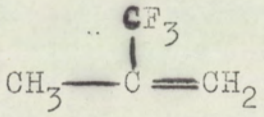
RESULTS FOR THE REACTION OF OXYGEN ATOMS WITH THE FLUORINATED ETHYLENES

4.1 INTRODUCTION

The rate constants for the reaction of oxygen atoms with ethylene and all the fluoroethylenes were measured at 23°C and 150°C.

Rate constants and activation energies were estimated relative to a common reference olefin,

2 trifluoromethyl propene

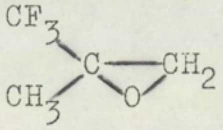


$$CH_3-\overset{CF_3}{\overset{|}{C}}=CH_2$$

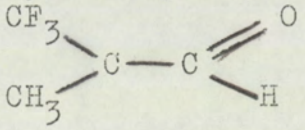
(hereafter referred to as 2 TFMP)

An extensive study has been made of the addition of oxygen atoms to 2 **TFMP**[54]. The advantages of using this olefin as a reference are:-

a) The products are almost exclusively the epoxide ans aldehyde



and



b) The yields of these products are almost pressure independent above pressures of 100mm.

c) The reactivity of the olefin with oxygen atoms is comparable to that of the fluorinated olefins.

4.2 ANALYSIS

All G.L.C. analysis was carried out using a 4m. 1/8" O.D. stainless steel colmmn packed with 20% di n-butylphthalate and 2% Carbowax 1000 at room temperature($23\pm2^{\circ}C$). Nitrogen was the carrier gas. This arrangement was found to give good separation of epoxide and aldehyde peaks and for most olefins, good separation of other products from epoxide and aldehyde, (exceptionally, the cases mentioned in section 4.4).

Carbon monoxide was measured with the copper oxide furnace. By correcting for the small amount of CO from the reference olefin (less than 2%) it was possible to estimate the carbon monoxide yield from the olefin being investigated. However, in the case of ethylene a rather more refined procedure was necessary. It was found that at liquid nitrogen temperatures ($77^{\circ}K$) the vapour pressure of ethylene was still appreciable (0·005mm.) and as a result, a small amount of this olefin was collected with the nitrogen by the Toepler pump. For this reason, the trap in the reaction system was kept at about $65^{\circ}K$ with liquid nitrogen cooled in a double-dewar (containing solid nitrogen in the outer jacket[104]).

In the case of ethylene, methane is also a product of the reaction with oxygen atoms. As a result, the non-condensibles from the reaction contained a small amount of methane which was not oxidised by the copper oxide furnace. Hence, methane yields were estimated by mass spectrometry, after copper oxide combustion. The samples were run on an AEI MS9 spectrometer using a direct entry to the source through a Varian leak valve in place of the normal solid sample probe. The instrument was calibrated with a mixture containing known amounts of nitrogen, carbon dioxide and methane.

Carbon dioxide gives peaks at 44 (CO_2^+)
28 (CO^+)
and 16 (O^+)

Nitrogen gives peaks at 28 (N_2^+) and 14 (N^+).

Methane gives peaks at 16 (CH_4^+)
15 (CH_3^+)
14 (CH_2^+)
13 (CH^+)
12 (C^+)

The proportion of CH_4 was estimated from the intensity of the 16 peak (resolved from O^+) relative to the intensity of the N_2 peak at 28 after correcting for the air background and CO^+ from CO_2 (via peak at 44^+). The test mixture gave the following results. If X is the component whose molar ratio to nitrogen is required, then

$$\text{Molar ratio} = \frac{X}{N_2} = \frac{\text{peak ht. of X (parent peak)}}{\text{peak ht. of } N_2 (m/e\ 28)} \times f_X$$

where f_X is a calibration factor for the parent peak X^+

For 44^+ of CO_2 $f_{CO_2} = 1.02$

" 16^+ of CH_4 $f_{CH_4} = 1.44$

Hence it was possible to calculate the proportion of methane and carbon dioxide in the non-condensibles collected.

The absence of 27,26, and 25 peaks in any of the samples examined showed that no appreciable amount of ethylene had been collected (these peaks would correspond to $C_2H_3^+$, $C_2H_2^+$, and C_2H^+).

4.3 RATE EQUATIONS

The rate constants for the reaction of ground-state oxygen atoms with several partially fluorinated olefins have been measured relative to a suitable reference olefin.

When mixtures of two olefins are irradiated in the presence of excess nitrous oxide, the reaction scheme is

a) $Hg(^1S_o) + h\nu\,(2537\text{Å}) \longrightarrow Hg(^3P_1)$

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

c) $O(^3P)$ + olefin (1) $\xrightarrow{k_1} \alpha_1 P_1 + \ldots..$

d) $O(^3P)$ + olefin (2) $\xrightarrow{k_2} \alpha_2 P_2 + \ldots..$

where α represents the fraction of oxygen atoms reacting with the olefin to produce product P.

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

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

Dividing (2) by (1)

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

where ΔP represents the rate of formation of product P. Also by steady state considerations

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

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 in reaction(b)
Substituting (5) into (3), we can express the ratio of rate constants in terms of one product as

$$\frac{k_2}{k_1} = \frac{[Ol_1]}{[Ol_2]} \cdot \left[\alpha_1 \frac{R_{N_2}}{P_1} - 1\right] \qquad (6)$$

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

Let ΔA_1 be the increase in peak area corresponding to the increase in product ΔP_1, then if detector calibration factor is f

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

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

ie. $$\alpha = \frac{\Delta P^*}{R_{N_2}^*} = f \cdot \left[\frac{\Delta A^*}{R_{N_2}^*} \right] = f . Q^* \qquad (6a)$$

The last expression defines Q and Q*.

Substituting (6a) into (3) and (6) respectively we obtain

$$\frac{[Ol_1]}{[Ol_2]} = \frac{k_2}{k_1} \cdot \frac{Q_2^*}{Q_1^*} \cdot \frac{A_1}{A_2} \qquad (7)$$

$$\frac{[Ol_2]}{[Ol_1]} = \frac{k_1}{k_2} \left[\frac{Q_1^*}{Q_1} - 1 \right] \qquad (8)$$

It should be noted that the above equations are derived assuming olefin concentrations remain constant throughout an irradiation. It is possible to correct for the small amount of olefin consumed (never more than 4%) by calculating the final concentration and using a mean value. Justification for this procedure is in the linear plots obtained.(section 4.5)

For the purpose of this work, equation (8) was used to calculate the ratio of the rate constants, separate plots being used for epoxide, aldehyde and where applicable carbon monoxide yields.

From the form of equation (8) a plot of $\frac{[Ol_2]}{[Ol_1]}$ vs $\frac{1}{Q_1}$ should give a straight line of gradient $\frac{k_1}{k_2} \cdot Q_1^*$ and intercept ${}^{k_1}/{k_2}$. Intercepts were generally estimated by feeding olefin ratios and 1/Q values into a Micro 16 computer programmed to calculate the least mean squares line.

Each plot should give the same rate constant ratio, but in practice some discrepancies are noted. This is usually due to peak overlap of the products from the olefin,, with epoxide and aldehyde peaks of the reference olefin.

4.4 RELATIVE RATE CONSTANTS FOR O(^{3}P) WITH THE FLUOROETHYLENES

Reaction at 23°C

Detailed results are collected in Appendix 2. All measurements are shown graphically at the end of this section. Tables 4.1 and 4.2 contain the derived relative rate constants using equation (8) with least squares treatment of the data. The rate constants quoted in Table 4.1 are relative to the reference olefin: 2 TFMP, and those in Table 4.2, relative to ethylene. The experimental errors quoted for the averaged value are based upon the difference in the relative rate constant as assessed from epoxide, aldehyde and occassionally carbon monoxide yields. In most cases the small yield of carbon monoxide from the olefin made the derived rate constant unreliable (see Table 4.3.) In this instance, the result has been ignored when calculating the average rate constant.

It was also found that in the case of ethylene, peaks from certain products of the reaction overlapped with aldehyde peak and for this reason, the average rate constant has been derived from the epoxide and carbon monoxide yields ~~above~~.

TABLE 4.1

Rate Constants for $O(^3P)$ with the Fluoroethylenes Relative to 2 TFMP (23 and 150°C)

Olefin	TEMP°C	k_{olefin} / k_{2TFMP}				other work Ref.56
		Product used for estimation			MEAN	
		Epoxide	Aldehyde	CO		
$CH_2=CH_2$	25±1°	2.15_2	1.68_8*	1.59_7	$1.81_2 \pm 0.3$	1.81
	150±1°	1.71_8	1.62_6*	1.37_3	$1.57_2 \pm 0.2$	
$CH_2=CHF$	24±1°	0.76_2	0.70_8	0.52_5*	$0.73_5 \pm 0.03$	0.69
	148±1°	0.81_9	0.80_8	0.82_6*	$0.81_4 \pm 0.01$	
$CF_2=CH_2$	25±2°	0.40_1	0.37_8	0.29_9*	$0.38_9 \pm 0.01$	0.39
	150±1°	0.49_2	0.43_7	0.43_4*	$0.46_5 \pm 0.03$	
Trans CHF=CHF	26±1°	1.04_1	0.99_6		$1.01_9 \pm 0.02$	0.97
	151±1°	1.14_8	1.09_2		$1.12_0 \pm 0.03$	
Cis CHF=CHF	26±2°	0.58_0	0.54_9		$0.56_4 \pm 0.01$	0.57
	151±1°	0.71_8	0.70_2		$0.71_0 \pm 0.01$	
$CF_2=CFH$	25±1°	1.07_3	0.97_6		$1.02_5 \pm 0.04$	1.02
	150±2°	1.03_0	1.03_0		1.03_0	
$CF_2=CF_2$	25±2°	3.14_0	3.03_6		$3.08_8 \pm 0.05$	2.90
	150±2°	2.04_5	2.14_9		$2.09_7 \pm 0.05$	

* indicates these values not included in the averaged result, as they are thought to be unreliable.

TABLE 4.2

Rate Constants for $O(^3P)$ with the Fluoroethylenes Relative to $CH_2=CH_2$ (23 and 150°C)

Olefin	This work 23°C	" 150°C	other work ref.56 23°C
$CH_2=CH_2$	(1.00)	(1.00)	(1.00)
$CH_2=CHF$	0.40_5	0.52	0.38
$CF_2=CH_2$	0.21_5	0.29_6	0.22
Trans CHF=CHF	0.56	0.71	0.54
cis CHF=CHF	0.31	0.45	0.32
$CF_2=CFH$	0.57	0.66	0.57
$CF_2=CF_2$	1.70	1.33	1.60

Absolute rate constants

Absolute rate constants may be calculated from the relative values by means of the absolute rate constant for reaction of oxygen atoms with ethylene. Two recent independent determinations[28,74] have been made using fast flow systems, with agreement within 35%. The mean of these two results at 300°K is

$$k_{C_2H_4} = 3.7 \times 10^{11}\ \text{cm.}^3\text{mol.}^{-1}\text{sec.}^{-1}$$

TABLE 4.3

Carbon Monoxide Yields (expressed as a percentage of nitrogen collected) for the Reaction of Oxygen Atoms with the Ethylenes.

Olefin	Carbon monoxide yield%)		Temp.(°C)
	this work	other work ref.99	
$CH_2=CH_2$	44.4	44.8	25
	45.3		148
$CH_2=CHF$	22.8	22.9	25
	24.7		150
$CF_2=CH_2$	13.5	14.5	23
	16.2		150
Trans CHF=CHF	1.5	3.8	24
	7.2		152
Cis CHF=CHF	2.3	3.2	24
	9.1		152
$CF_2=CFH$	3.0	2.3	23
	4.0		150
$CF_2=CF_2$	approx.0	approx.0	23
	0.8		145
2 TFMP	1.6	1.6	23
	2.0		150

4.5 ARRHENIUS PARAMETERS FOR THE REACTION BETWEEN OXYGEN ATOMS AND THE FLUORINATED ETHYLENES

Using the relative rate constants at the two temperatures quoted in the previous section, the activation energies and pre-exponential factors were calculated from the Arrhenius equation

$$k = A \exp(-E/RT)$$

The activation energies and 'A' factors relative to 2 TFMP and ethylene are shown in Table 4.4. The errors quoted are based on the discrepancies between values calculated separately from epoxide, aldehyde and in the case of ethylene, carbon monoxide yields.

TABLE 4.4

Pre-exponential Factors and Activation Energies of the Reactions between Oxygen Atoms and the Fluorinated Ethylenes

Olefin	$\frac{A_{ol.}}{A_{2\ TFMP}}$	$E_{ol}-E_{2TFMP}$ (kJmol.$^{-1}$)	$\frac{A_{ol.}}{A_{C_2H_4}}$	$E_{ol}-E_{C_2H_4}$ (kJmol.$^{-1}$)
$CH_2=CH_2$	0.98(±0.1)	-1.59(±0.3)	(1.00)	(0)
$CH_2=CHF$	1.03(±0.1)	+0.84(±0.3)	1.04(±0.2)	2.43(±0.6)
$CH_2=CF_2$	0.71(±0.1)	+1.42(±0.3)	0.72(±0.2)	3.01(±0.6)
cis CHF=CHF	1.23(±0.05)	+1.92(±0.1)	1.26(±0.2)	3.51(±0.4)
trans CHF=CHF	1.40(±0.05)	+0.79(±0.1)	1.43(±0.2)	2.38(±0.4)
$CF_2=CFH$	1.06(±0.1)	+0.04~~2~~(±0.4)	1.08(±0.2)	1.63(±0.7)
$CF_2=CF_2$	0.86(±0.1)	-3.14(±0.4)	0.88(±0.2)	-1.55(±0.7)

Absolute Arrhenius parameters

Westenburg [74] has made a detailed study of the $O(^3P)/C_2H_4$ reaction over the temperature range 195-715K using a fast flow technique. It was noted that an

Arrhenius plot showed definite curvature over the temperature range. However, linear behaviour was observed in the range 226-380 K and the reaction rates were reasonably described by the equation:-

$$k_{C_2H_4} = 5.0 \times 10^{12} \exp(-6270/RT)$$

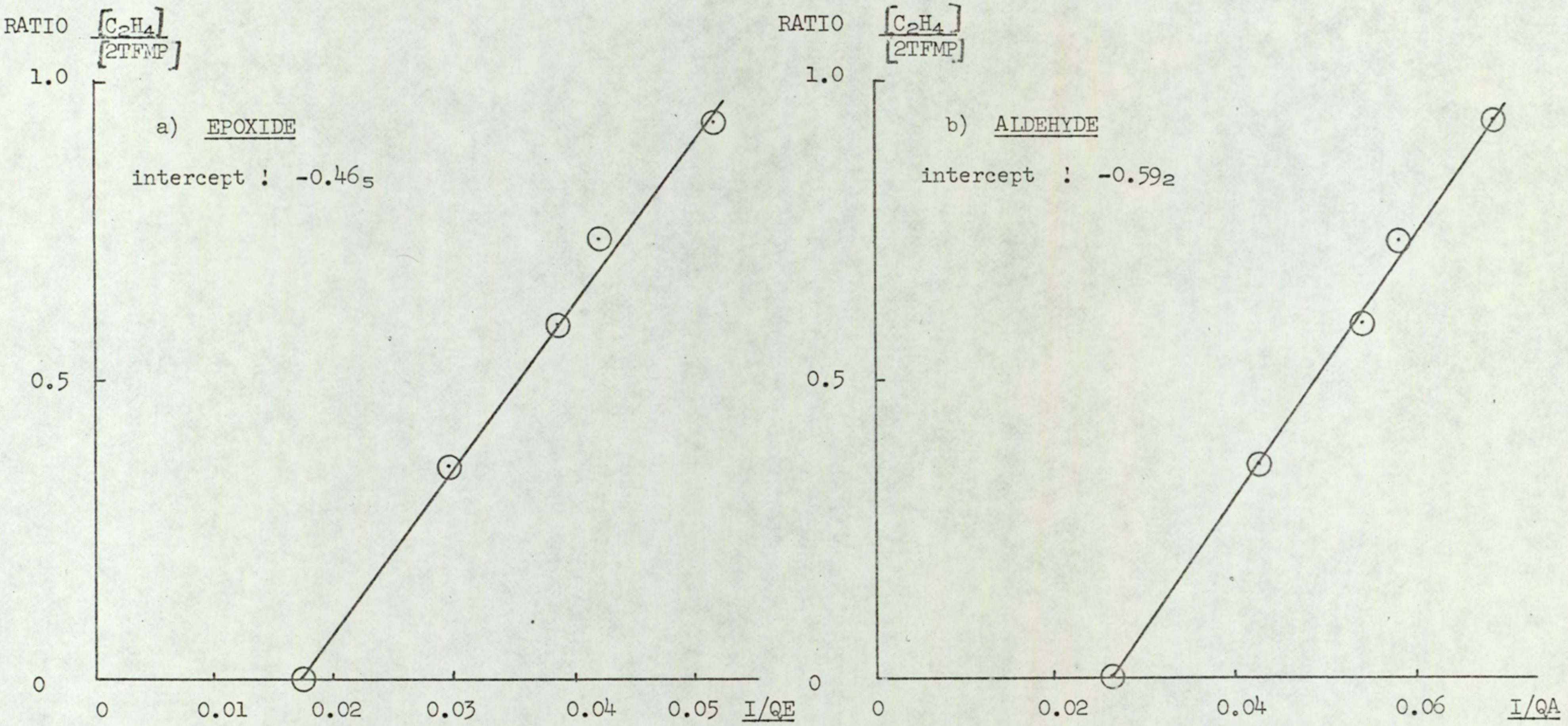
where the pre-exponential factor is in units of $cm^3.mol.^{-1}sec.^{-1}$ and activation energy in Joules $mol.^{-1}$. This is in reasonable agreement with an estimate by Elias[105] of the activation energy of the reaction being 6700 $Jmol.^{-1}$

Using the Westenburg absolute values of pre-exponential factor and activation energy the Arrhenius parameters of the fluoroethylene reactions have been placed on an absolute basis in Table 4.5 below.

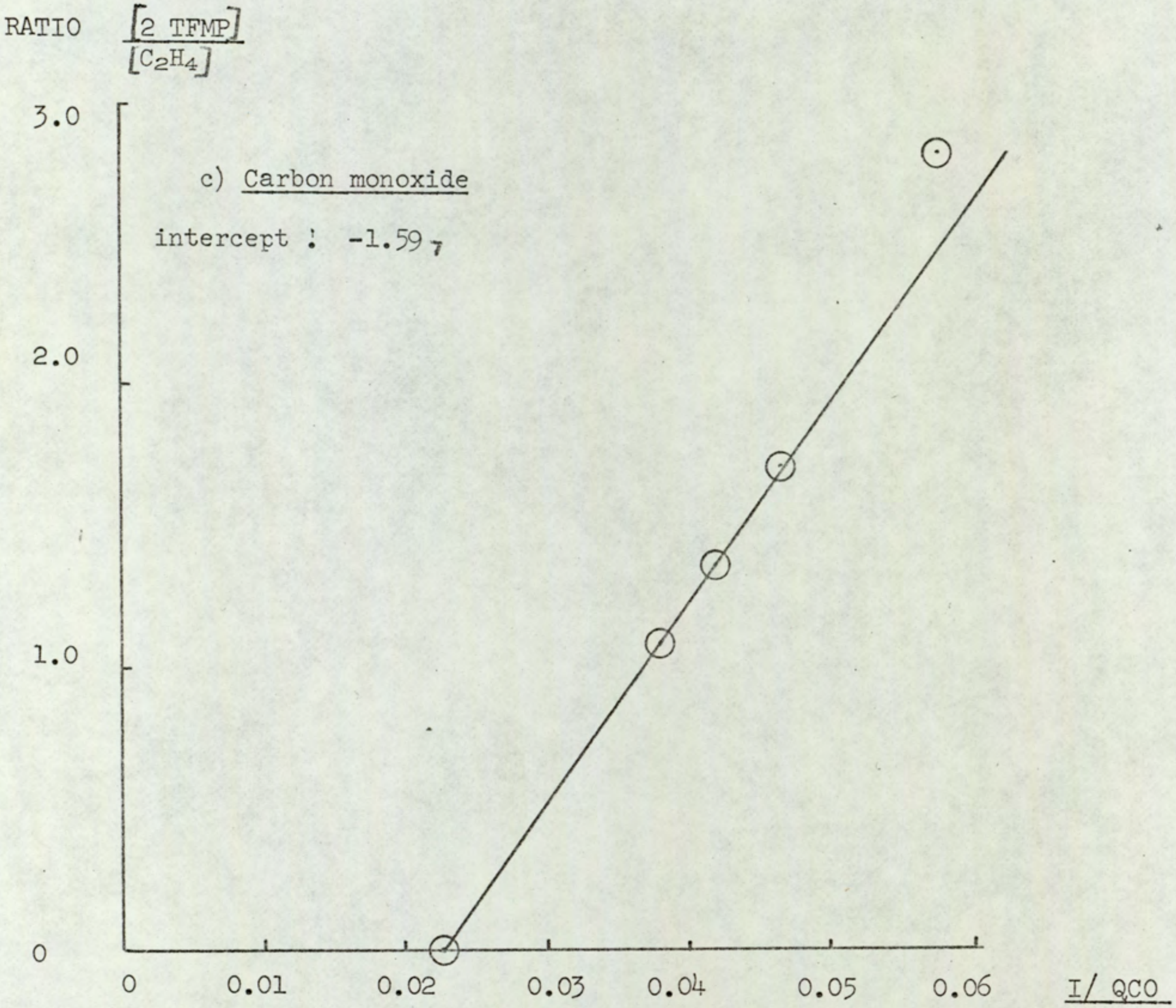
TABLE 4.5

Absolute Arrhenius Parameters of the $O(^3P)$/Fluoroethylene Reactions.

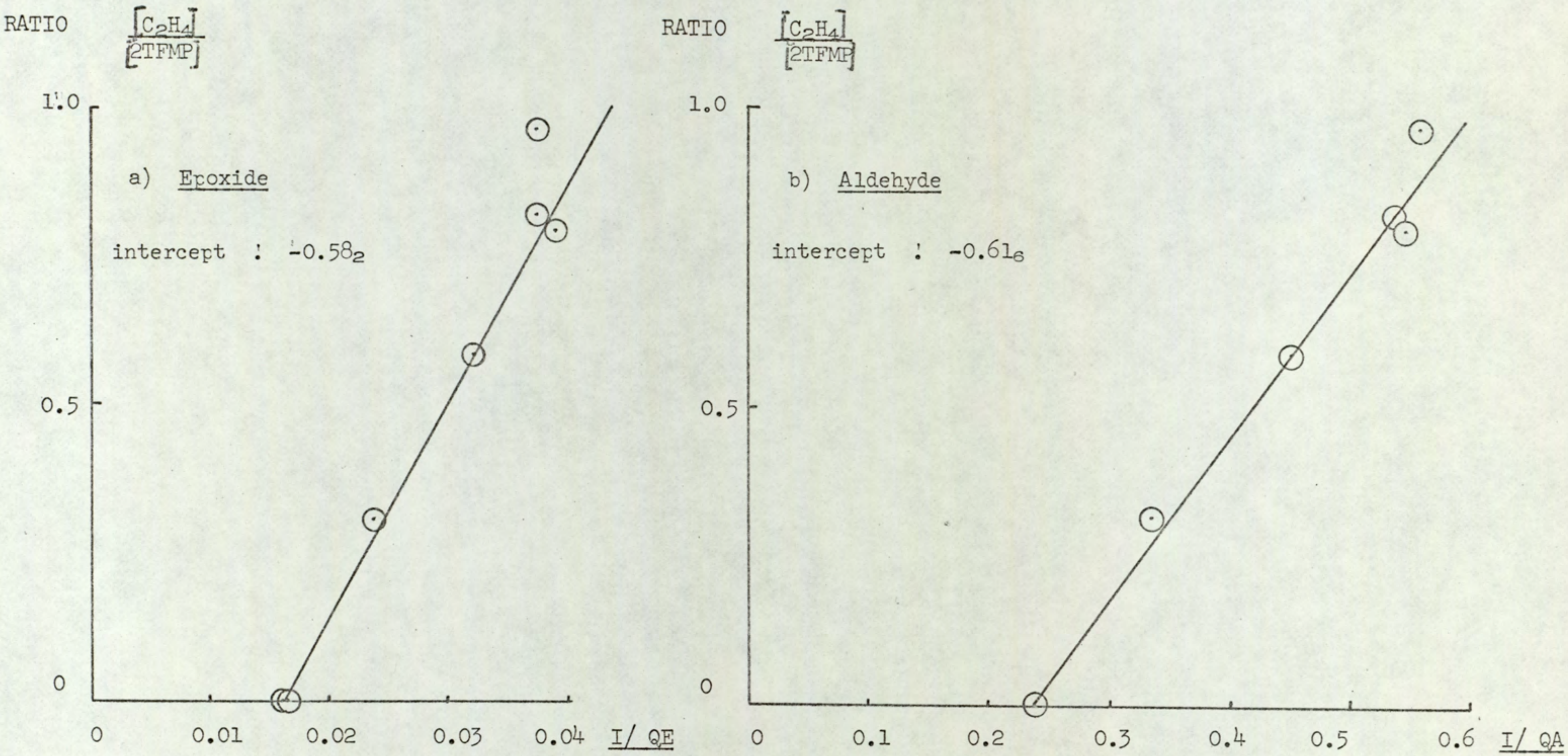
Olefin	A $cm^3.mol.^{-1}sec.^{-1}$ $\times 10^{-12}$	E($kJmol.^{-1}$)
$CH_2=CH_2$	5.0	6.27
$CH_2=CHF$	5.2 (±1.0)	8.70 (±0.6)
$CH_2=CF_2$	3.6 (±1.0)	9.28 (±0.6)
cis CHF=CHF	6.3 (±1.0)	9.75 (±0.4)
trans CHF=CHF	7.2 (±1.0)	8.65 (±0.4)
$CHF=CF_2$	5.4 (±1.0)	7.90 (±0.7)
$CF_2=CF_2$	4.4 (±1.0)	4.72 (±0.7)
2 TFMP	5.1 (±1.0)	7.86 (±0.3)



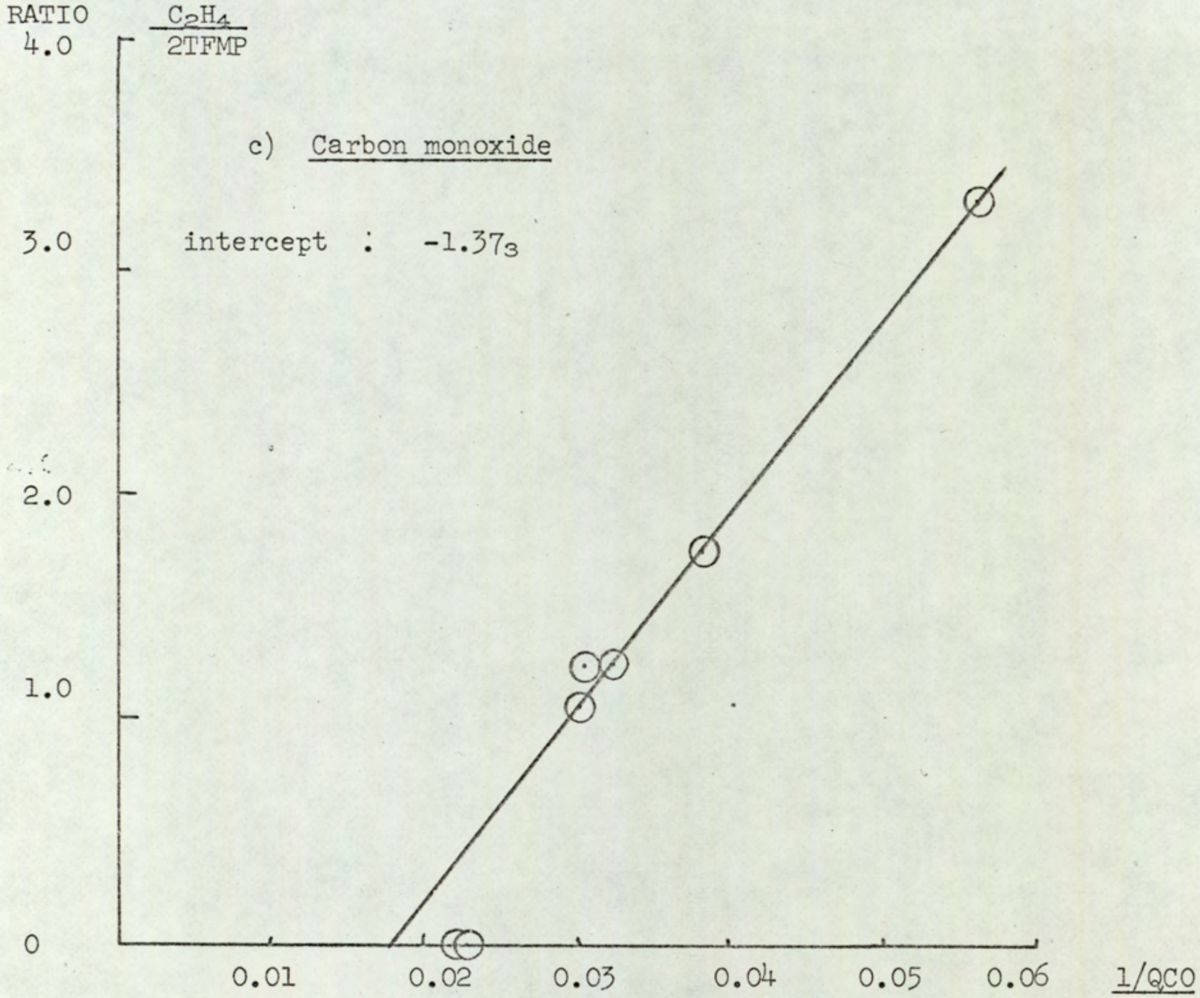
ETHYLENE vs 2TFMP AT 25°C



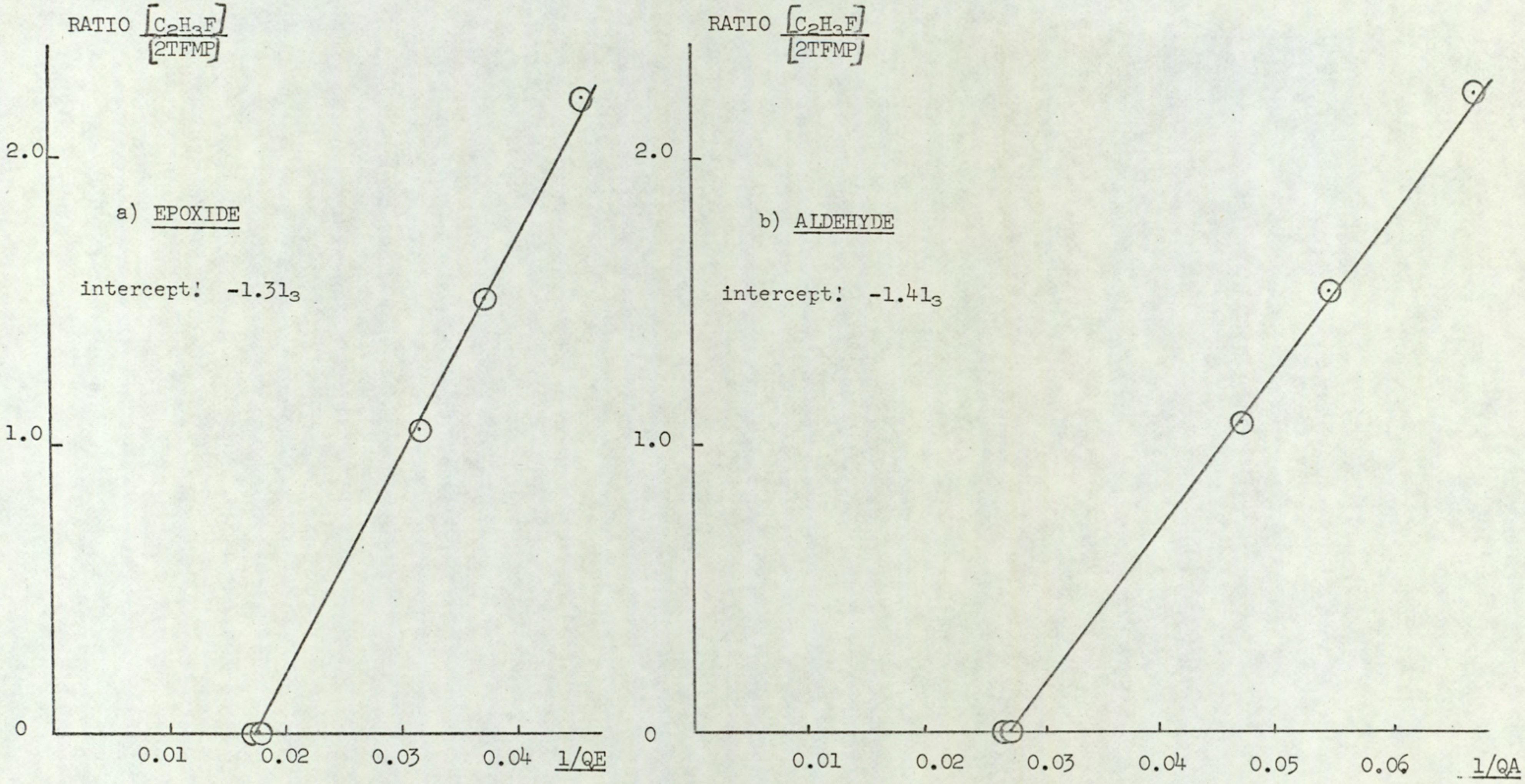
ETHYLENE vs 2TFMP AT 25°C



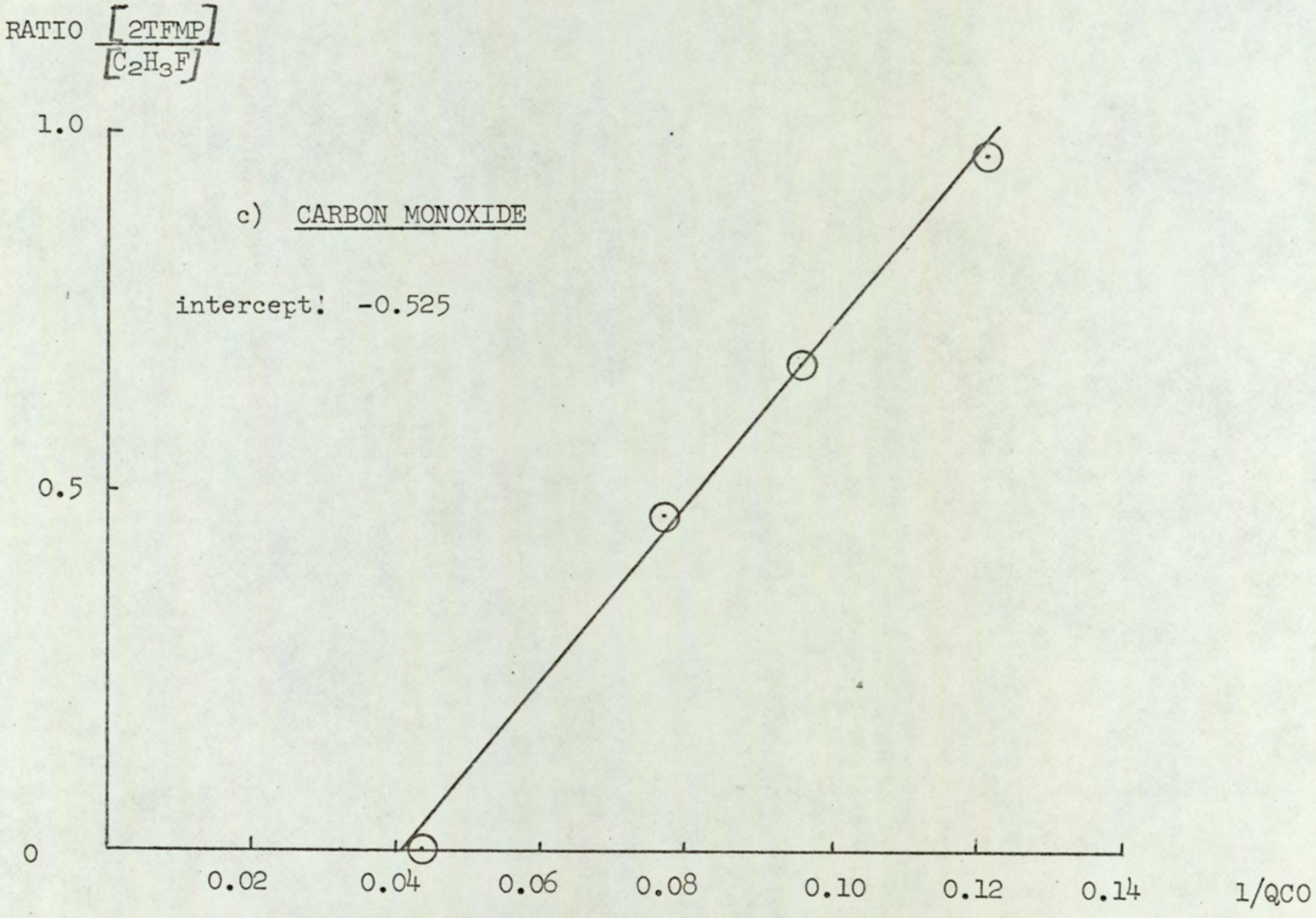
ETHYLENE vs 2 TFMP AT 150 C



ETHYLENE vs 2 TFMP AT 150 C



VINYL FLUORIDE vs 2TFMP AT 25°C



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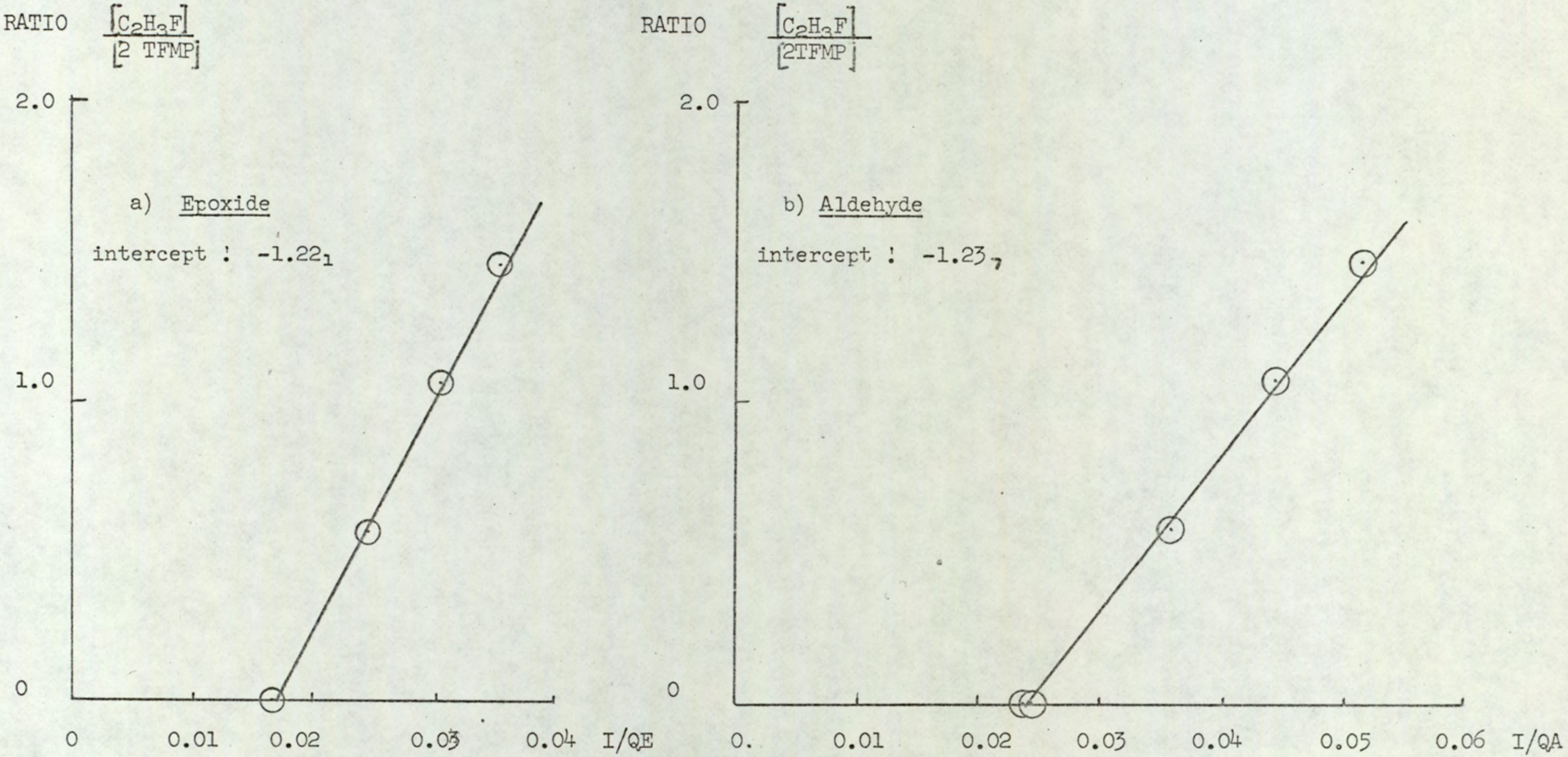
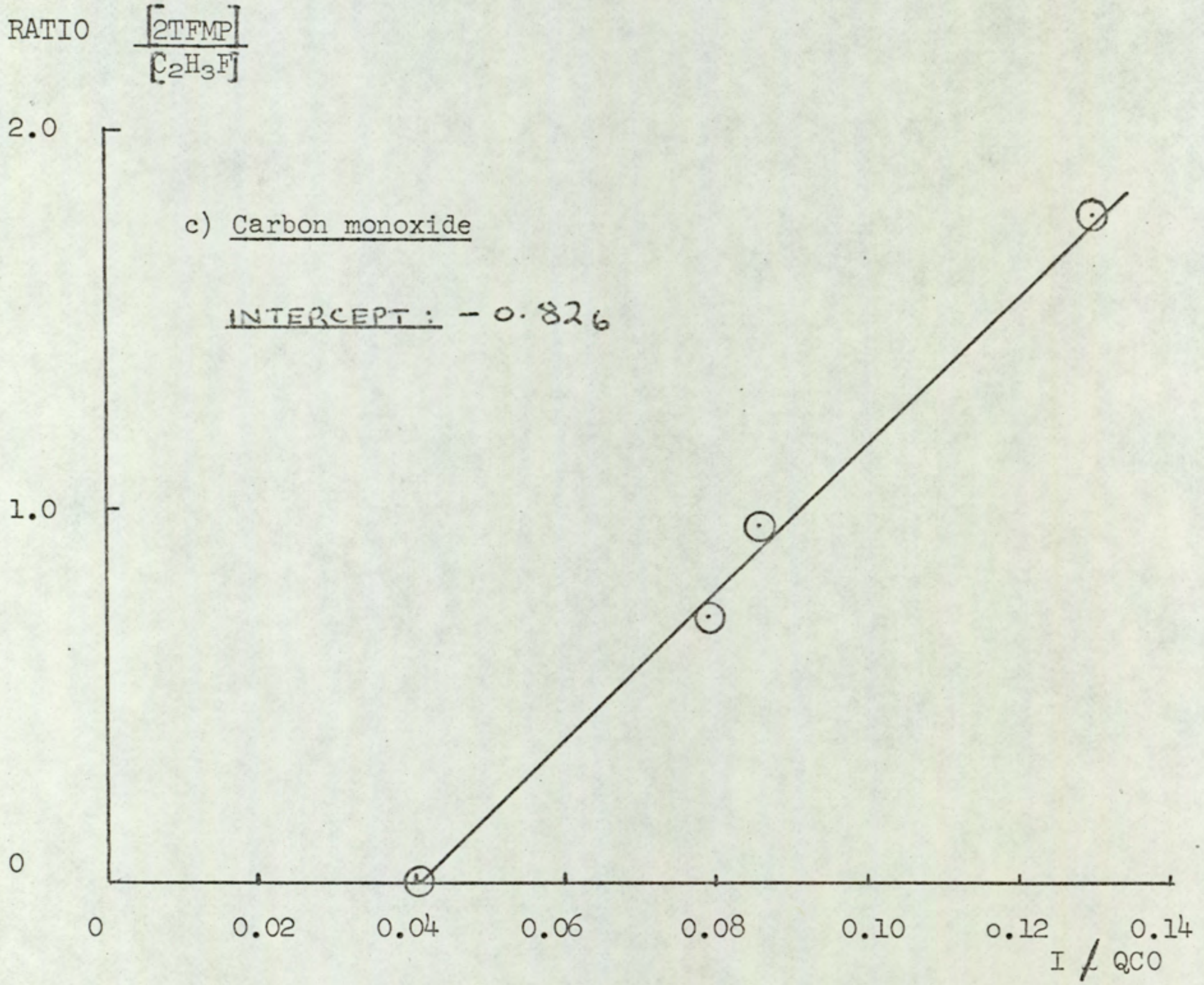
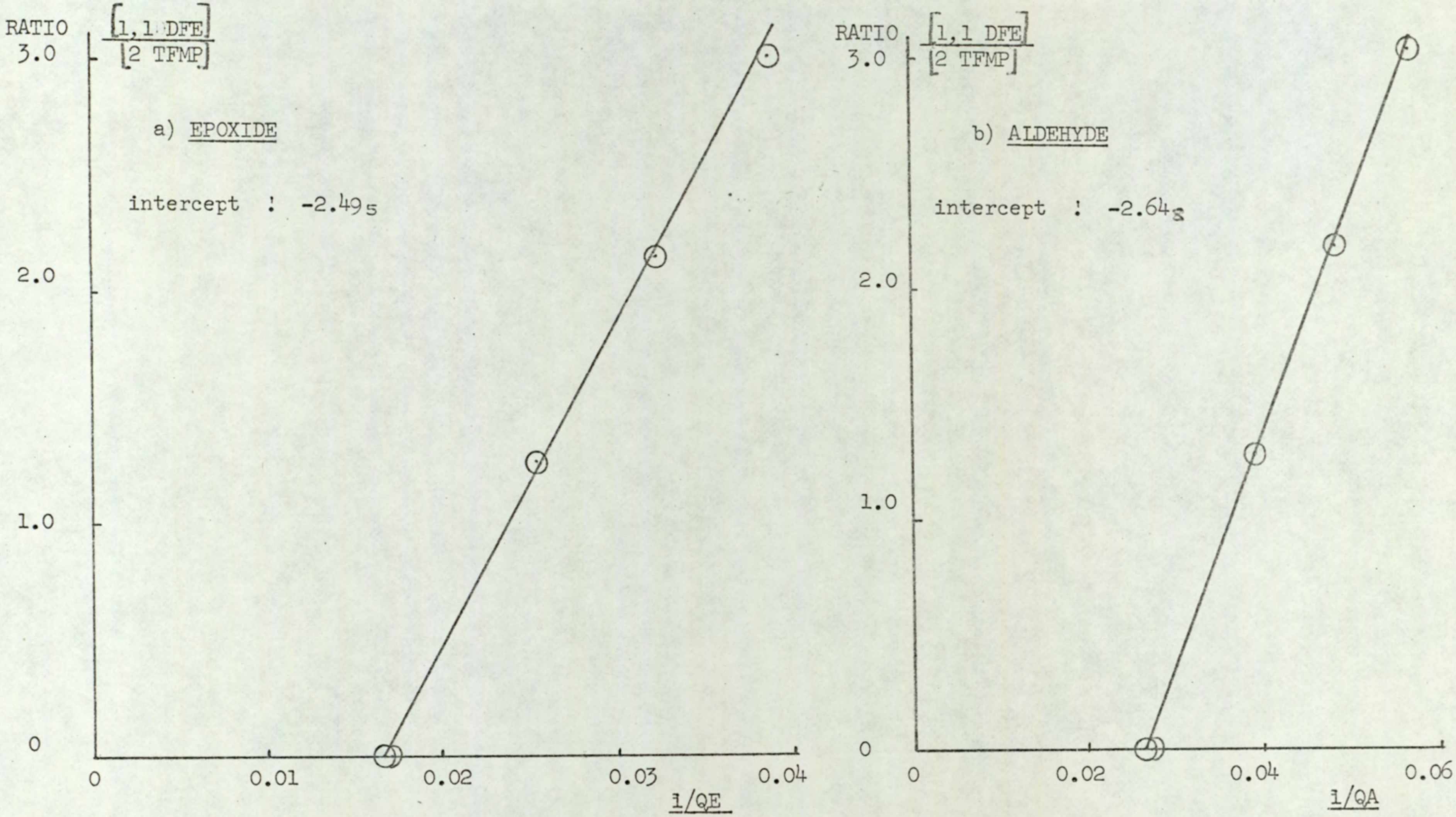


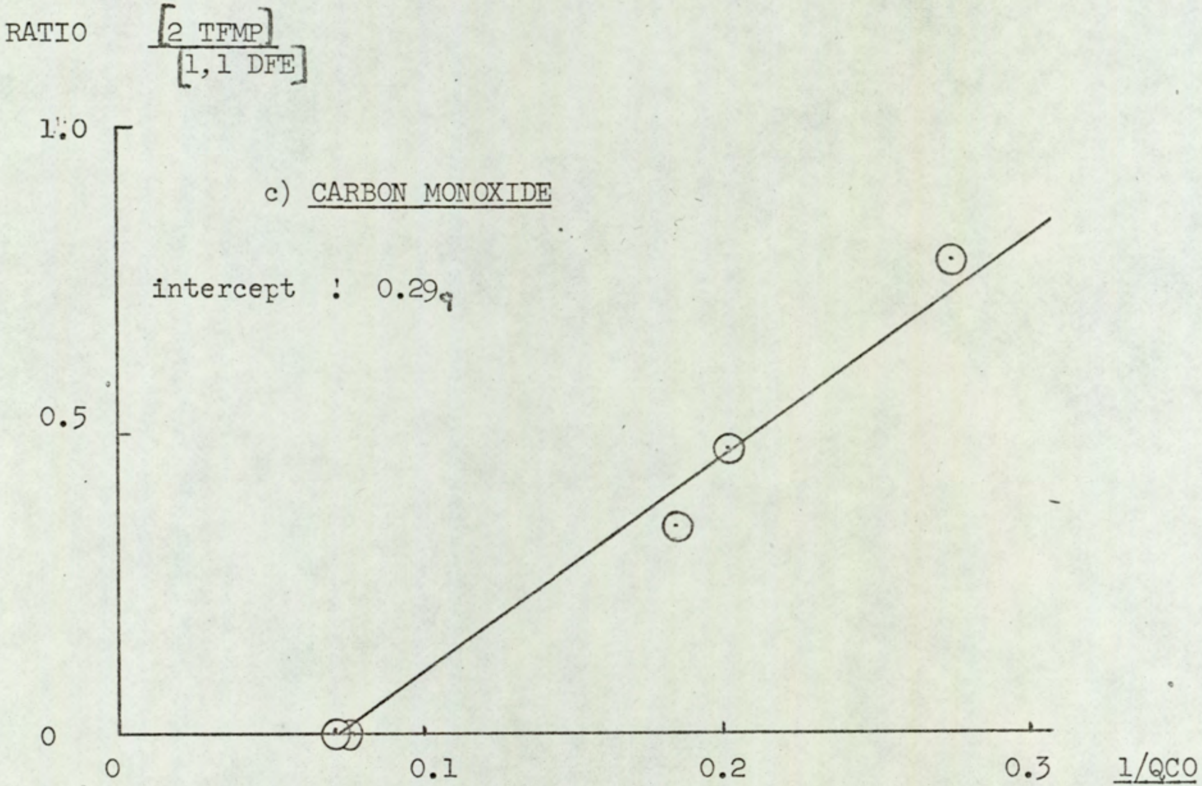
VINYL FLUORIDE vs 2TFMP AT 150°C



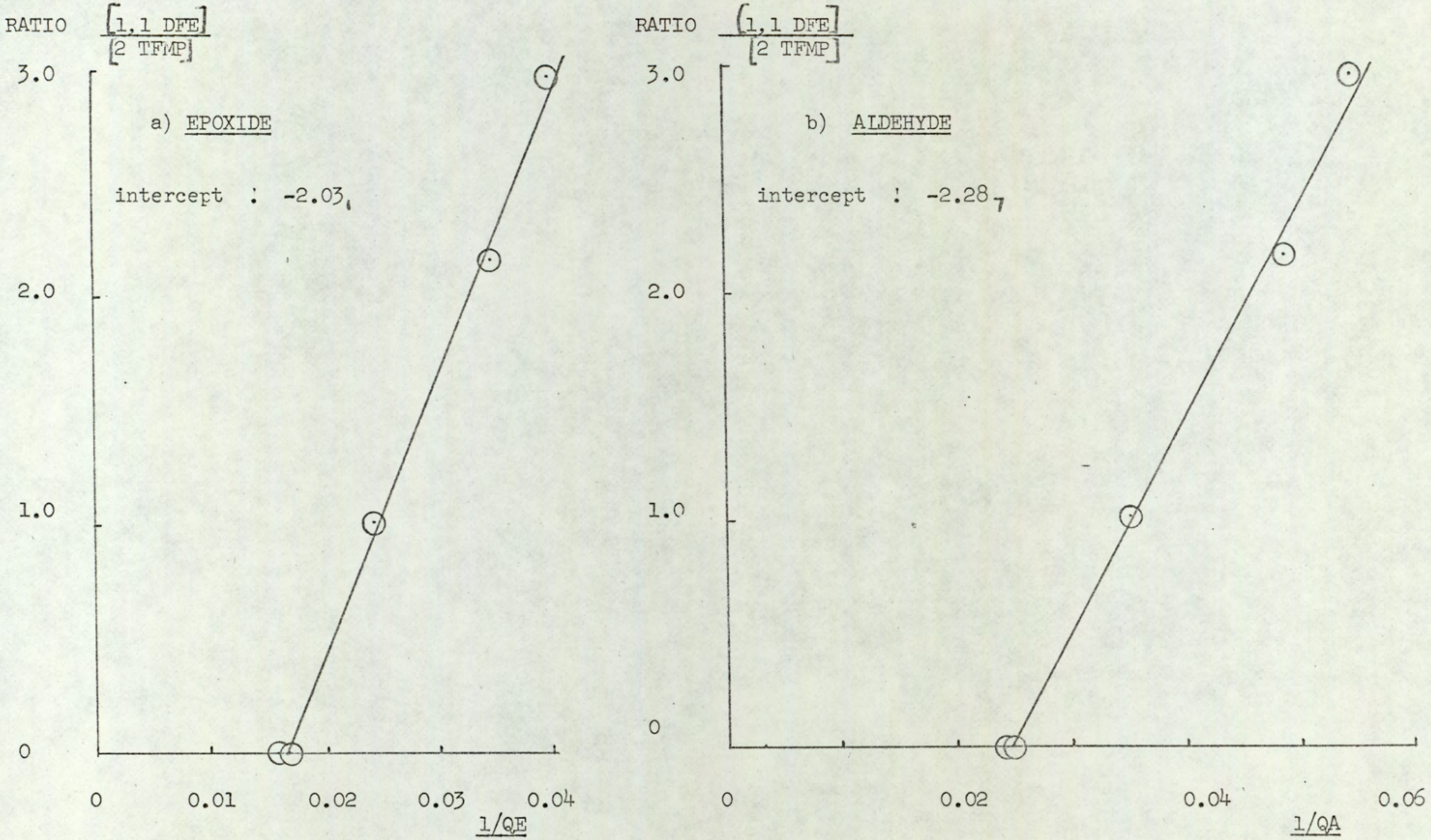
VINYL FLUORIDE vs 2TFMP AT 150°C



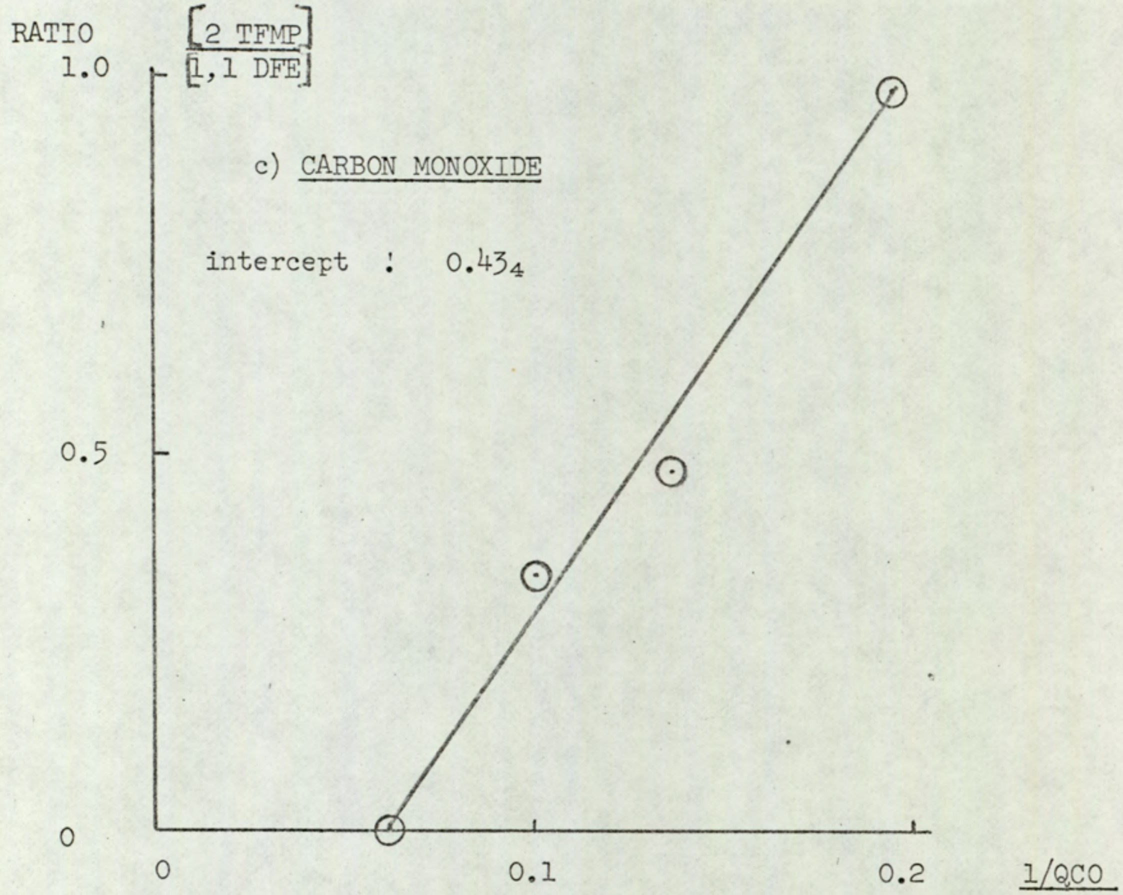
1,1 DIFLUOROETHYLENE vs 2 TFMP AT 25°C



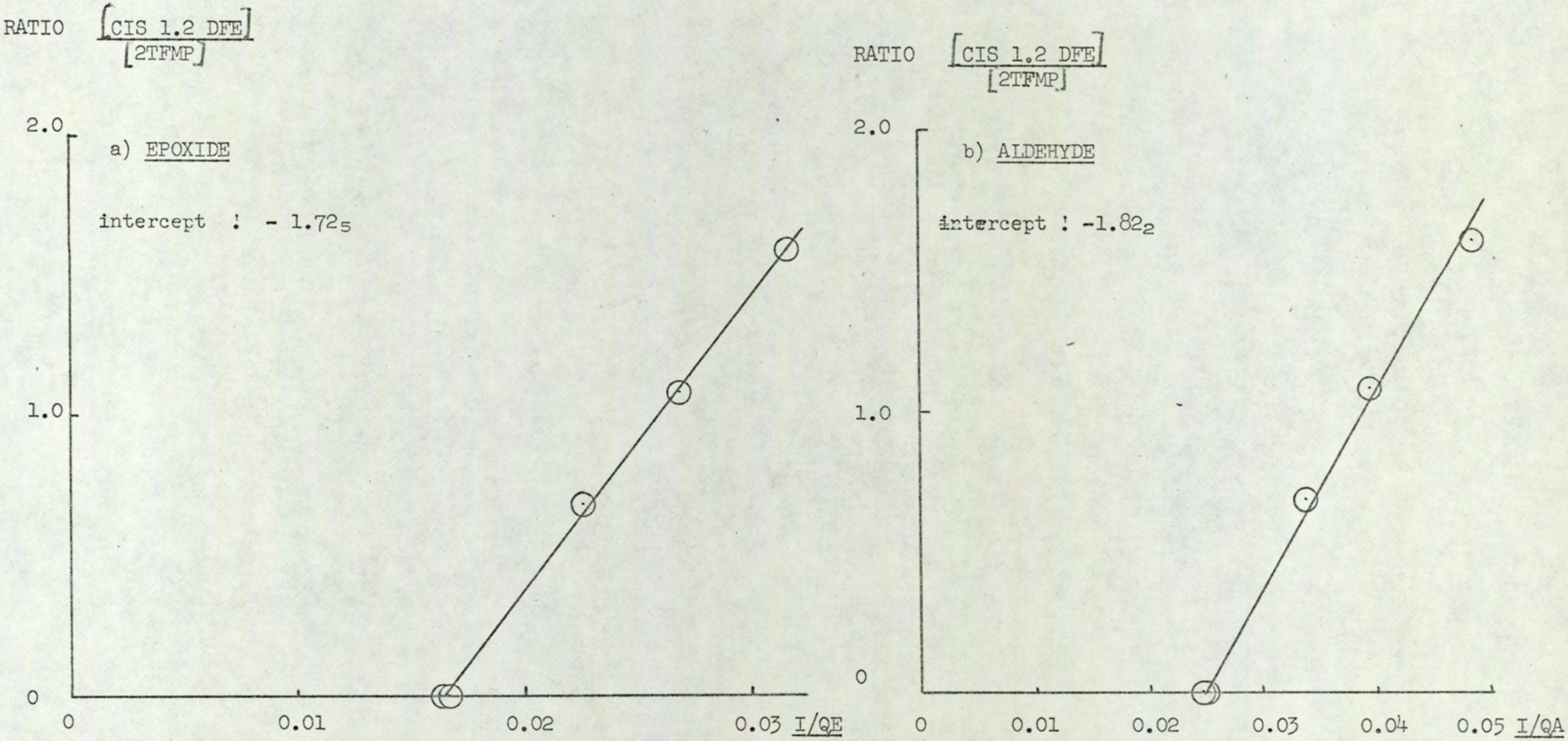
1,1 DIFLUOROETHYLENE vs 2 TFMP AT 25 °C



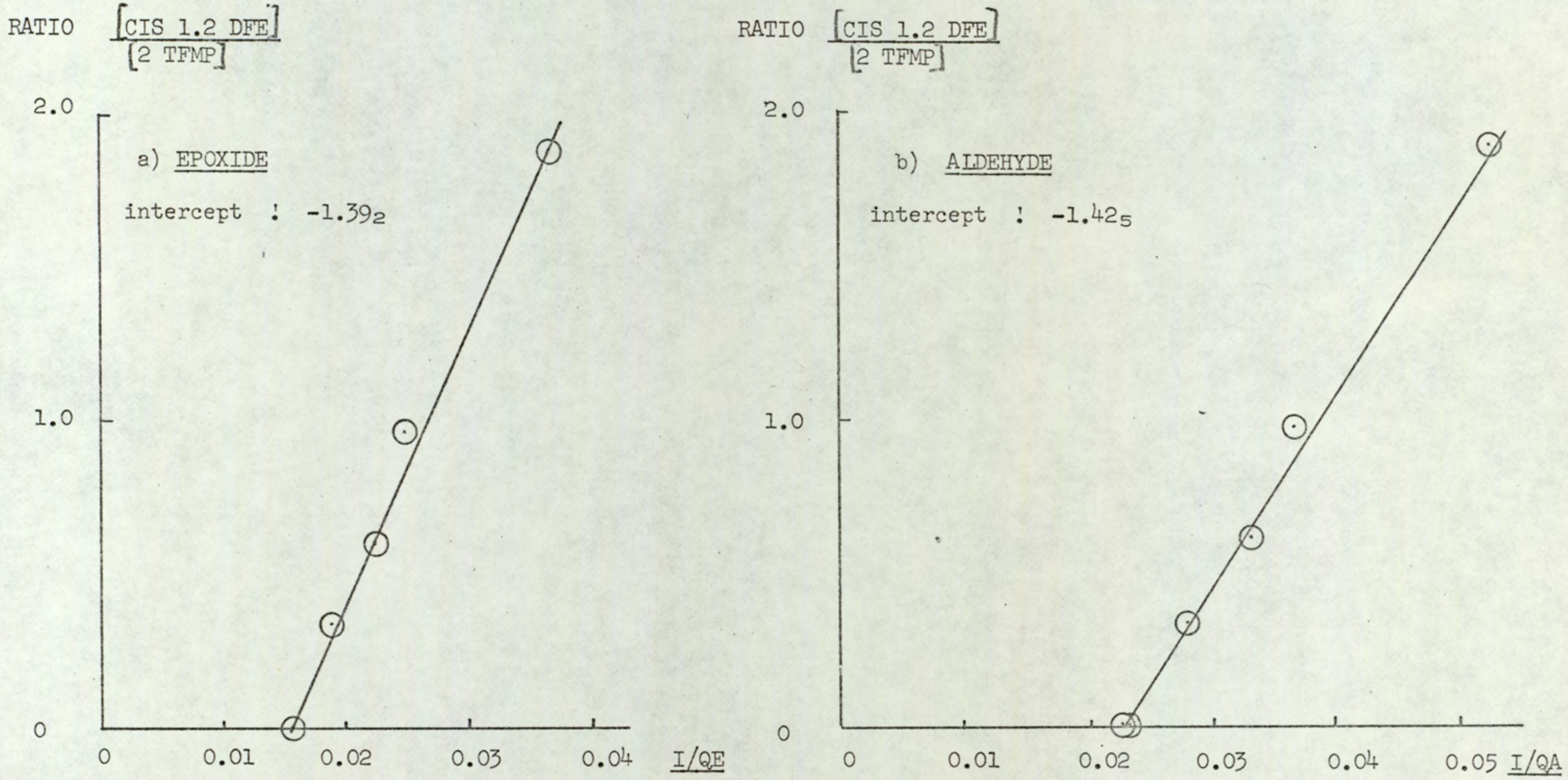
1,1 DIFLUOROETHYLENE vs 2 TFMP AT 150°C



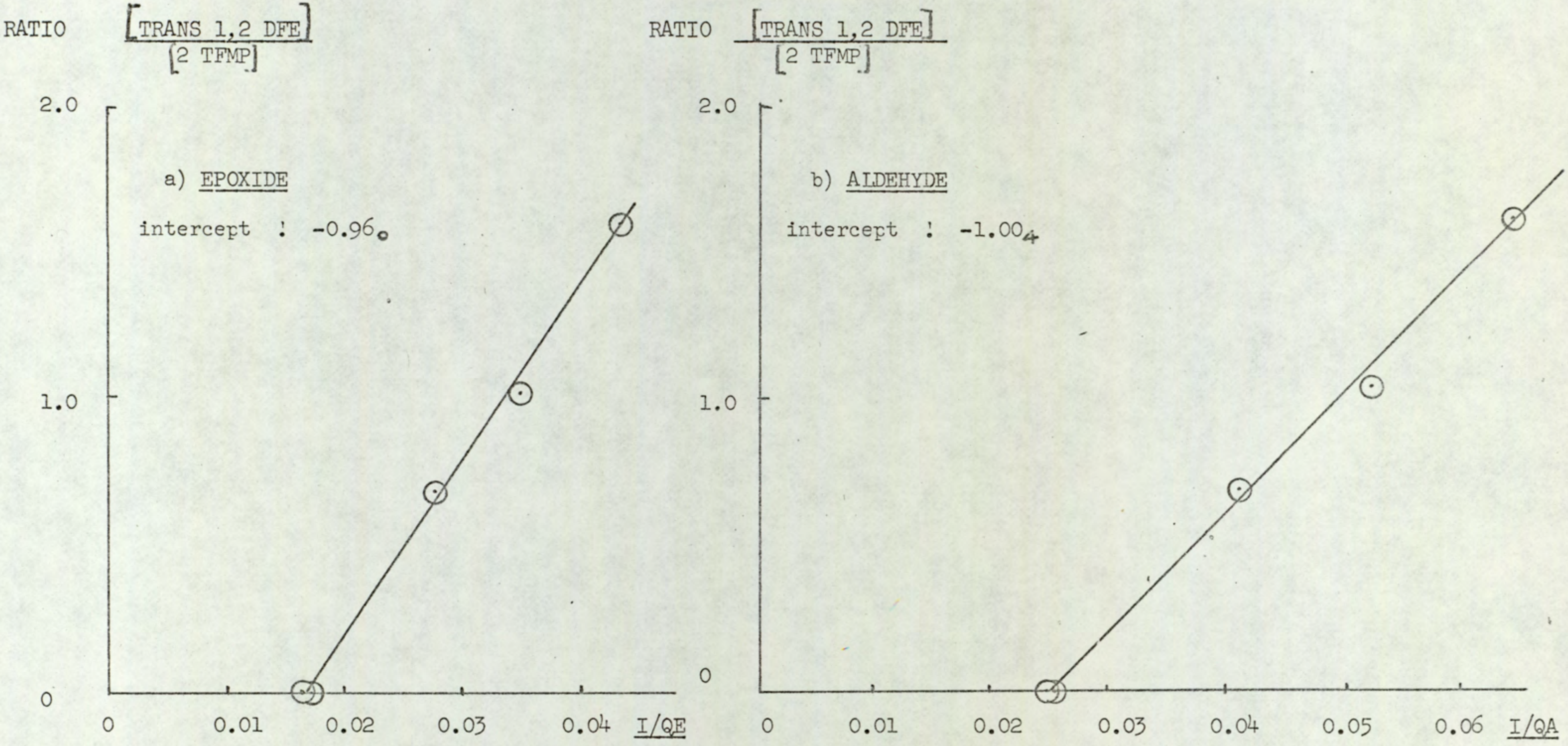
1,1 DIFLUOROETHYLENE vs 2 TFMP AT 150°C



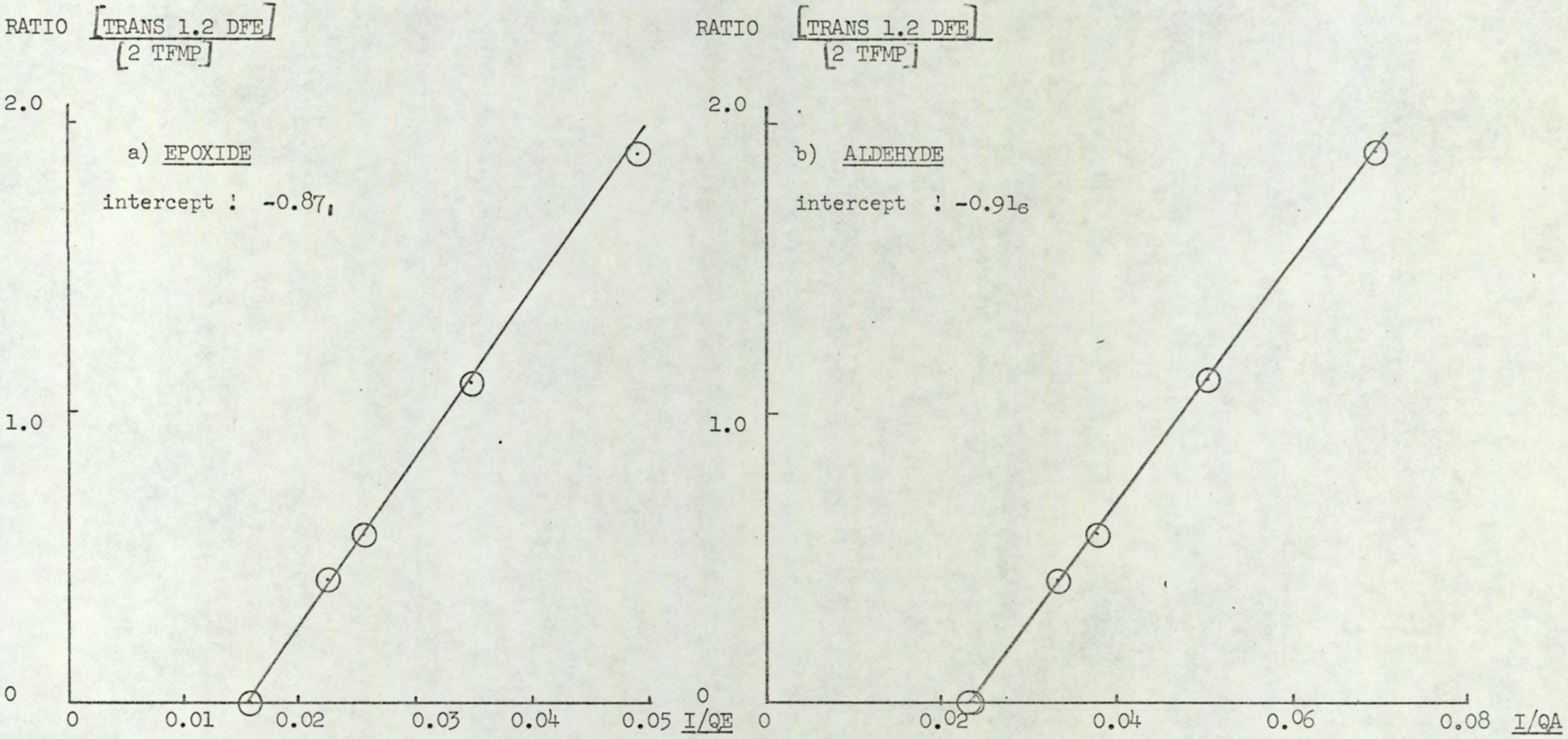
CIS 1.2 DIFLUOROETHYLENE vs 2TFMP AT 25°C



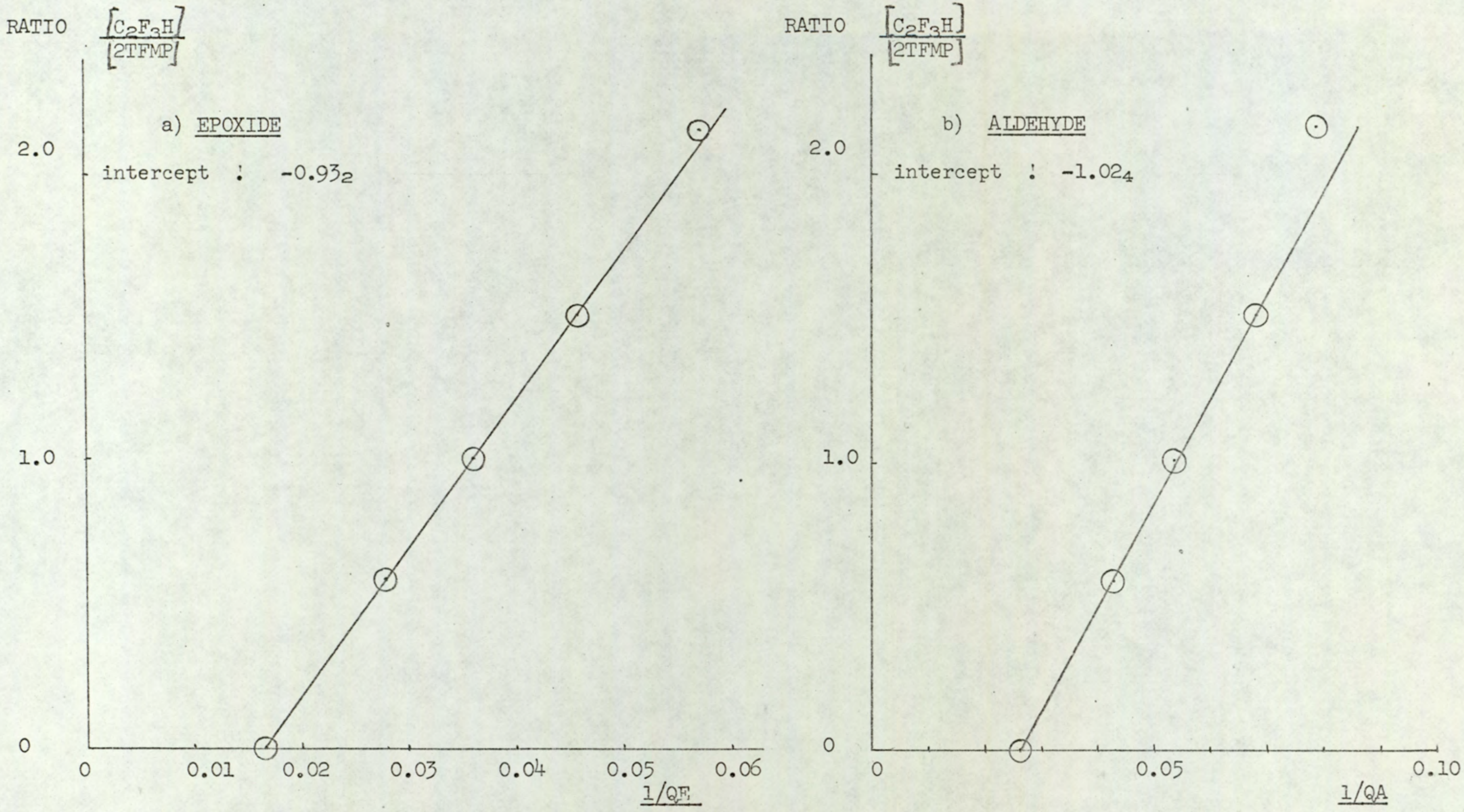
CIS 1.2 DIFLUOROETHYLENE vs 2TFMP AT 150°C



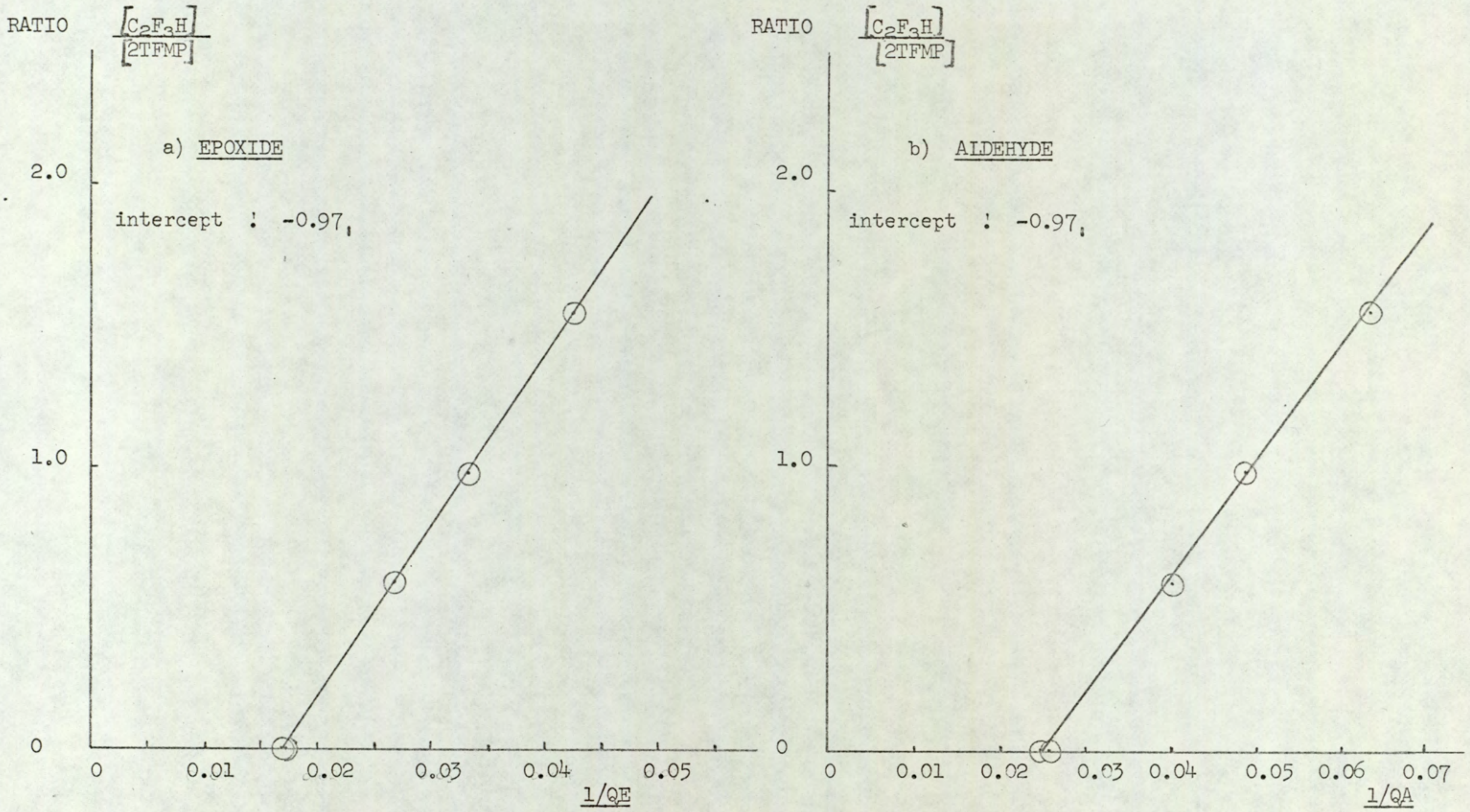
TRANS 1,2 DIFLUOROETHYLENE vs 2TFMP AT 25°C



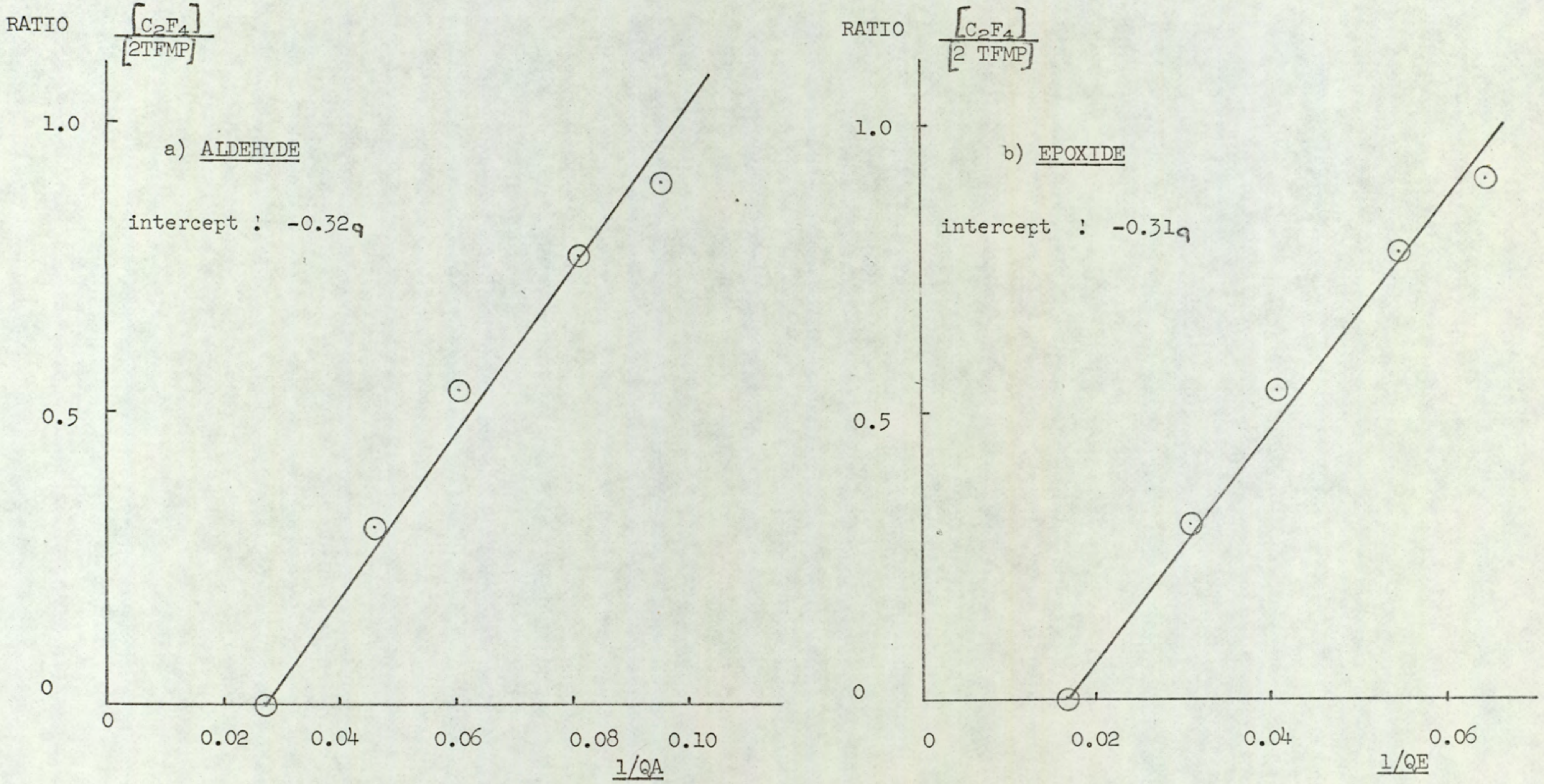
TRANS 1,2 DIFLUOROETHYLENE vs 2 TFMP AT 150°C



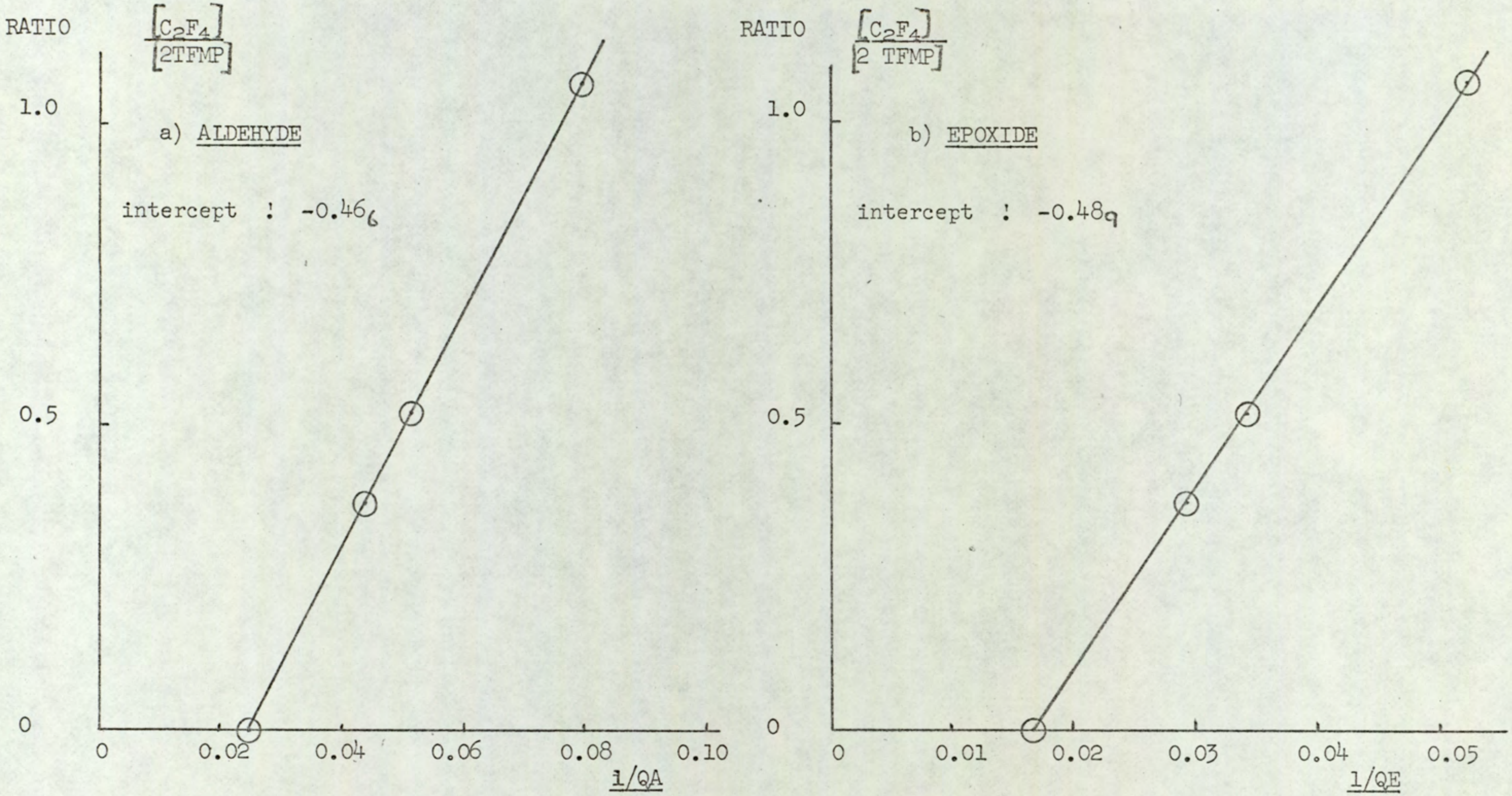
TRIFLUOROETHYLENE vs 2TFMP AT 25°C



TRIFLUOROETHYLENE vs 2TFMP AT 150°C



TETRAFLUOROETHYLENE vs 2TFMP AT 25°C



TETRAFLUOROETHYLENE vs 2 TFMP AT 150°C

CHAPTER FIVE

THERMOCHEMISTRY

5.1 INTRODUCTION

Thermochemistry is possibly one of the most important criteria in determining the feasibility of a reaction. For this reason, the heats of formation of products, reactants and related compounds have been extracted from the literature or estimated and are listed in this chapter for reference purposes. These will be utilised in the discussion section.

Three important and general sources of thermochemical data were

a) Stull,D.R.,Westrum,E.F. and Sinke,G.C.
'The Chemical Thermodynamics of Organic Compounds'
John Wiley and Son, 1st Edition, (1969).

b) Benson,S.W.
'Thermochemical Kinetics'
John Wiley and Son, 1st Edition,(1968)

c) Benson,S.W.
"Additivity Rules for Estimation of Thermochemical Properties."
Chem.Revs., 69, 279, (1969)

A fourth particularly useful source of estimated and experimental values for fluorine-containing compounds and radicals was the review article

d) Heicklen,J.
"Gas Phase Oxidation of Perhalocarbons."
Advances in Photochemistry,Vol.7,pps.57-147,(1969)

It will be realised that due to the degree of experimental error and scarcity of thermochemical information relating to fluorine containing compounds,much of the data in Table 5.1 is subject to some uncertainity. In Table 5.2 (a),(b),(c) and (d) correspond to the references given above,

5.2 METHODS OF ESTIMATING HEATS OF FORMATION

When the heat of formation of a compound has not been reported in the current literature, one or more of the following methods have been used to estimate the value.

1) Method of Group Contributions

A molecular property, such as the heat of formation of a compound, can be estimated by considering the property to be composed of contributions from groups comprising the molecule. A group is defined as a polyvalent atom (ligancy > 2), in a molecule together with all of its ligands. Thus $C-(H)_3(C)$ represents a carbon atom connected to three hydrogen atoms and another carbon atom (ie. a primary methyl group). Each such group contributes to the heat of formation of the whole compound.

Group values for ΔH^o_f contribution are shown below in Table 5.1 for a number of relevant groups. C_d represents dihedral carbon considered as a bivalent unit.

TABLE 5.1

Some Group Contributions to Heats of Formation

Group	ΔH_f^o kJmol.$^{-1}$
$C-(H)_3(C)$	-42
$C-(H)_2(C)_2$	-21
$C-(H)(C)_3$	-8
$C-(C)_4$	+2
$C_d-(H)(C)$	+36
$C-(F)_3(C)$	-662
$C-(F)_2(H)(C)$	-428
$C-(F)(H)_2(C)$	-217
$C-(F)_2(C)_2$	-405
$C-(F)(H)(C)_2$	-203
$C-(F)(C)_3$	-184
$C_d-(F)_2$	-324
$C_d-(F)(H)$	-157
$C_d-(F)(C)$	-130*

Values taken from Ref.(b)

* Estimated by the author.

2) Method of Structural Similarity

The heat of formation of a compound can be established by the following method. We select a compound of similar structure, whose heat of formation is known. We can then add or subtract contributions for groups that are either additional to or absent from the parent molecule.

For example if we wish to estimate the heat of formation of $CH_3CH_2CF=CF$, we can select $CHF=CF_2$, as the parent molecule (heat of formation = $-481 kJmol.^{-1}$) and a contribution for the two extra CH_2 groups in the fluorinated butene.

ie. $\Delta H_f^o (CH_3CH_2CF=CF_2) = -481 + 2 \times (-21)$

$= \underline{-523\ kJmol.^{-1}}$

If the group increment is not known then an alternative method is to assume that the difference in heats of formation of the trifluoroethylene and trifluorobutene is the same as the difference between the heats of formation of ethane and n-butane.

ie. $\Delta H_f^o (CH_3CH_2CF=CF_2) - \Delta H_f^o (CHF=CF_2)$

$= \Delta H_f^o (CH_3CH_2CH_2CH_3) - \Delta H_f^o (CH_3CH_3)$

$\Delta H_f^o (CH_3CH_2CF=CF_2) = -481 + 84 - 125$

$= \underline{-522\ kJmol.^{-1}}$

3) <u>Estimation of Ring Strain</u>

If the heat of formation of the cyclic compound is known then the ring strain can be calculated by subtracting the group contributions from the known heat of formation. Consider as an example, hexafluorocyclopropane.

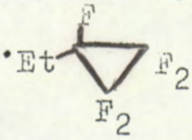
The heat of formation of cyclo C_3F_6 is approximately -940 kJmol.$^{-1}$. Then the ring strain will be

$\Delta H_f^o (\text{cyclo } C_3F_6) - 3 \times \Delta H_f^o (C-(C)_2(F)_2)$

$= -940 - 3 \times (-405)$

$= \underline{+\ 275\ kJmol.^{-1}}$

It has been assumed that all the derivatives of hexafluorocyclopropane have this ring stain

eg. 

has the same ring strain as cyclo C_3F_6.

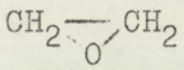
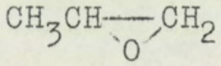
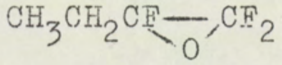
The numbers in the reference column of Table 5.2 correspond to the methods of estimation 1, 2, and 3 mentioned above.

TABLE 5.2

HEATS OF FORMATION OF VARIOUS COMPOUNDS

COMPOUND	ΔH_f^o (kJmol.$^{-1}$)	Reference
Alkanes		
CH_4	-75	a
C_2H_6	-84	a
C_3H_8	-104	a
cyclo C_3H_6	+55	a
CH_3F	-234	a
C_2H_5F	-266	a
$\overbrace{CF_2CF_2CF_2}$	-940	d
$\overbrace{CH_2CH_2CHF}$	-129 (±10)	1 & 3
$CH_3CH_2\underbrace{CF-CF_2-CF_2}$	-782 (±20)	1 & 3
Alkenes		
$CH_2=CH_2$	52	a
$CH_3CH=CH_2$	21	a
$CF_2=CF_2$	-648	b
$CF_2=CFH$	-481	b
$CH_2=CF_2$	-339	b
$CH_2=CHF$	-132	b
$CHF=CHF$	-314	1
$CH_3CF=CF_2$	-496 (±10)	1 & 2
$CH_3CH_2CF=CF_2$	-517 (±10)	1 & 2
$CH_3CH=CHF$(cis and trans)	-163 (±10)	1 & 2
$CF_3CF=CF_2$	-1110	a

TABLE 5.2 (cont.)

COMPOUND	H_f^o (kJmol.$^{-1}$)	Reference
Oxygen-containing compounds		
CF_2O	-640	a
$CHFO$	-403 (±20)	2 (three parents)
CH_2O	-117	a
CH_3CHO (g)	-167	a
C_2H_5OH (g)	-234	a
CH_3COF (g)	-439	a
CF_3OF	-758	d
CH_3CH_2COF (g)	-460 (±12)	2
 $\underbrace{CH_2-CH_2}_{O}$	-53	a
 $CH_3\underbrace{CH-CH_2}_{O}$	-105	a
 $CH_3CH_2\underbrace{CF-CF_2}_{O}$	-643 (±20)	1 & 3
Free Radicals		
Biradicals		
O:	+248	b
CF_2:	-163	d
CH_2:	+368	c
CHF:	+34 (±10)	
CF_3CF	-460	d
CH_3CH_2CF:	-18 (±10)	2 (two parent
Radicals		
$CH_3^{\cdot}$	+142 (±4)	c
$CF_3^{\cdot}$	-472 (±17)	d
$C_2H_5^{\cdot}$	+109 (±4)	c
$CF_2=CF^{\cdot}$	-217 (±10)	d
$CFO^{\cdot}$	+226 (±30)	d
$C_2H_5O_2^{\cdot}$	-8	b
$CH_3CH-CF=CF_2$	-375	2
$CF_3O^{\cdot}$	-640 (±25)	d
$^{\cdot}CH_2CF=CF_2$	-354 (±20)	2

5.3 BOND DISSOCIATION ENERGIES

A reference table of bond dissociation energies is shown below for some relevant molecules.[106,107,108]

TABLE 5.3

Bond Dissociation Energies

Carbon-Carbon Bonds	Bond Energy ($kJmol^{-1}$)
CH_3-CH_3	368
C_2H_5-CH_3	358
CF_3-CF_3	389
CH_2=CH_2	699
CH_2=CHF	523
CH_2=CF_2	552
CHF=CHF	414
CHF=CF_2	360
CF_2=CF_2	314
Bonds to Fluorine Atoms	
CH_3-F	452
C_2H_5-F	444
CF_3-F	519
Miscellaneous	
N_2-O	163
CH_3-H	435
CF_3-H	444

These bond dissociation energies are utilised in the discussion section.

CHAPTER SIX

DISCUSSION OF $O(^3P)$ + FLUOROETHYLENE RESULTS

6.1 GENERAL DISCUSSION

Reproduced as Table 6.1 is a summary of the results reported in sections 4.4. and 4.5.

TABLE 6.1

Summary of Rate Constants and Arrhenius Parameters of $O(^3P)$ + Fluoroethylene.

OLEFIN	k(23°C)	k(150°C)	$A/A_{C_2H_4}$	$E-E_{C_2H_4}$ kJmol^{-1}
C_2H_4	(1,0)	(1.0)	(1.0)	(0)
$CH_2=CHF$	0.40	0.52	1.04(±0.2)	2.43
$CH_2=CF_2$	0.22	0.30	0.72(±0.2)	3.01
cis CHF=CHF	0.31	0.45	1.26(±0.2)	3.51
trans CHF=CHF	0.56	0.71	1.43(±0.2)	2.38
$CHF=CF_2$	0.57	0.66	1.08(±0.2)	1.63
$CF_2=CF_2$	1.70	1.33	0.88(±0.2)	-1.55

Moss and Jennings[55] have previously determined the relative rate constant for 2 trifluoromethylpropene against butene-1 as 0.077. Cvetanovic[23] has found that the rate constant for butene-1 against ethylene is 5.8 and hence the relative rate constant for ethylene against 2 trifluoromethylpropene should be 2.2. The directly measured value from this work was found to be 1.81 which is in satisfactory agreement.

The only rate constant measured by other workers in the fluoroethylene series is tetrafluoroethylene. Heicklen[46] determined the rate constant for C_2F_4

relative to ethylene and obtained a value of 1.1(±0.1) measuring the yield of CF_2O by I.R. spectroscopy. Tyerman[109] also in a competitive study, measured the rate for C_2F_4 relative to C_2H_4 by following the CF_2 formed using UV spectroscopy. He obtained a value of 1.05(±0.5). From the results of this work and that of Moss[56] the results obtained were 1.70 and 1.60(±0.1) respectively. It is difficult to explain the apparent discrepancy which lies outside the experimental errors associated with the various methods used. Carefully purified batches of the olefins were used for the determination. Additionally, it is unlikely that interference by cross products from the mixed system are responsible for the discrepancies as G.L.C. determination would tend to give a lower relative reactivity.

It would appear that, in general, the relative reactivites of the fluoroethylenes with $O(^3P)$ are governed primarily by activation energy differences. With the exception of 1,1 difluoroethylene and the cis and trans isomers of 1,2 difluoroethylene, the 'A' factors relative to ethylene are unity within experimental error.

1,1 difluoroethylene displays a relatively low 'A' factor (0.72) whereas cis and trans 1,2 difluoroethylene appear to have high 'A' factors (1.26 and 1.43 respectively). As a result of the approximate constancy of 'A' factors the rates of the reactions are paralleled by the order of the activation energy differences. It should be noticed however that the order is reversed for 1,1 difluoroethylene and cis 1,2 difluoroethylene. This is due to the large difference in relative 'A' factors (about 0.5) for the two compounds. The general observation of constant 'A' factors has similarly been noted by Cvetanović[23] for the reaction of oxygen atoms with non-fluorinated olefins. (see Table 1.7)

The arguments put forward by. Moss and Jennings[54,55] to explain the reactivity differences of various fluorinated butenes and propylenes can be applied to the fluoroethylene system. The reasoning has been described in detail in section 1.5d. Briefly, it is suggested that fluorination initially decreases the reactivity by the $-I_\pi$ effect, withdrawing electrons from the system. However further fluorination can increase the π electron density of the system by $+I_\pi$ and + M effects, leading to an increase in reactivity. This, of course, assumes that reactivities are associated with electron density(formation of a π complex being the rate determining step.) One might argue that the above reasoning would necessarily imply that the π electron density initially decreases to a minimum for 1,1 difluoroethylene and then increases progressively with further fluorination. This is not reflected by the trend of ionisation potentials for the fluoroethylene which decreases regularly with increasing fluorination.[73]

In sections 6.2 - 6.5 an attempt is made to relate the order of relative reactivities to various properties of the individual flouroethylenes.

6.2 CORRELATION OF RATES WITH CALCULATED PHYSICAL PROPERTIES OF THE FLUOROETHYLENES

Useful information about the nature of the transition state is often gained by relating rates of radical reactions to physical properties of the reacting molecules. The physical properties of an olefin can be roughly divided into two classes.

1) Properties associated with individual atoms in the molecule. These include charge density at the atom in question, atom localisation energy and maximum free valence.

2) Properties associated with the molecule as a whole. These include ionisation potential, excitation energy and π bond order.

If the rates correlate well with atomic parameters the reaction generally proceeds through a σ complex located at the top of the potential energy pass. On the other hand, if the rates are related to double bond properties (the second class mentioned above), then it is likely that a π complex lies at the top of the potential energy curve. Cvetanović[14] has successfully correlated the oxygen atom reactions with bond properties of the olefins, strongly suggesting the formation of a π complex at a rate determining stage of the reaction.

Calculation of the physical parameters can be very tedious even for relatively simple molecules. The introduction of a fluorine (or any hetero atom) can complicate the problem still further. However, Kilcoyne[68] has calculated a number of useful parameters using Hückel theory. The results obtained must be accepted as extremely approximate. They are shown in Table 6.2

TABLE 6.2

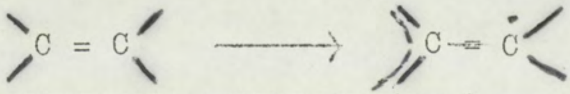
Parameters calculated by M.O. Theory for the Fluoroethylenes

Molecule	Charge Density		Atom Localisation Energy		Maximum Free Valence		Excit. Energy	bond order
1 2	q_1	q_2	L_1	L_2	F_1	F_2	$\in$	P_{12}
$CH_2=CH_2$	1.000	1.000	2.200	2.200	0.732	0.732	2.200	1.00
$CHF=CH_2$	1.093	0.934	2.629	2.159	0.591	0.742	2.134	0.983
$CF_2=CH_2$	1.179	0.872	3.077	2.121	0.478	0.770	2.076	0.962
cis & trans $CHF=CHF$	1.031	1.031	2.578	2.578	0.590	0.590	2.062	0.969
$CF_2=CHF$	1.121	0.972	3.018	2.533	0.461	0.594	2.000	0.951
$CF_2=CF_2$	1.065	1.065	2.966	2.966	0.449	0.449	1.926	0.935

A brief explanation of each of the parameters is useful.

a) Atom Localisation Energy (L_μ)

is the energy required to localise a π electron completely on carbon atom μ of the double bond. This can be visualised as the process



b) Maximum Free Valence (F_μ)

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

c) Excitation Energy ($\in$)

Ideally the excitation energy should be the difference in energy of the ground state olefin molecule and the lowest excitated triplet state. If calculated by Hückel theory, it is the difference in energy of ground state and the average of lowest excitated triplet and singlet states. This is because Hückel theory does not take into account electron spin.

d) Bond Order ($P_{\mu\nu}$)

is a measure of the π electron density in the bond between carbon atoms μ and ν (ie. a measure of the π charge in the bond between the two atoms.)

An attempt to correlate the rates of oxygen reactions with the various parameters listed in Table 6.2 has proved reasonably successful. The results are illustrated in graphical form in Figs.6.1 to 6.8.

For each of the parameters, charge density, localisation energy, maximum free valence, π bond order and excitation energy, it is possible only to correlate those olefins with a common terminal group(ie. those olefins with CF_2,CHF and CH_2 groups considered as three separate series of olefins.) The atomic parameters are considered for more and less substituted carbons. Necessarily, the variation of rates with these parameters must be opposite for the two ends of the molecule. This is because the atomic properties of the two carbons of the fluoroethylene are complementary eg. as localisation energy at the less substituted carbon decreases, the energy at the opposite end increases.

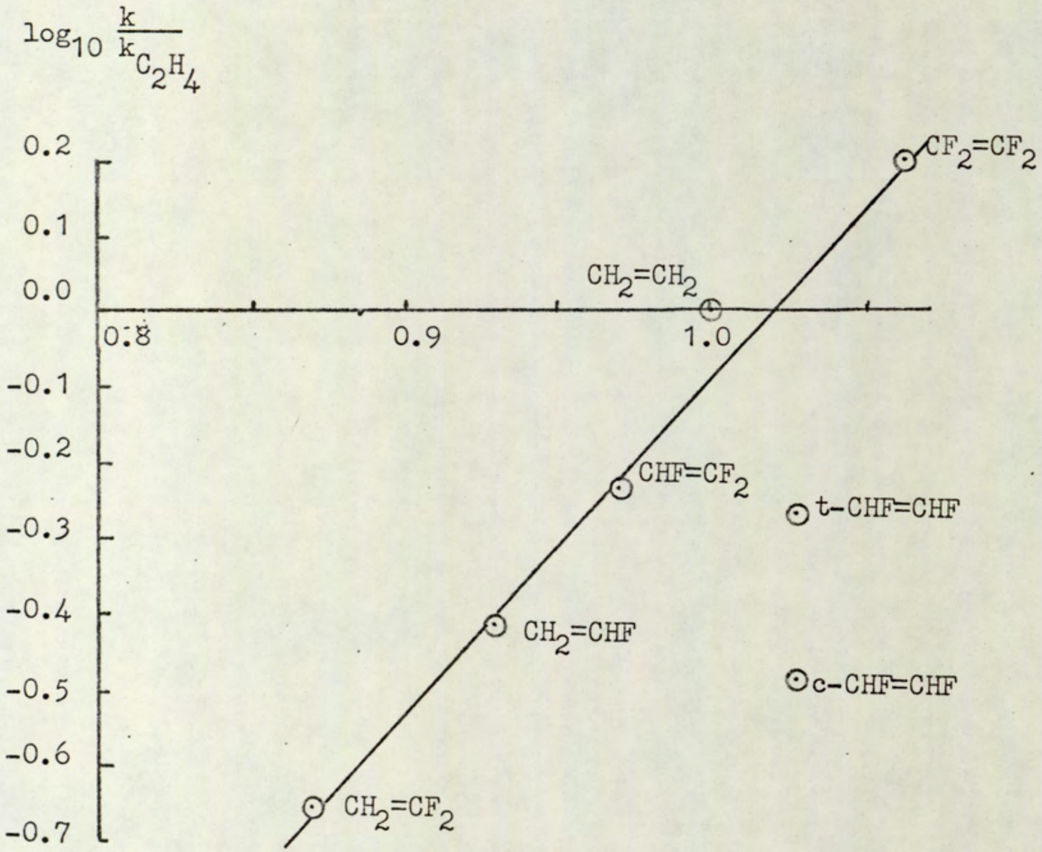


FIG. 6.1 LESS SUBSTITUTED CARBON

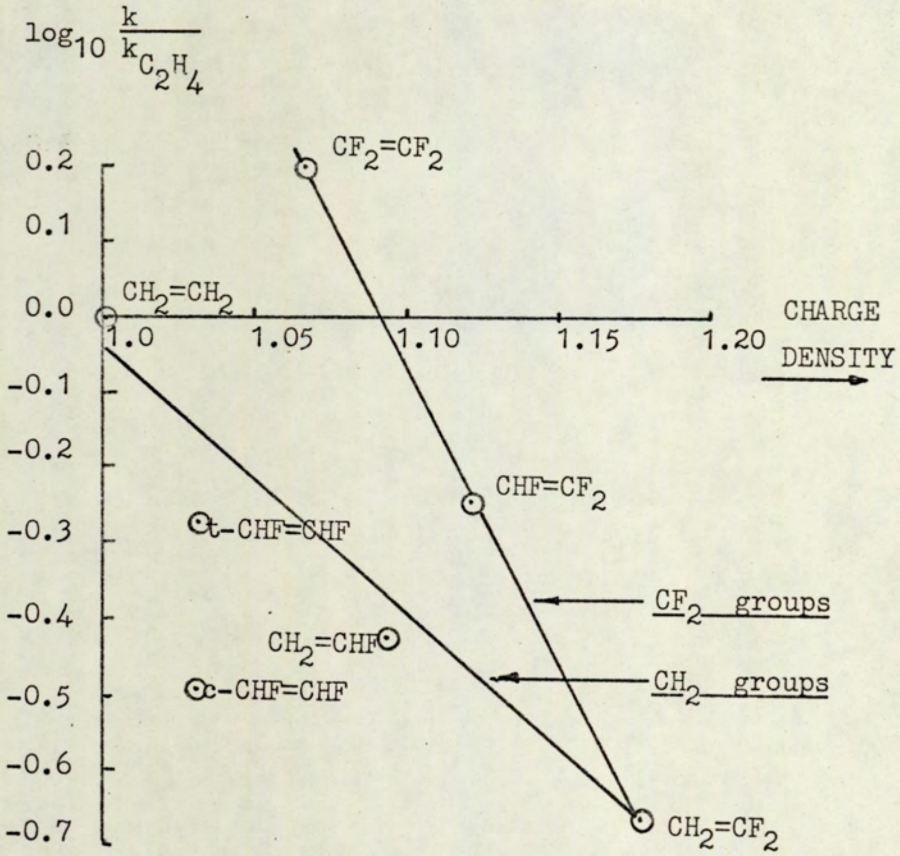


FIG. 6.2 MORE SUBSTITUTED CARBON

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

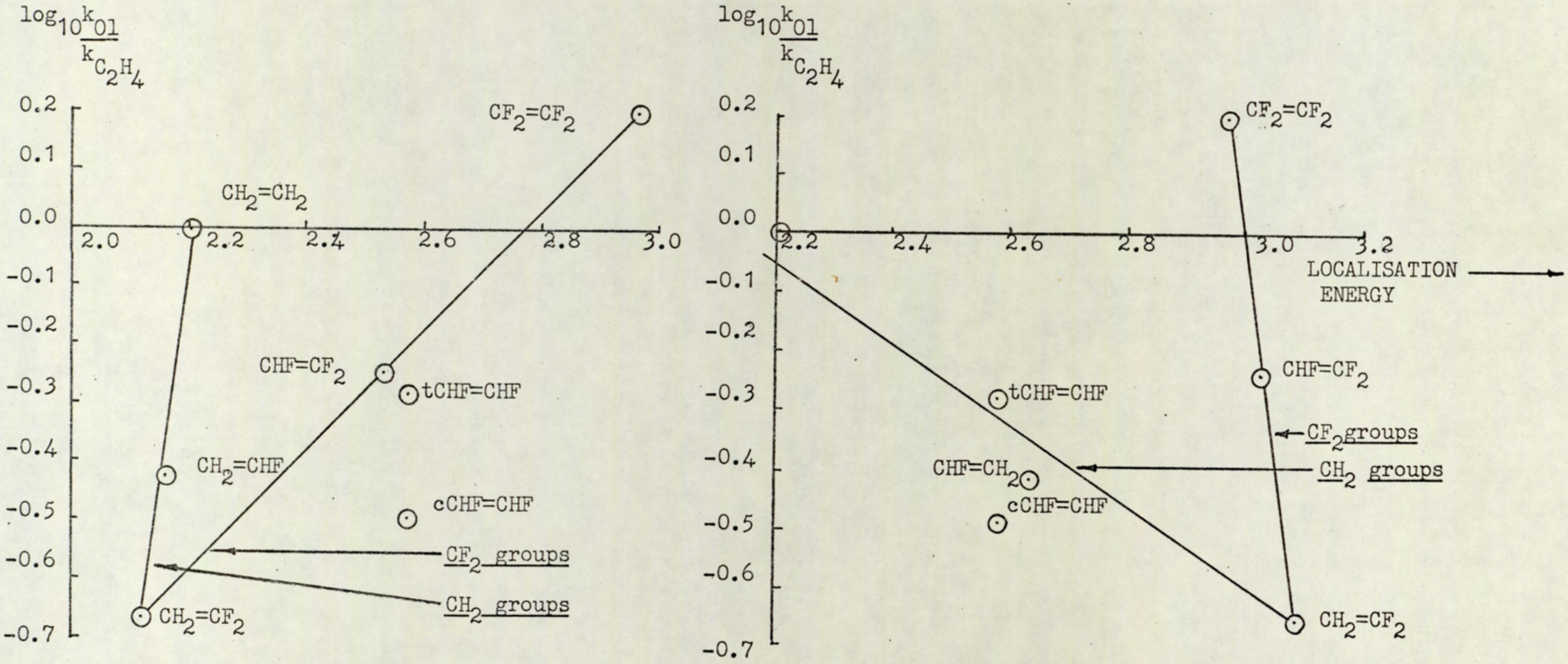


FIG. 6.3 LESS SUBSTITUTED CARBON

FIG. 6.4 MORE SUBSTITUTED CARBON

PLOTS OF $\log_{10} k$ AGAINST LOCALISATION ENERGY

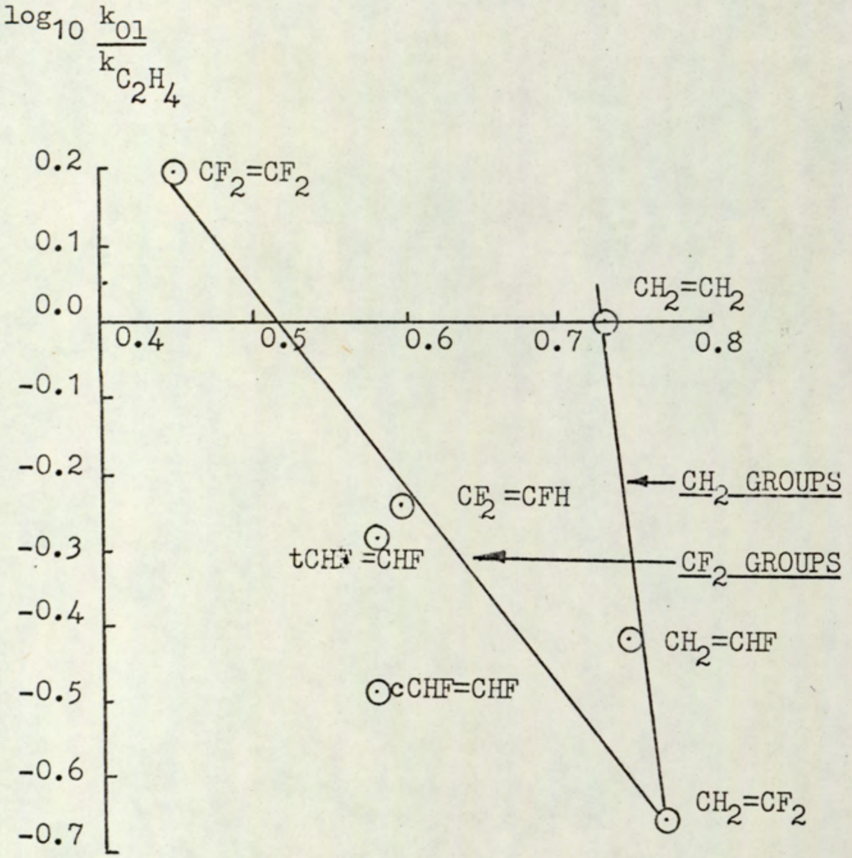


FIG. 6.5 LESS SUBSTITUTED CARBON

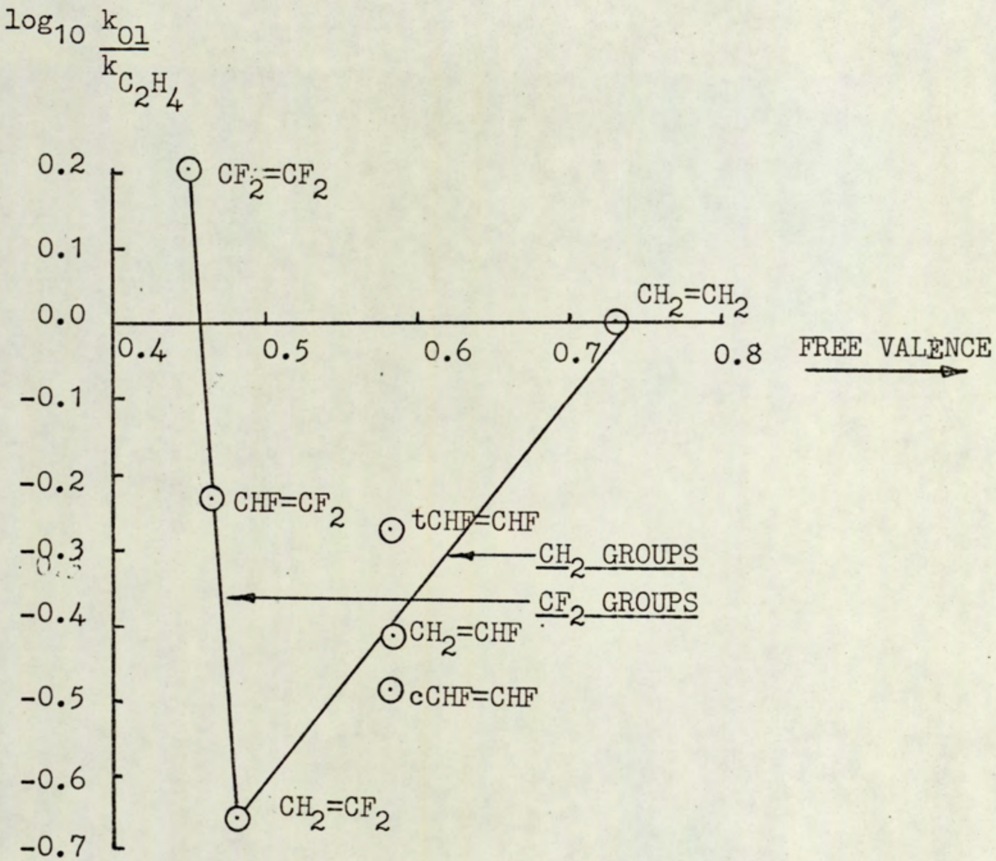


FIG. 6.6 MORE SUBSTITUTED CARBON

PLOTS OF $\log_{10} k$ AGAINST MAXIMUM FREE VALENCE

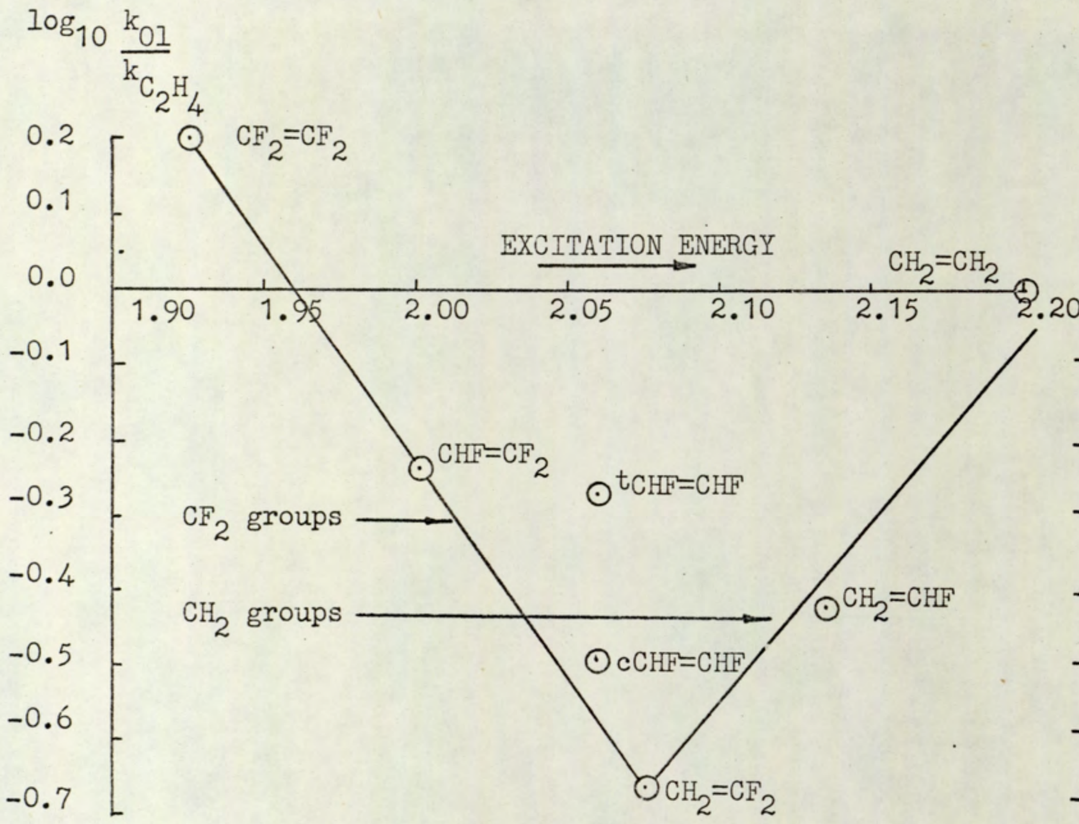


FIG. 6.7 $\log_{10} k$ vs. EXCITATION ENERGY

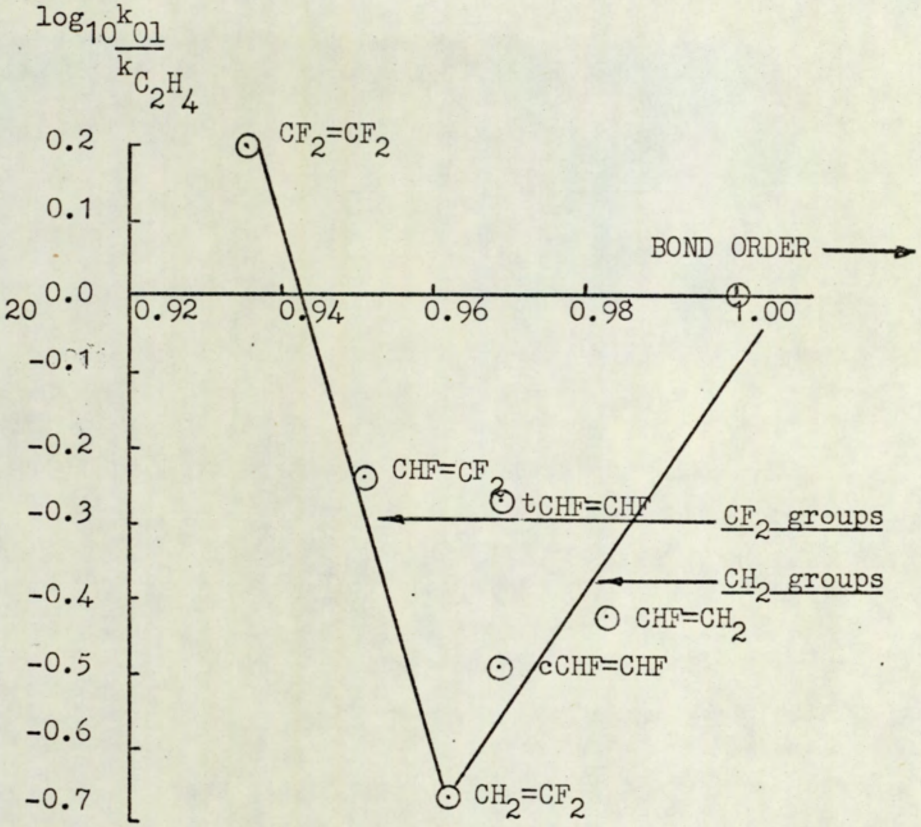


FIG. 6.8 $\log_{10} k$ vs. BOND ORDER

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

6.3 COMPARISONS BETWEEN OXYGEN ATOMS AND OTHER RADICAL SPECIES

In Table 6.3, the rates of reaction of $O(^3P)$ with the fluoroethylenes are compared with rates for other radical species.

TABLE 6.3

Relative Reactivities of Fluoroethylenes with Atoms and Radicals.

	$O(^3P)$	$O(^3P)$	$O(^3P)$	$S(^3P)$	CCl_3		CF_3	CH_2	Hg (^3P)	I.P.
	25°	150°	25°	20°	25°	164°	164°	25°	25°	(eV)
$CH_2=CH_2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	10.66
$CH_2=CHF$	0.41	0.52	0.38	0.42	0.68	0.71	0.47	0.60	0.79	10.45
$CH_2=CF_2$	0.22	0.30	0.22	0.10	0.12	0.25	.47	0.33	0.62	10.45
c.CHF=CHF	0.31	0.45	0.32							
t.CHF=CHF	0.56	0.71	0.54							
$CHF=CF_2$	0.57	0.66	0.57	0.07	0.05	0.27		0.16	0.41	10.33
$CF_2=CF_2$	1.70	1.33	1.60	0.09	0.23	1.21	0.12	0.10	0.21	10.12
Reference	This work		56	66	67	67	70	71	72	73

It can be seen that electrophilic species such as $S(^3P)$, CF_3 and $Hg(^3P_1)$ do not show the same trends in reactivity as are exhibited by oxygen atom reactions. As pointed out previously the rates of oxygen atom reactions (at both temperatures) fall with increasing fluorination to a minimum for 1,1 difluoroethylene; further fluorination then increases the rate for the olefin. In marked contrast, the rates of the other electrophilic species mentioned above, progressivly decrease with increasing fluorination.

A useful procedure when searching for a correlation between rates of different radical species is to plot the logarithm of the rates against each other.

This is called a free energy plot. The theory of the procedure has previously been described in section 1.4. A good free energy plot often suggests that the reactions proceed through a similar transition complex. A detailed analysis of log-log plots for the species listed in Table 6.3 yielded the following information.

a) A good correlation between rates of methylene and Hg($^3P_1$) with the fluoroethylenes.

b) An approximate correlation of the CF_3 and CCl_3 reactions.

c) No correlation of oxygen atoms rates with other radical species.

It would appear that methylene and Hg($^3P_1$) reactions are in some way related. It is also possible that CCl_3 and CF_3 reactions are related. Indeed Tedder and Walton[117] have pointed out that the reactions of CCl_3, CF_3 and C_3F_7 with the fluoroethylenes follow the same trends.

Unfortunately the free energy plots do not reveal any useful information on the mechanism of the oxygen atom reactions. It has been noticed, however, that methylene and Hg($^3P_1$) reactions relate well with bond properties of the fluoroethylenes. Plots of excitation energy and bond order against the logarithm of the rate constants for the two reactions reveal a linear relationship. A similar correlation has been noted for ionisation potential with the rate constants.

6.4 GENERAL CONCLUSIONS

Although there seems to exist a relationship of both bond and atomic properties with the oxygen rate constants (section 6.2) the evidence presented above points more towards a σ than a π transition state. The arguments against a π complex are as follows:-

1) As mercury and methylene reactions correlate well with π bond order, excitation energy and ionisation potential there is every reason to believe the reaction proceeds through a π transition state. However, the complete lack of correlation in the free energy plots of these two species with oxygen atom reactions, would tend to suggest that the transition states are different, especially when one considers that triplet mercury atoms behave as an electrophilic species[13].

2) Even though Figs. 6.7 and 6.8 do show a correlation between bond properties and rate constants of fluoroethylenes with a common reaction centre, this relationship is probably fortuitous. The idea of a reaction proceeding through a π transition state (ie. rate associated with the double bond properties) and yet at the same time being influenced by the nature of the group at one end of the double bond (rate associated with atom properties) seems rather unlikely. Conceivably this might suggest an intermediate transition state, but it is also unlikely that the π and σ character could be separated by the method mentioned above.

Evidence for a σ transition state seems somewhat stronger.

1) The good correlation of charge densities, atom localisation energies and maximum free valence with rate constants can be incorporated into a general theory of a σ transition state.

2) The idea of dividing the fluoroethylenes into separate categories with common reaction sites simplifies the correlation considerably. The idea of separate reaction sites also is in keeping with reaction taking place at a particular carbon, and not with the double bond. This method has been usefully employed by Kilcoyne[68] to relate hydrogen atom reactions with fluoroethylenes to a σ transition state. At this point it is necessary to formulate a more concrete theory in keeping with the observed correlations.

If the oxygen atom reactions are influenced by similar factors to the reaction of alkyl radicals with olefins, then one of the major considerations is the stability of the radical formed. Cvetanović[123] has pointed out that the carbon with the higher free valence is most likely to determine the initial position of attack in σ transition state reactions Examination of Table 6.2 reveals that the less substituted carbon has the higher free valence and hence is more susceptible to attack by the oxygen atoms. However it must be noted that the rates of the oxygen atom reactions are not related to the maximum free valence of this carbon atom (rates increasing with decreasing free valence as is seen from Fig.6.5).

Careful examination of Fig.6.4 reveals that the expected correlation does exist between the localisation energy at the more substituted carbon and the rates of the oxygen atom reactions (rate decreasing with increasing localisation energy). Any different interpretation (eg. attack at the more substituted carbon) gives the opposite correlation to that expected with free valence and localisation energies. The following conclusions have therefore been drawn.

1) the position of initial attack is dictated by the free valence of the respective carbon atoms in the fluoroethylene molecule ie. attack at the <u>less</u> substituted end.

2) the rates of reaction appear to be related to the localisation energy (energy to localise a electron) at the more substituted carbon.

3) the rates of the oxygen atom reactions with the fluoroethylenes are best correlated by considering those olefins with a <u>common reactive centre</u>, rather than by considering progressive fluorination of ethylene.

Cvetanović[23] has proposed a tentative potential energy diagram for the reaction between oxygen atoms and hydrocarbon olefins. This is shown in Fig. 6.9. He visualises the activation energy ΔE as being the result of initial electrostatic repulsion between the electron rich oxygen radical and double bond of the olefin. At C a state is reached where electrostatic repulsion is balanced by the charge tranfer process, electrons being donated by the double bond to the oxygen atom to give a loose π complex. A is presumably a

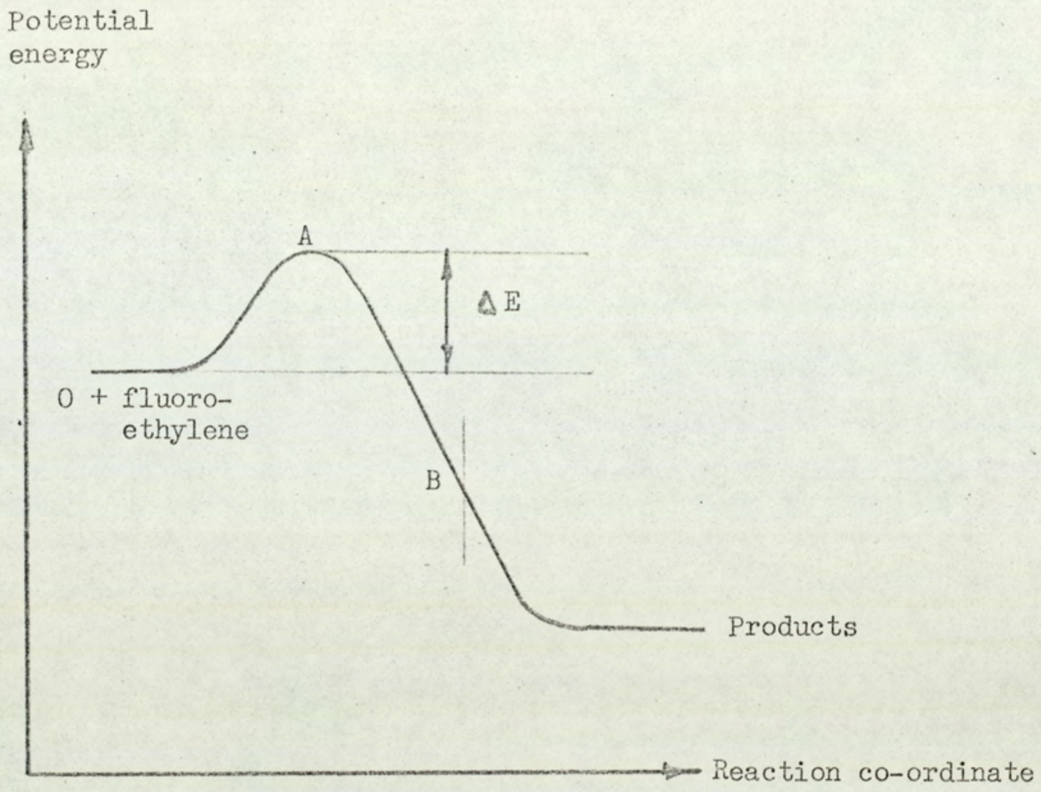


FIG. 6.10 TENTATIVE POTENTIAL ENERGY DIAGRAM FOR THE $O(^3P)$ - FLUOROETHYLENE REACTION

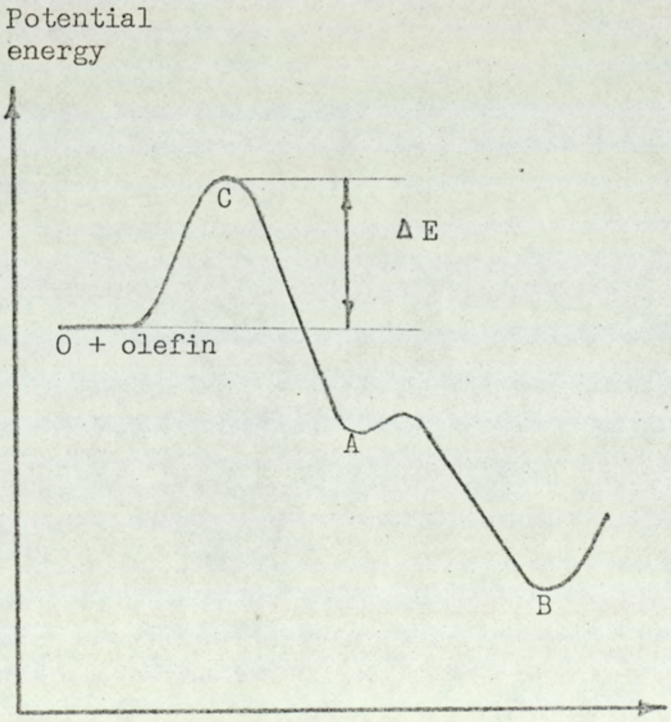
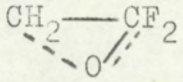


FIG. 6.9 TENTATIVE POTENTIAL ENERGY DIAGRAM FOR THE $O(^3P)$ - OLEFIN REACTION

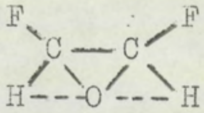
π complex in which the initial repulsion has been overcome and B then corresponds to the biradical intermediate, relatively stable, which undergoes further rearrangement to give the products.

It should be noted that at C, the oxygen atom has not yet become localised on any particular carbon atom, but is rather removed from the olefin molecule and loosely associated with the double bond.

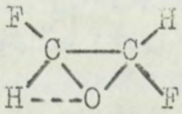
It seems probable from the conclusions of this work that a rather different reaction scheme operates for the fluoroethylene system. This is illustrated in Fig.6.10. It is proposed that A corresponds to the formation of the biradical (not the π transition state advanced by Cvetanovic for the hydrocarbon olefins.) This biradical is considered to be formed by addition of oxygen to the less subsitituted end. It would seem reasonable to assume that initial attack is at the less substituted end because of electrostatic repulsion experienced if the oxygen atom approaches the more fluorinated carbon. For example, with 1,1 difluoroethylene the biradical formed would be $\dot{C}F_2-CH_2-\dot{O}$. This does not necessarily mean that the <u>products</u> formed are associated with addition at the less substituted end of the molecule. Cvetanovic[23] has mentioned that for the hydrocarbon olefins the factors controlling the rates of the reaction are not the same as those governing the nature of the products. It is possible that the oxygen atom subsequently becomes attached to the other (more substituted) carbon which might be visualised as passing through an intermediate state  (B)

However, as a detailed product analysis of those systems has not been undertaken, it is difficult to predict to which end of the molecule the oxygen eventually attaches itself. It seems unlikely from the foregoing discussion that the Klein model[39,40,41] is involved in the rate determining process (ie. formation of A in Fig.6.10). As previously mentioned, the transition state proposed is one in which loose bonds are formed with hydrogen on the same side of the molecule as the oxygen becomes attached,

eg. with cis and trans 1,2 difluoroethylene, the envisaged transition states would be



cis complex



trans complex

On the Klein theory oxygen bonds are formed to both carbon atoms simultaneously, contrary to the observations in this system in which rates are dictated by properties of the <u>less</u> substituted carbon.

However, Klein complexes have been successfully employed to explain the nature of the products of O(^{3}P) - olefin reactions and there seems no reason why the Klein transition state could not be important in some later stage of the product forming process(point B of Fig.6.10).

6.5 THE REACTIVITY DIFFERENCES OF CIS AND TRANS 1,2DIFLUOROETHYLENE

In this section an attempt is made to discover the factors responsible for the difference in reactivity of the cis and trans isomers of 1,2 difluoroethylene with oxygen atoms.

The differences in reactivity can be due to

i) steric differences (associated with 'A' factors)
ii) energetic differences (associated with activation energies.)

Table 6.1 shows that the difference is a mixture of both factors. The trans isomer reacts faster with oxygen atoms because of the larger 'A' factor and also because of the lower activation energy.

Moss[56] has considered the problem by the following approach:-

From a detailed experimental study of the isomerisation equilibrium[121]

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

$$\Delta H^{o}_{c \rightarrow t} = +3890 \text{ Jmol.}^{-1} \quad (298\text{K})$$

$$\Delta S^{o}_{c \rightarrow t} = +0.56 \text{ JK}^{-1}\text{mol.}^{-1} \quad (298\text{K})$$

the cis isomer is thermodynamically more stable. From a knowledge of the ratio of the rate constants at room temperature, certain deductions can be made of the differences in the transition states for the two isomers. Using the information above

$\Delta G^{o}_{c \rightarrow t} = 3725 \text{ Jmol.}^{-1}$ at 298K. Now if the transition states for both isomers are identical the situation can be represented by the free energy diagram of Fig.6.11(a). Alternatively the free energy difference

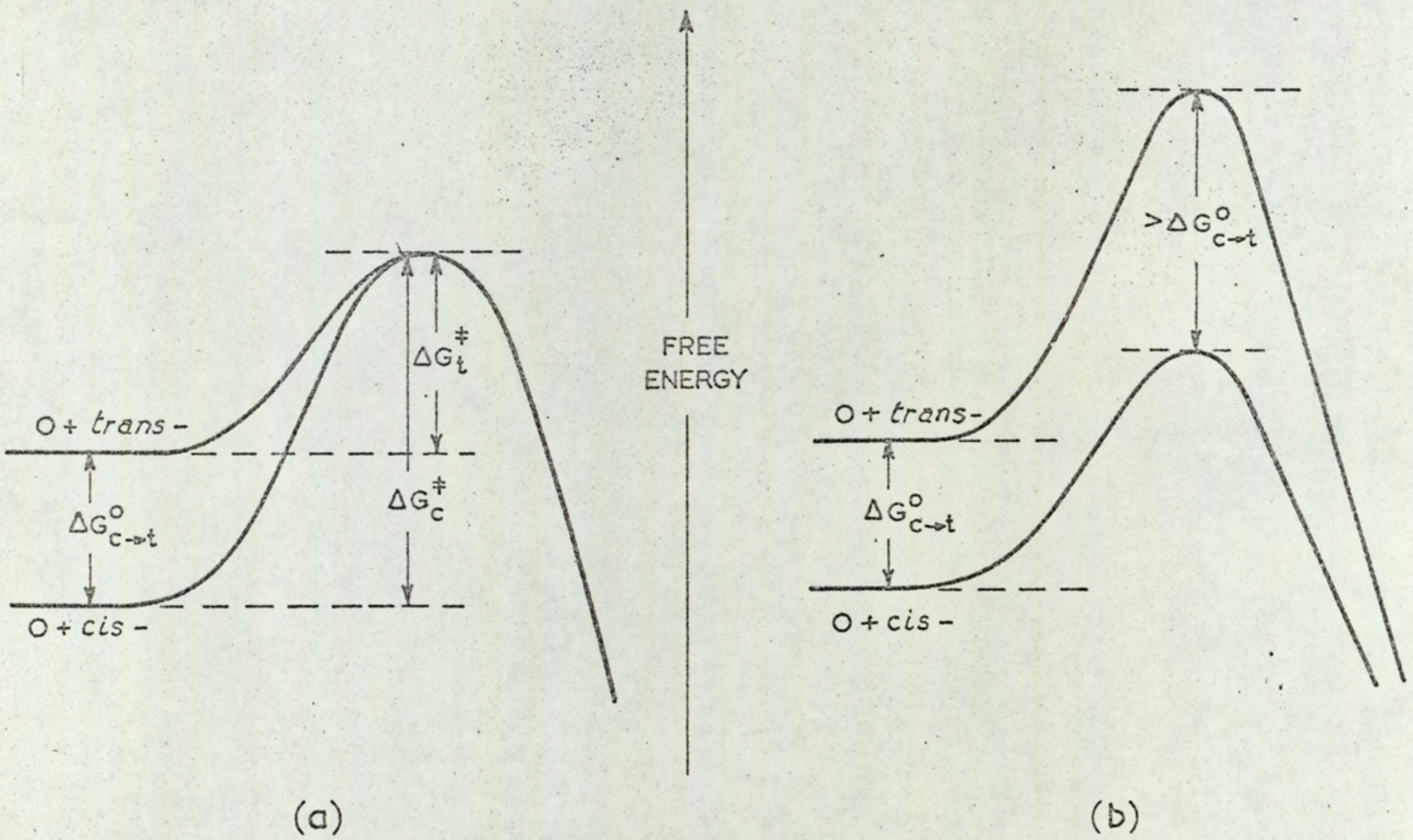


Fig. 6.11 SCHEMATIC REACTION PATHS FOR THE $O(^3P)$ - 1,2 DIFLUOROETHYLENE REACTION

of the ground state molecules may be retained or enhanced in the complexes as illustrated in Fig. 6.11(b) If (b) is the true situation then $\Delta G^{\neq}_{t} \geq \Delta G^{\neq}_{c}$ and the reactivity of the cis isomer is greater than or equal to the trans isomer. ie. $k_c / k_t \geqslant 1.0$.

If (a) is valid then $\dfrac{k_c}{k_t} = \exp\left[\dfrac{-\Delta G^{o}_{c \to t}}{RT}\right]$

(ie. $k_c / k_t = K_T$, the equilibrium constant for cis → trans isomerisation at temp. T).

$$= \underline{0.21 \text{ at } 298K}$$

Experimentally, k_c/k_t as measured in this work is 0.60 which indicates that the transition states lie somewhere between the two extremes.

More specifically, $\dfrac{k_{cis}}{k_{trans}} = e^{-(\Delta G^{\neq}_{c} - \Delta G^{\neq}_{t})/RT}$

At 298K, $k_c / k_t = 0.60$ and hence

(1) $\underline{\Delta G^{\neq}_{cis} - \Delta G^{\neq}_{trans} = +1270 \text{ Jmol.}^{-1}}$ (298K)

ie. the free energy difference in the transition state is less than the free energy difference of the ground state molecules by 1270 Jmol.$^{-1}$

ie. $\underline{G^{\neq}_{cis} - G^{\neq}_{trans}} = -3725 + 1270 = \underline{-2455 \text{ Jmol.}^{-1}}$

Similarly using the ratio of the rate constants at 424K measured in this work

$$k_{cis} / k_{trans} = 0.634$$

(2) $\underline{\Delta G^{\neq}_{cis} - \Delta G^{\neq}_{trans} = +1610 \text{ Jmol.}^{-1}}$ (424K)

Using $(\Delta G^{\neq}_{cis} - \Delta G^{\neq}_{trans}) = (\Delta H^{\neq}_{cis} - \Delta H^{\neq}_{trans}) - T(\Delta S^{\neq}_{cis} - \Delta S^{\neq}_{trans})$

We obtain the two simultaneous equations (3) and (4)

(3) $1270 = (\Delta H^{\neq}_{cis} - \Delta H^{\neq}_{trans}) - 298(\Delta S^{\neq}_{cis} - \Delta S^{\neq}_{trans})$

(4) $1610 = (\Delta H^{\neq}_{cis} - \Delta H^{\neq}_{trans}) - 424(\Delta S^{\neq}_{cis} - \Delta S^{\neq}_{trans})$

Solving, we have

$$\underline{(\Delta H^{\neq}_{cis} - \Delta H^{\neq}_{trans}) = 465\ \text{J mol.}^{-1}} (\pm 100\ \text{J mol.}^{-1})$$

and $$\underline{(\Delta S^{\neq}_{cis} - \Delta S^{\neq}_{trans}) = -2.7\ \text{J mol.}^{-1}\text{K}^{-1}} (\pm 1.0\ \text{J mol.}^{-1}\text{K}^{-1})$$

(limits of error have been assessed from the experimental errors incurred in measuring cis and trans rate constants at 298 and 433 °K)

The results indicate

a) the enthalpies of the transition state are 465 J mol.^{-1} closer together than the ground state molecules.

b) the entropies of the transition state are 2.7 $\text{J mol.}^{-1}\text{K}^{-1}$ further removed than the ground state molecules.

The results are illustrated in Figs.6.12 and 6.13. A contrasting system is the $O(^3P)$ - butene-2 reaction In this case, the trans isomer of butene-2 is the more stable but is the more reactive[14] with oxygen atoms. Thermodynamic data[122] indicates that

$$\Delta G^{o}_{f\ cis} - \Delta G^{o}_{f\ trans} = 2880\ \text{J mol.}^{-1}$$

The ratio of the rate constants for cis and trans butene-2 determined by Cvetanovic[14] was 0.86(k_{cis}/k_{trans}) at 298 K. Using the same method of calculation as previously described for 1,2 difluoroethylene, we find that the difference in free energy of the transition states is 3252 J mol.^{-1}. This is illustrated in Fig.6.14. It can be seen that the free energy difference between transition states is <u>greater</u> than that between the ground state molecules whereas for cis and trans 1,2 difluoroethylene the converse is evident.

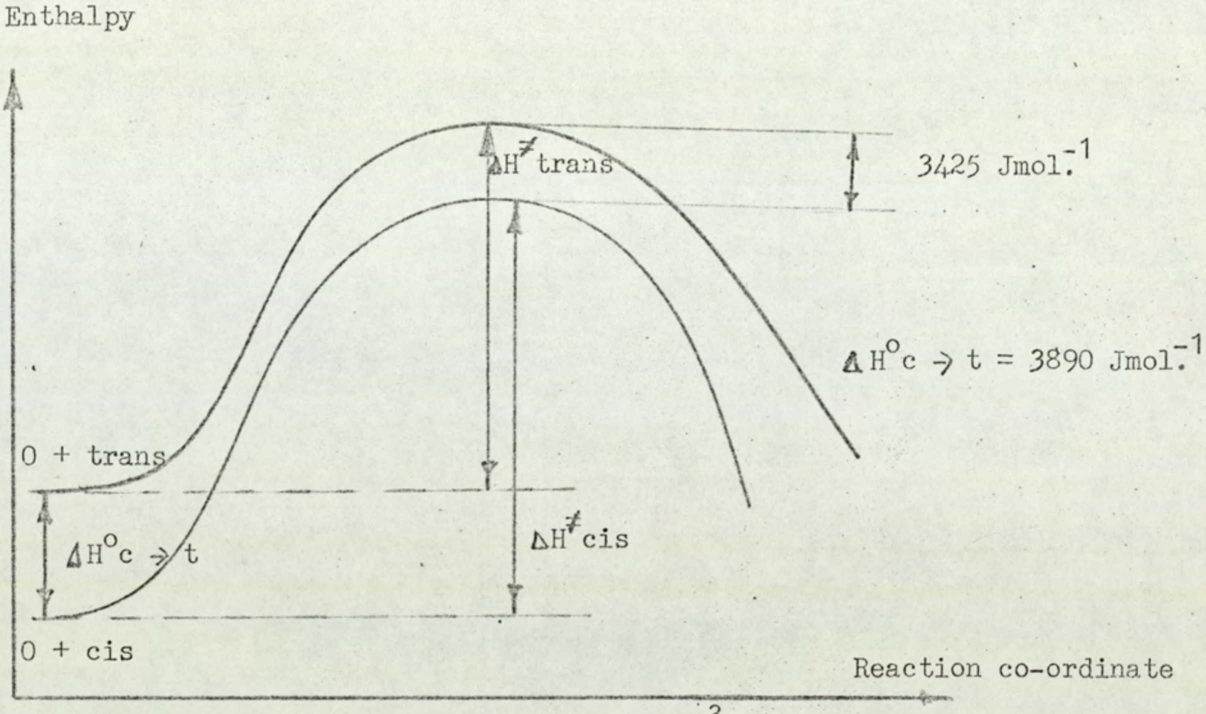


FIG. 6.12 SCHEMATIC ENTHALPY DIAGRAM FOR $O(^{3}P)$ + 1,2 DIFLUOROETHYLENES

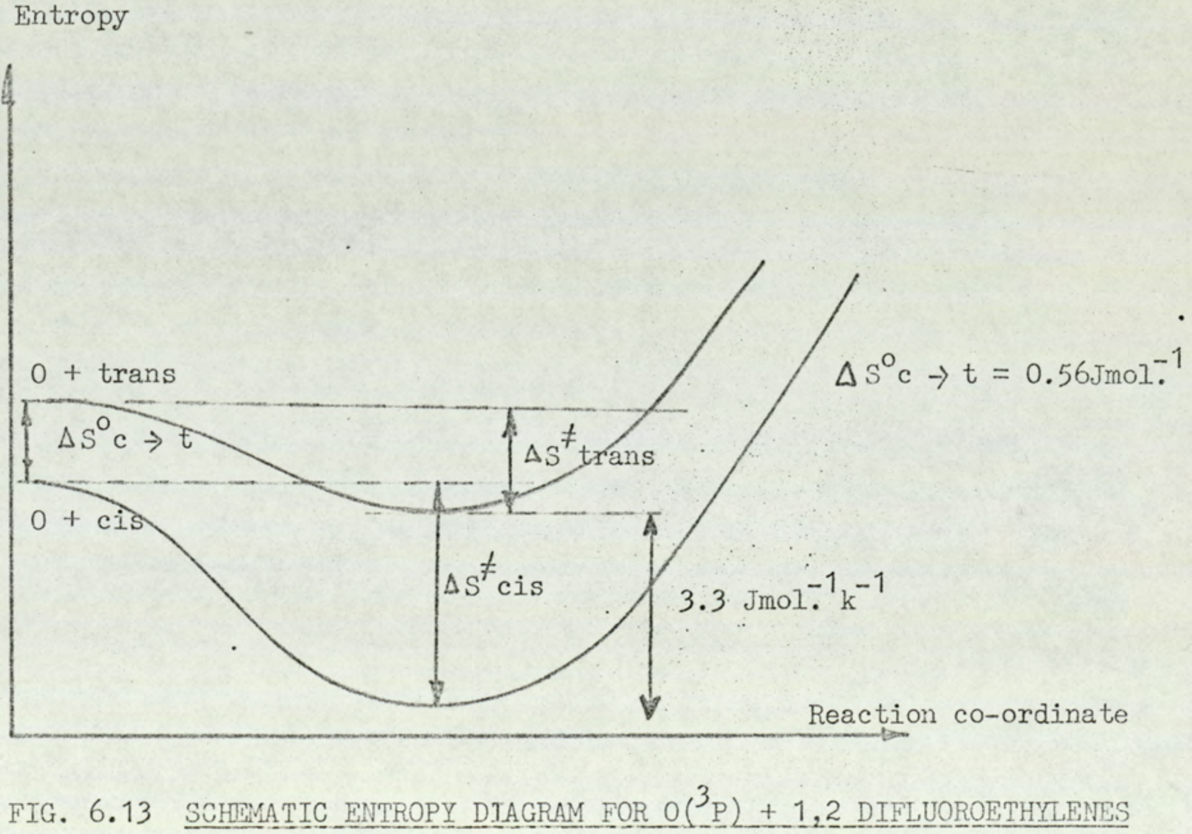


FIG. 6.13 SCHEMATIC ENTROPY DIAGRAM FOR $O(^{3}P)$ + 1,2 DIFLUOROETHYLENES

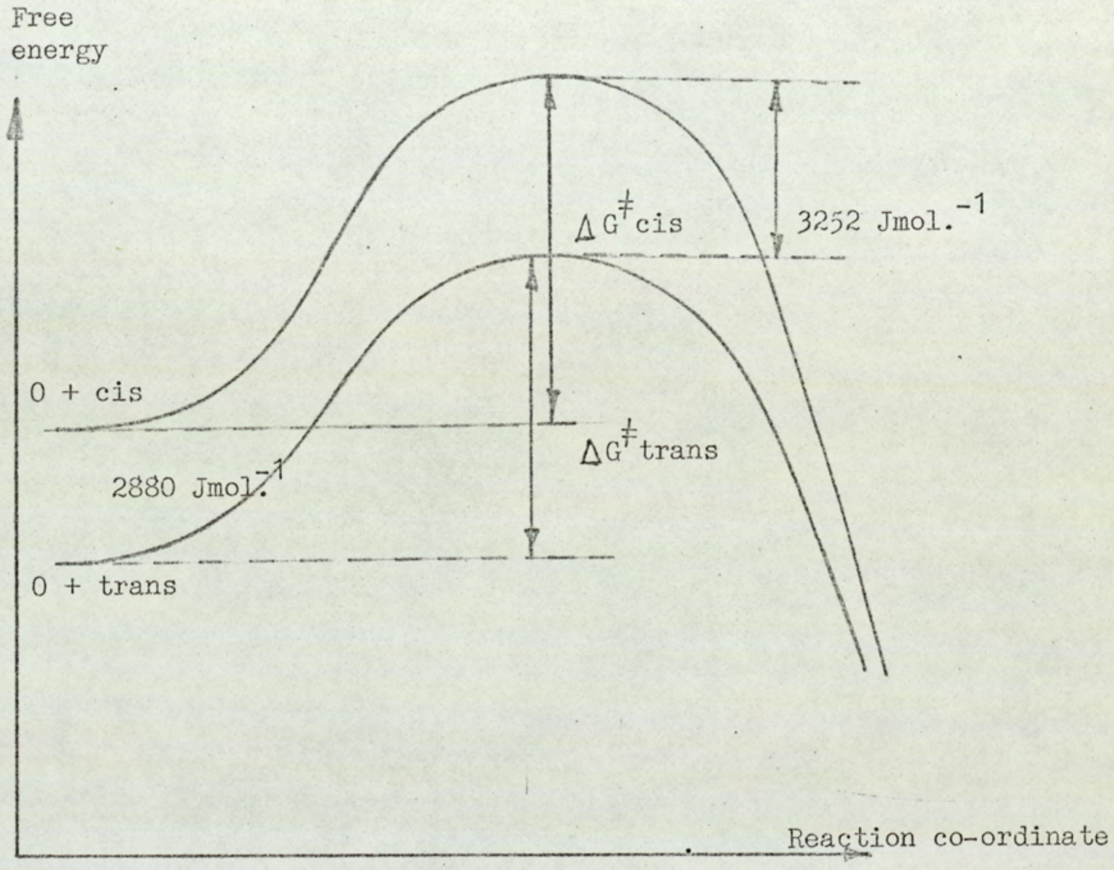


FIG.6.14 FREE ENERGY DIAGRAM FOR THE O(^{3}P)/ BUTENE-2 REACTION

The enthalpy diagram (Fig. 6.12) for cis and trans 1,2 difluoroethylene, is in one respect not compatable with the transition state being the biradical. If the biradical corresponds to the highest point of the enthalpy curve then we would expect all configurational differences to be eliminated ie. cis and trans isomers passing through a common transition state. However, it can be seen that energy differences associated with configurational factors are <u>retained</u> in the transition state. It seems difficult to explain this in terms of the discussion in the previous sections.

CHAPTER SEVEN

DISCUSSION OF THE O(^{3}P) + 1,1,2 TRIFLUOROBUTENE-1 REACTION

SECTION A : IN THE ABSENCE OF MOLECULAR OXYGEN

7.1 PRODUCTS AND YIELDS

The main products of the reaction are cis and trans 1 fluoropropene and carbonyl fluoride. Minor products include fluorocyclopropane, propionyl fluoride ethane, ethylene and propane.

The quantum yields of each of these products from a typical run at room temperature and 250mm. pressure are shown in Table 7.1 below.

TABLE 7.1

Quantum yields of products O(^{3}P) + 1,1,2 TFB reaction at 23°C and 250mm. pressure.

Product	Quantum Yield
Ethylene	0.0068
Ethane	0.011
Propane	0.0036
cis 1 fluoropropene	0.65
trans 1 fluoropropene	0.31
Fluorocyclopropane	0.042
Propionyl fluoride	0.023
Carbonyl fluoride	0.89

In the following discussion, an attempt is made to formulate a mechanism which satisfactorily explains product formation and certain other aspects of the reaction.

7.2 PRIMARY PROCESSES

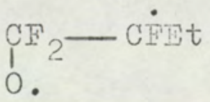
The reaction of oxygen atoms with non-fluorinated olefins has been discussed previously (Section 1.4). Cvetanović proposed the initial adduct as a biradical with oxygen attached to the less substituted carbon of the double bond. The main possible reactions of the biradical were;

a) ring closure to epoxide.

b) intramolecular migration of an alkyl group or hydrogen atom to form aldehydic or ketonic products, with the <u>same</u> number of carbon atoms as the olefin.

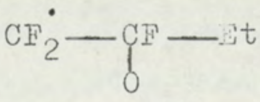
c) fragmentation to products with a <u>smaller</u> number of carbon atoms than the original olefin.

The reaction of oxygen atoms with small olefins proceeds with predominant fragmentation (reaction c) because excess energy of the biradical cannot be accomodated by the few vibrational modes of the molecule. Using Cvetanović's scheme, we would expect two possible biradicals for the $O(^3P)$/1,1,2 TFB reaction;



$\underset{\underset{O\cdot}{|}}{CF_2}-\dot{C}FEt$

and



$\dot{C}F_2-\underset{\underset{O}{|}}{CF}-Et$

(A) (B)

It is difficult to predict which biradical is formed in accordance with Cvetanović's theory as the "less substituted carbon" is rather an ambiguous expression when applied to 1,1,2 TFB; one carbon of the double bond is substituted with two fluorines, the other with one fluorine and an ethyl group.

No identified products of the 1,1,2 TFB reaction had more than three carbon atoms and no detectable amounts of epoxide were formed. This suggests that reactions a) and b) of the biradical (mentioned above) are not important in this system and it would seem likely that(A) or (B) fragment almost completely. Predominant fragmentation would appear peculiar to the fluorinated double bond rather than related to the molecular size of the olefin (non-fluorinated butenes give high yields of epoxide and four carbon carbonyl compounds in their reactions with oxygen atoms[23]).

Heicklen[46-50] has noted that small perfluoro-olefins with a terminal double bond yield carbonyl fluoride a quantum yield near to unity. In the case of tetrafluoroethylene, primary processes considered most likely were

$$O + C_2F_4 \longrightarrow CF_2O + CF_2:$$

or $$O + C_2F_4 \longrightarrow C_2F_4O^* \longrightarrow CF_2O + CF_2:$$

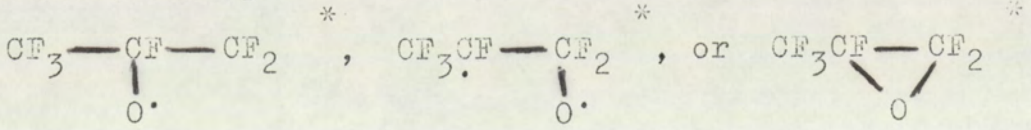
With perfluoropropylene [46,52,53], primary processes proposed were

$$O + C_3F_6 \longrightarrow CF_2O + CF_3CF:$$

$$O + C_3F_6 \longrightarrow CF_3CFO + CF_2:$$

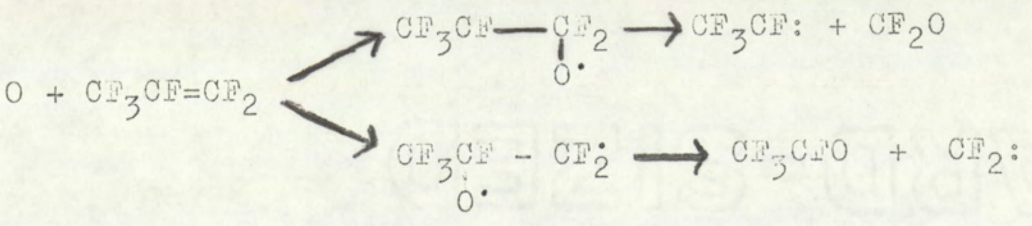
$$O + C_3F_6 \longrightarrow C_3F_6O^*$$

The structure of the oxygen-containing intermediate has not been elucidated but is probably the excited biradical or epoxide



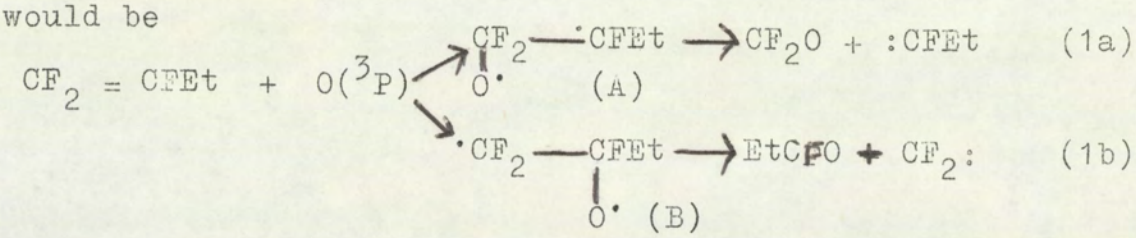
$$CF_3-\underset{\overset{|}{O^{\cdot}}}{CF}-CF_2^{\;*}\ ,\quad CF_3\underset{\cdot}{C}F-\underset{\overset{|}{O^{\cdot}}}{CF_2}^{\;*}\ ,\ \text{or}\quad CF_3\underset{\diagdown\, O\, \diagup}{CF-CF_2}^{\;*}$$

Cvetanović's and Heicklen's schemes are broadly compatible if we consider the overall reaction as



$$\begin{array}{lll} & \nearrow CF_3CF-\underset{\overset{|}{O^{\cdot}}}{CF_2} & \longrightarrow CF_3CF: + CF_2O \\ O + CF_3CF{=}CF_2 & & \\ & \searrow CF_3\underset{O^{\cdot}}{CF} - \dot{C}F_2 & \longrightarrow CF_3CFO + CF_2: \end{array}$$

By analogy, the corresponding 1,1,2 TFB reaction would be



$$CF_2 = CFEt + O(^3P) \rightarrow \underset{O^{\cdot}}{CF_2}-\dot{C}FEt\ \text{(A)} \rightarrow CF_2O + :CFEt \quad (1a)$$

$$CF_2 = CFEt + O(^3P) \rightarrow {}^{\cdot}CF_2-\underset{O^{\cdot}}{CFEt}\ \text{(B)} \rightarrow EtCFO + CF_2: \quad (1b)$$

ie.addition to the terminal fluorinated carbon gives carbonyl fluoride and the carbene EtCF:, whereas addition to the other carbon of the double bond is expected to yield propionyl fluoride and CF_2:. In the absence of oxygen the yields of carbonyl fluoride and propionyl fluoride are probably indicative of the extent of addition to the two respective carbons of the double bond. As the quantum yield of propionyl fluoride is is very small (0.02) and carbonyl fluoride relatively large (0.9) most oxygen atoms add to 1,1,2 TFB with formation of biradical (A).

The small pressure dependence of carbonyl fluoride quantum yields (Fig. 3.7) would indicate that intermediate (A) is very short-lived and is not collisionally deactivated within the pressure range investigated in this study.

If we accept reaction 1a as the main primary process, it is necessary to consider some possible reactions of the carbene EtCF:.

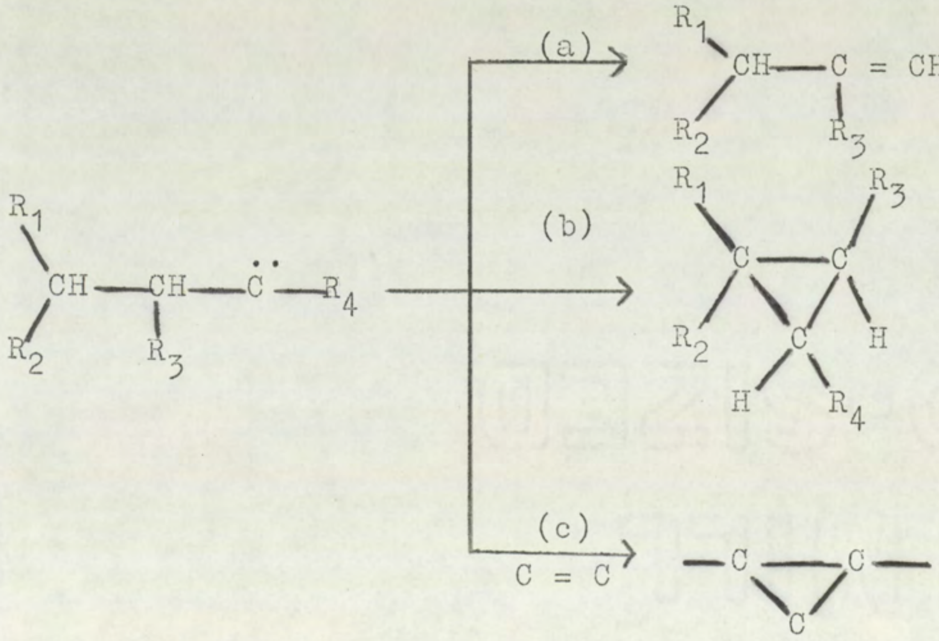
7.3 REACTIONS OF THE CARBeNE ($C_2H_5CF:$)

Heicklen [48,49,50] verified that difluorocarbenes formed in the reaction of $O(^3P)$ with tetrafluoroethylene is in the triplet state (from the reactivity of $^3CF_2$ with molecular oxygen, not shown by the corresponding singlet series .) This is in accordance with spin conservation rules

$$O(^3P) + C_2F_4 \longrightarrow CF_2O + {}^3CF_2:$$

Heichlen[46,52,53] has similarly postulated that $:CF_2$ and $CF_3CF:$ formed in the perfluoropropylene reaction (section 7.2) are also in the triplet state. From these considerations, there is good reason to believe that the carbene, $C_2H_5CF:$ from reaction 1a is also formed in the triplet state.

Carbenes exhibit a variety of reactions[125]. The three most important are outlined below



Reaction a) refers to hydrogen atom shift, a well-known reaction of alkyl and dialkyl carbenes. The reaction proceeds intramolecularly and predominates when the carbene is substituted with straight chain groups (ie. R_2 and R_3 are hydrogen).

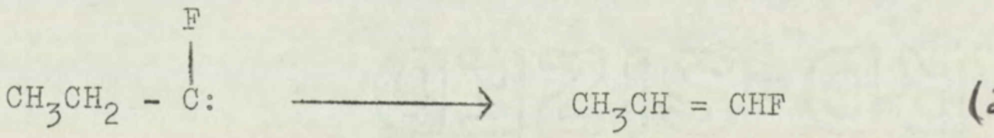
Reaction b) illustrates cyclisation of the carbene, the carbenyl carbon inserting into a suitable C - H bond, by an intramolecular mechanism. This reaction is increasingly predominant with increasing branching of the substituted alkyl groups. Relative yields of substituted cyclopropane increase in the order R = nbutyl < isobutyl < neopentyl.

Reaction c) represents the well known addition of carbenes to olefins to give cyclopropane derivatives.

These three reactions have been used to explain a number of products observed in the present system.

a) Hydrogen atom shift

The analogous reaction for ethylfluorocarbene is

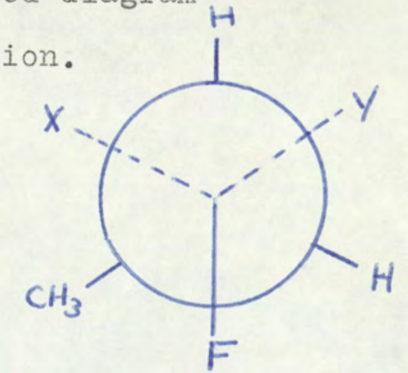


$$CH_3CH_2 - \overset{F}{\overset{|}{C}}: \longrightarrow CH_3CH = CHF \qquad (2)$$

cis and trans 1 fluoropropene

Reaction 1a predicts that the carbene and carbonyl fluoride are formed in equivalent amounts. It has been observed that carbonyl fluoride and 1 fluoropropene yields are almost identical. This suggests that the carbene isomerises overwhelmingly to form 1 fluoropropene by reaction 2

The ratio of cis to trans 1 fluoropropene was found to decrease with increasing temperature (Fig.3.10) and with decreasing pressure(Fig.3.9). These observations have been explained by the ideas outlined below. Rotation of carbene molecule is illustrated diagramatically assuming a tetrahedral configuration.



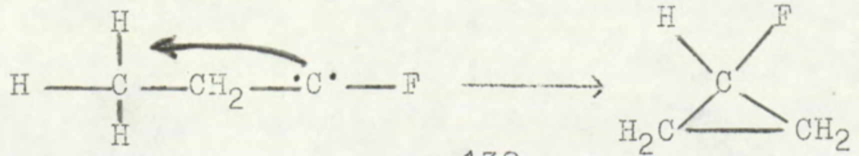
X and Y represent the two vacant valencies on the carbenyl carbon. It can be seen that isomerisation of the carbene yields cis 1 fluoropropene if the fluorine atom is in close proximity to the methyl group at the time of hydrogen atom transfer. It is thought that in this position a certain amount of attraction is experienced due to the proximity of the methyl hydrogens and the fluorine atom. If the carbene is formed by reaction 1a without excess energy (in equillibrium with the surroundings) then we anticipate the attraction to result in a predominant amount of the cis isomer being formed. However, if the carbene is given progressively more energy, the attraction effect will assume less and less importance and hydrogen atom transfer occurs with the molecule in a random orientation. This would be observed as a decrease in the cis/trans ratio.

The pressure dependence of the isomer ratio seems to be best interpreted as progressive removal of excess energy from the carbene by collision, yielding at high pressure, the carbene in thermal equilibrium with the surroundings and therefore a higher yield of cis-olefin.

Increasing the reaction temperature, on the other hand, increases the energy of the biradical resulting in a decrease of the cis/trans ratio.

b) Cyclisation

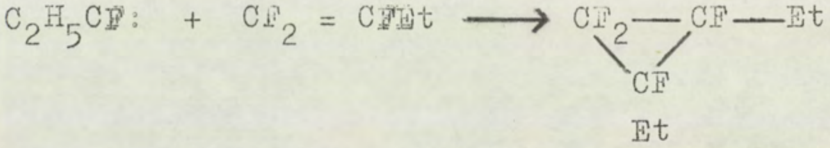
Cyclisation of ethylfluorocarbene is expected to yield fluorocyclopropane as shown below.



As fluorocyclopropane and 1 fluoropropene are formed intramolecularly from a common intermediate (the carbene) one would expect factors affecting the yield of the intermediate to produce correspondingly affected yields of both products. For example, the pressure dependence of 1 fluoropropene is paralleled by the pressure dependence of fluorocyclopropane. However, diminished yields of fluorocyclopropane at high conversions are explained by competition of 1 fluoropropene with 1,1,2 TFB for oxygen atoms.

c) Addition to an olefin

A possible reaction is



Although this compound was not specifically identified as one of the reaction products, it is possible that a small amount formed would correspond to one of the two trace products observed in the high boiling point region of the Porapak Q chromatogram (Fig. 3.1). Difficulty of synthesis prevented subsequent confirmation.

The addition process was considered unimportant in the overall reaction due to relatively fast isomerisation of the carbene. The high quantum yield of 1 fluoropropene confirms this supposition. In addition extensive fluorination of the double bond would be expected to reduce the rate of thecarbene addition by a relatively large factor.[99]

7.4 FORMATION OF MINOR PRODUCTS

Fluorocyclopropane formation has been discussed in Section 7.3. The remaining minor products are ethane, ethylene and propane, identified by the techniques outlined in Chapter 3.

A number of runs carried out at low conversions (less than 1%) confirmed that all three minor products were formed by primary processes. Each product exhibits a marked pressure dependence, yields of each increasing with decreased pressure (Fig.3.8). This behaviour is similar to that noted by Cvetanović[23] for fragmentation products of the non-fluorinated olefin reactions with oxygen atoms. In Cvetanović's scheme, increased yields of fragmentation products are attributed to the inefficiency of collisional stabilisation of "hot" intermediates at low pressure, excess energy being dissipated by fragmentation of the primary adduct.

With these ideas in mind, the formation of each minor product is discussed.

a) <u>Ethane</u>

One possible source of ethane is from the combination of two methyl radicals. For example, the process might be

$$O + CF_2 = CFC_2H_5 \longrightarrow CH_3^{\cdot} + \text{fragments}$$

followed by $CH_3 + CH_3 \longrightarrow C_2H_6$

As oxygen atom concentration is directly proportional to lamp intensity, reducing the lamp intensity by a factor of 10 would result in a 10 fold reduction of methyl radicals from the first reaction, although the <u>quantum yield</u> is unaffected $\left(\text{as } \phi_{CH_3} = \frac{R_{CH_3}}{R_{N_2}} \right)$

However, the ethane formation process is reduced by a factor or 100, giving a quantum yield of ethane 10 times less than that at full lamp intensity. This direct dependence of ethane quantum yield with lamp intensity is contraryto observation (Section 3.5). In addition, radical-radical combination processes are highly inefficient at low pressure. Pressure dependence curves indicate ethane yields <u>increasing</u> at lower pressures. For this reason, the above scheme has been dismissed as a likely source of ethane.

Abstraction of a methyl group (from 1,1,2 TFB) by by a methyl radical has also been discounted because of the absence of methane amongst the reaction products. Formation of ethane from ethyl radicals seems the only logical alternative. Radical formation processes are conceivably

$$O + C_2H_5CF = CF_2 \longrightarrow C_2H_5^{\cdot} + \text{fragments} \qquad (3)$$

and/or $Hg^* + C_2H_5CF = CF_2 \rightarrow C_2H_5^{\cdot} + Hg(^1SO) + \text{fragments}$ (4)

followed by

$$C_2H_5^{\cdot} + RH \longrightarrow C_2H_6 + R^{\cdot} \qquad (5)$$

If reaction (4) is to be important, one would expect the mercury photosensitised decomposition of 1,1,2 TFB to yield ethane as one of the major products. One run carried out using 1,1,2TFB alone revealed ethane to be one of the products. However, if reaction 4 is the major source of ethyl radicals, variation of the 1,1,2 TFB/N_2O ratio should affect the observed quantum yield of ethane as the olefin competes with nitrous oxide for quenching of triplet mercury atoms. Comparing runs 51 and 52 of Table 3.9 reveals the expected variation is not observed.

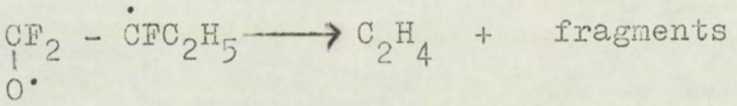
The major source of ethane seems to be the primary reaction (3) between oxygen atoms and 1,1,2 TFB, followed by the hydrogen abstraction (5).

b) Ethylene

The time dependenece of ethylene quantum yield (Fig. 3.5) shows a linear rate of formation in the early stages of reaction and an enhanced rate at higher conversion. This is indicative of primary formation coupled with a secondary source of ethylene, becoming more important at high conversions.

Primary sources of ethylene are first considered.

$$C_2H_5\ddot{C}F \longrightarrow C_2H_4 + CHF \qquad (6)$$



$$\underset{O^{\cdot}}{CF_2} - \dot{C}FC_2H_5 \longrightarrow C_2H_4 + \text{fragments} \qquad (7)$$

$$Hg^* + CF_2 = CFEt \longrightarrow C_2H_4 + \text{fragments} \qquad (8)$$

If the carbene is formed 'hot' we would expect that at higher pressures progressively more carbene molecules are collisionally deactivated. The deactivated carbene probably isomerises to 1 fluoropropene in preference to ethylene (reaction (6)). A decrease in ethylene quantum yield with increasing pressure, in accordance with 6, is indicated in Fig.3.8.

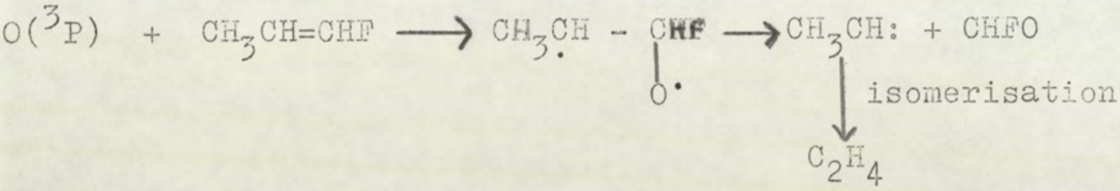
It would seem experimentally impossible in this system to distinguish between reactions 6 and 7. The variation of ethylene quantum yield with pressure could be explained by a similar argument to that of the elimination mechanism.

Reaction 8 has been discounted for two reasons. The mercury photosensitised decomposition of 1,1,2 TFB was found to proceed without formation of ethylene. Secondly the absence of variation of ethylene quantum yield with varied 1,1,2TFB/N_2O ratio (Table 3.9) is contrary to the expected behaviour.

The most likely secondary source of ethylene is the reaction of oxygen atoms with 1 fluoropropene

$$O \;+\; CH_3CH = CHF \longrightarrow CHFO \;+\; C_2H_4$$

It can be seen this is analogous to the reaction of $O(^3P)$ with 1,1,2TFB



$$O(^3P) \;+\; CH_3CH{=}CHF \longrightarrow CH_3\dot{C}H - \underset{\displaystyle O^{\bullet}}{\underset{|}{CHF}} \longrightarrow CH_3CH{:} \;+\; CHFO$$

$$CH_3CH{:} \xrightarrow{\text{isomerisation}} C_2H_4$$

Isomerisation of methyl carbene $CH_3CH{:}$ is known to predominantly yield ethylene.[126] As confirmation, a single run with N_2O and a mixture of cis and trans 1 fluoropropene yielded ethylene as the major product observable.

Thes scheme can only become appreciable as a source of ethylene when 1 fluoropropene has reached sufficient concentration to compete effectively with 1,1,2 TFB for available oxygen atoms as discussed in Chapter 3. Further consideration of these processes is included in Section 7.6.

c) Propane

Three possible routes to formation are

$$CH_3 \;+\; C_2H_5 \longrightarrow C_3H_8 \qquad (9)$$

$$C_3\dot{H}_7 \;+\; RH \longrightarrow C_3H_8 + R^{\cdot} \qquad (10)$$

$$C_2H_5^{\cdot} + CH_3\ H_2CF = CF_2 \longrightarrow C_3H_8 + {}^{\cdot}CH_2CF = CF_2 \qquad (11)$$

Reaction (9) is discounted both on observed invariance of propane yields with reduced light intensity and decreased yields at high pressure.

A likely source of propyl radicals (for reaction 10) is not apparent. The structure of 1,1,2 TFB is such that a non-fluorinated C_3 fragment cannot be formed without breaking a C-F bond, which is energetically unfavourable,

Reaction (11) is thought to be the onlypossible source of propane. Abstraction of a methyl group from 1,1,2 TFB yields an allylic-type radical which are known to be exceptionally stable due to resonance.

$$\cdot CH_2CF = CF \longleftrightarrow CH_2 = CF - CF_2^{\cdot}$$

Further evidence in support of this mechanism is offered in Section 7.6.

SECTION B

THE REACTION IN THE PRESENCE OF MOLECULAR OXYGEN

Molecular oxygen is well known as a radical scavenger. An investigation of the reaction $O(^3P)$ with 1,1,2 TFB in the presence of molecular oxygen was undertaken in the hope of identifying those products formed by a radical process. In particular, it was anticipated the results would indicate the reactivity of the carbene, $C_2H_5CF:$, with molecular oxygen. It is realised that oxygen is capable of quenching excited states and could possibly diminish yields of some productsfor this reason (as opposed to reaction). This possibility is hopefully minimised by adding only small amounts of molecular oxygen to the system. The results of this investigation are discussed in the subsequent sections.

7.5 PRODUCTS AND YIELDS

It was found that yields of some products were dependent on oxygen concentration. These have been discussed in greater detail in section 3.7 but the results are summarised in Table 3.9 reproduced below for ease of reference.

The main points evident from the table are

1) The quantum yields of carbonyl fluoride and propionyl fluoride are greatly enhanced in the prescence of oxygen and are dependent upon oxygen concentration.

2) Cis and trans 1 fluoropropene yields are unchanged in the presence of oxygen.

3) Ethane and propane are not formed with oxygen present, ethanol and acetaldehyde are additional products of the reaction.

TABLE 3.9

Effect of Oxygen/Olefin Ratio Upon the Quantum Yield of Products

Run	O_2 (mm)	TFB (mm)	QUANTUM YIELDS						
			ethylene	ethane	propane	CIS 1FP	TRANS 1FP	propionyl fluoride	CF_2O
50	0	12	0.0085	0.0106	0.0043	0.72	0.34	0.02	0.98
51	0	13	0.0080	0.0110	0.0042	0.65	0.31	0.02	1.00
52	0	6.2	0.0086	0.0103	0.0037	0.65	0.31	0.02	0.98
53	4.5	13	0.0065	0	0	0.66	0.31	0.38	1.85
54	9.1	13.2	0.0067	0	0	0.65	0.31	0.34	1.71
55	0	13.8	0.0092	0.0099	0.004	0.63	0.29	0.02	1.00
56	0.4	13.2	0.0068	0.0027	0.001	0.66	0.32	0.32	1.55

7.6 INFLUENCE OF OXYGEN ON YIELDS OF MINOR PRODUCTS

Ethane and propane

Ethyl radicals react with molecular oxygen giving as the main products ethanol and acetaldehyde in approximately equal amounts.[102,124]

$$2C_2H_5^{\bullet} + O_2 \longrightarrow CH_3CHO + C_2H_5OH$$

Disappearance of ethane and appearance of ethanol and acetaldehyde (also in equal amounts) ~~unless~~ when oxygen is added strongly suggests that the source of ethane is indeed ethyl radicals.

Propyl radicals also can react with oxygen by an analogous process to form propionylaldehyde and propanol The absence of even traces of these two compounds amongst the reaction products confirms that propane is <u>not</u> formed from propyl radicals (reaction 10 Section 7.4). It would seem that abstraction of a methyl group from 1,1,2 TFB by an ethyl radical is the most plausible route to formation of propane.

If all reactions of ethyl radicals lead to to propane and ethane,

$$\phi_{C_2H_5} = \phi_{C_3H_8} + \phi_{C_2H_6}$$

and if, in the presence of oxygen, all ethyl radicals are consumed by oxygen, then

$$\phi_{C_2H_5^{\bullet}} = \phi_{CH_3CHO} + \phi_{C_2H_5OH}$$

It has been observed that quantum yields of propane and ethane are typically 0.004 and 0.012 (at 250mm pressure Fig. 3.8). At the same pressure, but in the presence of oxygen, the yields of ethanol and acetaldehyde were both 0.14

$$\emptyset_{C_2H_6} + \emptyset_{C_5H_6} = 0.016$$

whereas $$\phi_{CH_3CHO} + \phi_{C_2H_5OH} = 0.28$$

One explanation of this anomaly is that not all ethyl radicals react to form ethane and propane but can be consumed by an alternative route. It is thought likely that in this system (O_2 absent) that some ethyl radicals are able to add to the olefin

$$C_2H_5^{\bullet} + CF_2{=}CFEt \longrightarrow CEt - CF_2 - {}^{\bullet}CFEt$$
$$\text{or} \quad {}^{\bullet}CF_2 - CF(Et)_2$$

Although the possible products from this reaction have not been specically identified, it is conceivable that they correspond to unidentified peaks on the chromatogram (Fig. 3.1). However, it seems unlikely that the quantum yield of ethyl radicals could be as high as 0.3 (suggested by acetaldehyde and ethanol yields) when one considers the yields of 1 fluoropropene and carbonyl fluoride are both close to unity. The only alternative explanations are that either more ethyl radicals are formed in the presence of oxygen or that acetaldehyde and ethanol can also be formed directly by an alternative mechanism (such as O_2 with the carbene or biradical). From the thermochemical viewpoint, the latter explanation is considered more likely. This problem remains unresolved at present.

Ethylene

The primary sources of ethylene considered most likely from the foregoing discussion were

$$C_2H_5CF: \longrightarrow C_2H_4 + CHF: \qquad (6)$$

and $$\underset{\underset{O^{\bullet}}{|}}{CF_2} - {}^{\bullet}CFC_2H_5 \longrightarrow C_2H_4 + \text{fragments} \qquad (7)$$

Yields of ethylene in the presence of oxygen will be dependent entirely on the stationary state concentration of biradical and carbene with oxygen present. For this reason, ethylene yields are considered in the section dealing with reactivity of carbene and biradical with oxygen.

7.7 YIELDS OF MAJOR PRODUCTS IN THE PRESENCE OF MOLECULAR OXYGEN

Any mechanism proposed must explain the following:

1) An unchanged yield of 1 fluoropropene
2) Greatly increased yields of propionyl fluoride and carbonyl fluoride.

The number of possible processes in the presence of oxygen is considerable. It is necessary at an early stage to establish which of these processes are likely to be important in the overall reaction scheme.

a) Quenching Processes

With oxygen present, triplet mercury can be quenched by three reactions:-

$$Hg^* + O_2 \longrightarrow O_2^* + Hg(^1S_0) \qquad 12a$$

$$Hg^* + Ol \longrightarrow Ol^* + Hg(^1S_0) \qquad 12b$$

$$Hg^* + N_2O \longrightarrow N_2 + O + Hg(^1S_0) \qquad 12c$$

Reaction 12c has been well described elsewhere in this thesis. As all runs in the presence of molecular oxygen were under conditions of a great excess of nitrous oxide (greater than 20 : 1) this route must constitute the major quenching process.

The rate of the quenching process 12b relative to nitrous oxide quenching has not been measured. Examination of Table 7.2 (containing the quenching rate constants of some perfluoro-olefins relative to N_2O) reveals that those olefins with a fully fluorinated double bond have rate constants less than that of nitrous oxide (with the exception of perfluoro 1,3 butadiene). This would suggest that 1,1,2 TFB has a quenching rate constant less than that of nitrous oxide.

In all runs with added oxygen, the ratio of olefin to N_2O was never greater than 1 : 20. Reaction 12b would hence not be expected to account for more than 5% of the total quenching process.

TABLE 7.2

Rate Constants for Reaction of $Hg(^3P_1)$ with various Molecules relative to N_2O

Molecule	k/k_{N_2O}	Reference
O_2	1.00	110
O_2	1.26	111
C_2F_4	0.31	112
C_2F_4	0.35	113
C_2F_4	0.36	15
C_2F_4	0.43	72
C_3F_6	0.27	53
C_4F_8-2	0.51	114
c - C_4F_6	0.71	115
1,3 C_4F_6	1.38	116

Quenching of triplet mercury by oxygen (reaction 12a) has been investigated previously[118]. The excited O_2 molecule formed is considered to be sufficiently excited to react with an unexcited O_2 molecule to yield O_3 and $O(^3P)$. However the value of the quenching rate constant indicated in Table 7.2 would suggest this reaction could be responsible for no more than 5% of the total quenching process for N_2O/O_2 ratios operative in this study. It would appear, in conclusion, that excited olefin and O_2 molecule reactions such as

$$O1^* + O_2 \longrightarrow \text{products}$$

and $$O1 + O_2^* \longrightarrow \text{products}$$

cannot possibly account for the greatly increased yields of propionyl fluoride and carbonyl fluoride in this system.

b) Ozone formation

The reaction of oxygen atom with molecular oxygen is known to yield ozone.

$$O + O_2(M) \longrightarrow O_3(M)$$

The results of earlier research[119] indicate the above reaction is relatively unimportant even for oxygen pressures of 1 atmosphere. This is primarily due to the difficulty of pressure stabilisation of the ozone molecule formed. Ozone reactions are not thought to to be important in this system and are unable to explain enhanced yields of CF_2O and C_2H_5CFO.

An unchanged 1 fluoropropene yield in the presence of oxygen can be interpreted in two ways:

The first is that intermediates leading to 1 fluoropropene do not react with oxygen either because the lifetime of the intermediate is too short or that reaction is unfavourable. This explanation does not account for greatly increased yields of propionyl fluoride and carbonyl fluoride.

The alternative explanation is that oxygen <u>can</u> react with the intermediates but the same or similar intermediates are regenerated at some laterstage in in the reaction, together with the carbonyl and propionyl fluoride. This chain-type process is thought to be the more likely of the two alternatives. Some possible reactions are outlined below.

<u>Reaction of Oxygen with Intermediates</u>

The two main intermediates are the carbene and biradical adduct $CH_3CH_2CF:$ and $C_2H_5\dot{C}F - \dot{C}F_2O$. Four possible reactions are

$$CH_3CH_2CF: \; + \; O_2 \rightarrow C_2H_5CFO_2: \xrightarrow{+\,1,1,2\ TFB} C_2H_5CF: \; + \; CF_2O \; + \; C_2H_5CFO \qquad \textbf{13a}$$

$$C_2H_5CF: \; + \; O_2 \longrightarrow C_2H_5CFO \; + \; O \qquad \textbf{13b}$$

$$C_2H_5\dot{C}F\text{-}CF_2\dot{O} \; + \; O_2 \longrightarrow C_2H_5CFO_2: \; + \; CF_2O \qquad \textbf{13c}$$

$$\xrightarrow{+\,1,1,2TFB} C_2H_5CF: \; + \; CF_2O \; + \; C_2H_5COF$$

$$C_2H_5\dot{C}F\text{-}CF_2\dot{O} \; + \; O_2 \longrightarrow C_2H_5CFO \; + \; CF_2O \; + \; O \qquad \textbf{13d}$$

Reactions 13a and 13c both generate the carbene $CH_3CH_3CF:$ (the precursor to 1 fluoropropene) as well as carbonyl and propionyl fluoride.

Reactions 13b and 13c regenerate oxygen atoms.

Heichlen has studied the reactions of oxygen atoms with tetrafluorethylene [100,112] in the presence of oxygen. It was found that triplet CF_2 was able to react with O_2 to yield CF_2O_2:. On the other hand, singlet CF_2: is remarkably inert to O_2 even at oxygen pressures of 1 atmosphere. In the present study there is every reason to believe the triplet carbene CH_3CH_2CF: is able to react by an analogous route to $^3CF_2$:.

The importance of reactions 13c and 13d depends largely upon the existence and lifetime of the biradical which must be sufficiently long lived to experience a collision with an oxygen molecule. If fragmentation of the biradical to the carbene occurs faster than reaction with oxygen then reactions 13 a and b become necessarily more important than 13c and d . Heichlen[49,100] has included the analogous reaction to 13c

$$C_2F_4O: + O_2 \rightarrow CF_2O + CF_2O_2$$

as an integral part of the reaction mechanism for the O_2/ O / C_2F_4 system.

Derivation of Rate Equations

In the remainder of this section, rate equations will be derived for various possible reaction schemes. The four schemes based on reactions 13a - d are outlined in Fig. 7.1. The reactions in the schemes have been renumbered to simplify the rate equations. The intermediates listed below have been assigned the following identities for further simplification.

X = EtCF:

Y = $EtCFO_2$

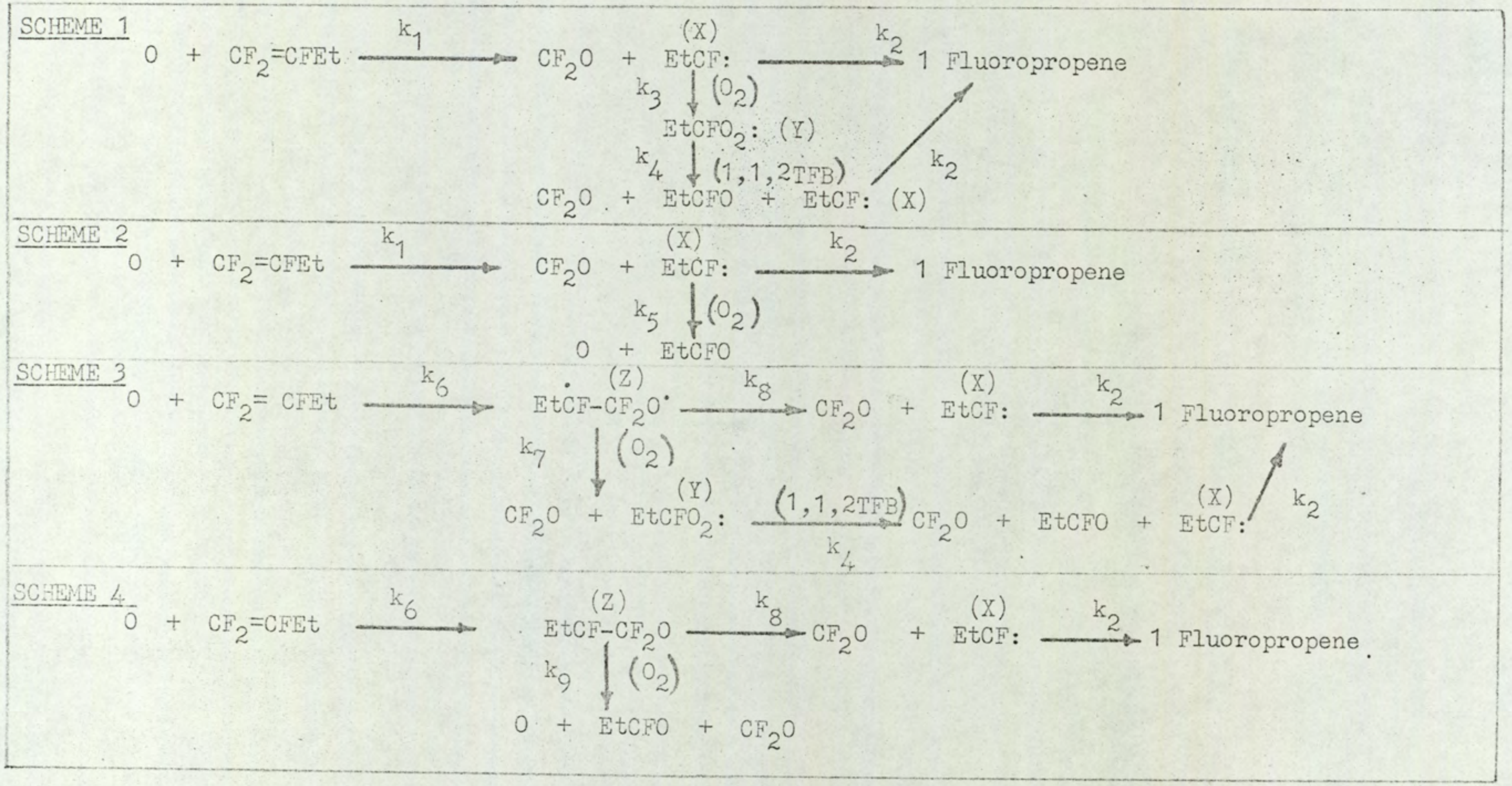


FIG. 7.1 POSSIBLE REACTION SCHEMES FOR THE REACTION OF O(^{3}P) WITH 1,1,2TFB IN THE PRESENCE OF OXYGEN

$Z = Et\dot{C}F - CF_2\dot{O}$

and $Ol = 1,1,2$ TFB

a) SCHEME 1 (Fig. 7.1)

Considering concentration of the carbene X :

$$\frac{d(X)}{dt} = R_1 - R_2 + R_4 - R_3 = 0$$ under steady state conditions

$$\text{ie.} \quad R_1 - R_2 + R_4 = 0 \qquad (1)$$

For intermediate Y :

$$\frac{d(Y)}{dt} = R_3 - R_4 = 0$$ (steady state condition)

$$R_3 - R_4 = 0 \qquad (2)$$

For oxygen atom concentration :

$$\frac{d(O)}{dt} = R_{N_2} - R_1 = 0 \qquad (3)$$

Substituting (2) into (1) and adding (3) we obtain

$$R_{N_2} = R_2 \qquad (4)$$

ie. Rate of formation of 1 fluoropropene is equal to rate of formation of nitrogen ie. independent of oxygen concentration.

From (4) we have

$$R_{N_2} = k_2 [X]$$

$$\text{ie.} \quad [X] = R_{N_2} / k_2 \qquad (5)$$

Also from (2) we have

$$k_3 [X] \, O_2 = k_4 [Y] [Ol]$$

Substituting for **X** from (5)

$$[Y] = \frac{R_{N_2} k_3}{k_2 k_4} \cdot \frac{[O_2]}{[Ol]} \qquad (6)$$

$$R_{CF_2O} = R_1 + R_4 = R_{N_2} + k_4 [Y] [Ol]$$

$$= R_{N_2} \left[1 + \frac{k_3}{k_2} [O_2] \right]$$

$$\phi_{CF_2O} = \frac{R_{CF_2O}}{R_{N_2}} = 1 + \frac{k_3}{k_2}[O_2] \qquad (7)$$

Similarly

$$R_{CH_3CH_2CFO} = R_{PF} = R_4 = k_4[Y][O1]$$

$$= R_{N_2}\frac{k_3}{k_2}[O_2]$$

Hence $$\phi_{PF} = \frac{k_3}{k_2}[O_2] \qquad (8)$$

ie. increases in the quantum yields of propionyl fluoride and carbonyl fluoride are directly proportional to oxygen concentration.

Using the methods illustrated for scheme 1 we obtain the following stationary state concentrations and quantum yield expressions for the remaining schemes.

Scheme 1

$$[X] = R_{N_2}/k_2$$

$$[Y] = \frac{R_{N_2}k_3[O_2]}{k_2k_4[O1]}$$

$$\phi_{CF_2O} = 1 + \frac{k_3}{k_2}[O_2]$$

$$\phi_{PF} = \frac{k_3}{k_2}[O_2]$$

$$\phi_{1FP} = 1$$

Scheme 2

$$[X] = R_{N_2}/k_2$$

$$\phi_{CF_2O} = 1 + \frac{k_5}{k_2}[O_2]$$

$$\phi_{PF} = \frac{k_5}{k_2}[O_2]$$

$$\phi_{1FP} = 1$$

Scheme 3

$$[X] = R_{N_2}/k_2$$

$$[Y] = \frac{R_{N_2} k_7 [O_2]}{k_4 [O] (k_8 + k_7 [O_2])}$$

$$[Z] = R_{N_2}/(k_8 + k_7 [O_2])$$

$$\phi_{CF_2O} = 1 + \frac{k_7 [O_2]}{k_8 + k_7 [O_2]}$$

$$\phi_{PF} = \frac{k_7 [O_2]}{k_8 + k_7 [O_2]}$$

$$\phi_{1FP} = 1$$

Scheme 4

$$[X] = R_{N_2}/ k_2$$

$$[Z] = R_{N_2}/k_8$$

$$\phi_{CF_2O} = 1 + \frac{k_9 [O_2]}{k_8}$$

$$\phi_{PF} = \frac{k_9 [O_2]}{k_8}$$

$$\phi_{1FP} = 1$$

It is noted that all four reaction schemes satisfactorily explain 1 fluoropropene yields which are independent of oxygen concentration. However, schemes 1,2 and 4 all predict that increased yields of propionyl and carbonyl fluoride are <u>directly</u> proportional to oxygen concentration. Examination of Table 3.9, reveals that varying oxygen concentration by a factor of over 20 times has a very small effect on the quantum yields of CF_2O and EtCFO. For this reason these schemes are regarded as being inadequate to explain the observations in this system.

Reaction scheme 3 seems rather more promising.

If $k_7 \gg k_8$, the expected behaviour is a fast linear growth in the quantum yield of both CF_2O and EtCFO at low oxygen concentrations (where $k_8 > k_7\, O_2$) At high oxygen concentrations when $k_7[O_2] \gg k_8$, the form of the quantum yield equations predicts a limiting value of 2 for ϕ_{CF_2O} and 1 for ϕ_{PF} . This behaviour is more in line with observation than that predicted by the other three schemes. For this reason, scheme 3 is believed to be operative in this system.

One reaction not yet considered but thought possible is decomposition of intermediate Y($EtCFO_2$:) to yield the carbene and oxygen.

$$EtCFO_2: \xrightarrow{k_{10}} EtCF: + O_2 \qquad (10)$$

Inclusion of this reaction in scheme 3 yields the following results:-

$$[X] = R_{N_2}/k_2$$

$$[Y] = \frac{R_{N_2} k_7 [O_2]}{(k_7[O_2] + k_8)(k_{10} + k_4[Ol])}$$

$$[Z] = R_{N_2}/(k_7[O_2] + k_8)$$

$$\phi_{CF_2O}\,(A) = 1 + \frac{k_7[O_2]\ k_4[Ol]}{(k_8 + k_7[O_2])(k_{10} + k_4[Ol])} \qquad (A)$$

$$\phi_{PF}\,(B) = \frac{k_7 k_4 [O_2][Ol]}{(k_8 + k_7[O_2])(k_{10} + k_4[Ol])} \qquad (B)$$

$$\phi_{FP} = 1$$

It can be seen that at constant olefin concentration, the variation of CF_2O and C_2H_5CFO quantum yields with oxygen are basically the same as for scheme 3. However, the limiting values at high $[O_2]$ for ϕ_{CF_2O} and ϕ_{PF} now become

$$\underset{(\lim [O_2] \to \infty)}{\phi_{CF_2O}} = 1 + \frac{k_4[Ol]}{k_{10} + k_4[Ol]} \quad (k_7[O_2] \gg k_8)$$

and $$\emptyset_{PF} \; (\text{lim.} [O_2] \to \infty) = \frac{k_4 [Ol]}{k_{10} + k_4 [Ol]} \qquad (k_7 [O_2] \gg k_8)$$

Bearing in mind that quantum yields of carbonyl fluoride are subject to relatively high uncertainty (±0.05)the results of runs 53-56 (Table 3.9) can be fitted with behaviour anticipated from the above reaction scheme

Run No.	(O_2) mm	$\emptyset_{CF_2O}$	$\emptyset_{PF}$
55	0	1.00(±0.05)	0.02
56	0.4	1.55(±0.05)	0.32
53	4.5	1.84(±0.05)	0.38
54	9.1	1.71(±0.05)	0.34

The results would suggest that the assumption of $k_7 [O_2] \gg k_8$ is valid for $[O_2] > 0.4$ mm. Further inclusion of the reverse of reaction (10) (reaction of the carbenes with oxygen) modifies the quantum yield equation to

$$\emptyset_{CF_2O} = \emptyset_{CF_2O}\,(A) + \frac{k_{10}^{-1} . k_4 [O_2][Ol]}{k_2 (k_{10} + k_4 [Ol])}$$

$$\emptyset_{PF} = \emptyset_{PF}\,(B) + \frac{k_{10}^{-1}\, k_4 [O_2][Ol]}{k_2 (k_{10} + k_4 [Ol])}$$

$$\emptyset_{1\,1FP} = 1$$

where $\emptyset_{CF_2O}\,(A)$ and $\emptyset_{PF}\,(B)$ represent quantum yields of CF_2O and EtCFO derived from the previous scheme (equations A and B respectively). The form of the equations above indicate that the quantum yields of CF_2O and EtCFO are increased (over and above those of the previous scheme) linearly with oxygen concentration (olefin concentration constant). However observed constant quantum yields at high oxygen concentration suggests that this linear proportion is not significant (implying the reaction of the carbene with oxygen does not play an important part in the overall reaction scheme.)

It has been noted that all reaction schemes predict

$$\phi_{CF_2O} = 1 + \phi_{PF}$$

Examination of Table 3,9 reveals this not to be the case. It was found that all likely mechanisms by which ϕ_{CF_2O} was increased to greater than unity also required an equal increase in the propionyl fluoride quantum yield. One possible explanation of this discrepancy is error incurred in the estimation of the propionyl fluoride calibration factor, It will be remembered from section 3.2 a factor was calculated for propionyl fluoride, assuming the response of CH_3CH_2CFO to be approximately the same as ethane. If the factor for propionyl fluoride is substantially greater than ethane, this would explain the apparent low yield of propionyl fluoride. An alternative explanation is rapid decomposition of propionyl fluoride as it is formed (formyl fluoride CHFO, is known to decompose completely within 24 hours at room temperature[96]). Difficulty of preparation and purification of an authentic sample (section 2.4c) for calibration purposes prevented subsequent clarification of this point.

Ethylene yields in presence of O_2

The two sources of ethylene considered were

$$\underset{(Z)}{CH_3CH_2\dot{C}F - CF_2\dot{O}} \xrightarrow{k_a} C_2H_4 + \text{fragments} \qquad (a)$$

$$\text{and} \quad \underset{(X)}{C_2H_5CF:} \xrightarrow{k_b} C_2H_4 + CHF: \qquad (b)$$

From the discussion in this chapter all schemes leave $[X]$ unchanged in the presence of oxygen.

As $R_{C_2H_4} = k_b[X]$, the rate predicted is unchanged with oxygen present.

However, if ethylene is formed by reaction (a)

$$R_{C_2H_4} = k_a[Z] = \frac{k_aR_{N_2}}{(k_8 + k_7[O_2])} \qquad ([Z] \text{ taken from scheme 3})$$

If $k_7[O_2] \gg k_8$ as already supposed at $[O_2] > 0.4$mm then $R_{C_2H_4} = \frac{k_aR_{N_2}}{k_7[O_2]}$. This predicts a rate dependent upon O_2 concentration. Examination of Table 3.9 reveals $\phi_{C_2H_4}$ is <u>independent</u> of O_2 which supports reaction (b).

7.9 THERMOCHEMISTRY

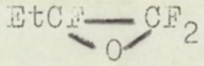
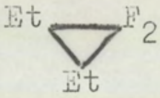
The feasibility of various reactions already described in this chapter have been assessed purely on their ability to explain product formation and the influence of factors, such as pressure, on the yields. However, it is important at this stage to consider the additional criterion of thermochemistry.

Below in Table 7.3 are listed some reactions considered important in sections 7.2 - 7.4 with corresponding estimated heats of reaction. Heats of formation of reactants and products are taken from Table 5.2. Unfortunately, difficulty was encountered in the estimation of heats of formation of many of the fluoro-oxygen radicals and biradicals. For this reason, the list is restricted to those reactions occurring in the absence of molecular oxygen. It should be noted that the reactions have been renumbered for ease of classification.

It appears from the results shown in Table 7.3 that most of the included reactions are favourable on thermochemical grounds (the majority being exothermic). The reactions are briefly discussed below, classified in the manner illustrated in the Table.

TABLE 7.3

POSSIBLE PROCESSES IN THE ABSENCE OF OXYGEN AND THEIR HEATS OF REACTION

	Reaction	ΔH $(kJmol.^{-1})$
1a	$Hg^* + N_2O \longrightarrow Hg(^1S_0) + N_2 + O(^3P)$	-221
1b	$Hg^* + EtCF{=}CF_2 \longrightarrow Hg(^1S_0) + CF_2{=}CF^{\cdot} + C_2H_5$	+40
1c	$Hg^* + EtCF{=}CF_2 \longrightarrow Hg(^1S_0) + CF_2{=}CFH + C_2H_4$	-281
2a	$O + EtCF{=}CF_2 \longrightarrow CF_2O + C_2H_5CF:$	-389
2b	$O + EtCF{=}CF_2 \longrightarrow C_2H_5CFO + CF_2:$	-354
2c	$O + EtCF{=}CF_2 \longrightarrow$  $EtCF{-}CF_2$ (O)	-374
2d	$O + CH_3CH{=}CHF \longrightarrow CHFO + C_2H_4$	-286
3a	$CH_3CH_2CF: \longrightarrow$ cis and trans $CH_3CH{=}CHF$	-145
3b	$CH_3CH_2CF: \longrightarrow$ cyclo C_3H_5F	-1q1
3c	$CH_3CH_2CF: \longrightarrow C_2H_4 + CHF:$	+68
3d	$CH_3CH_2CF: + EtCF{=}CF_2 \longrightarrow$ 	-90
4a	$C_2H_5^{\cdot} + EtCF{=}CF_2 \longrightarrow C_3H_8 + {}^{\cdot}CH_2CF{=}CF_2$	-50
4b	$C_2H_5^{\cdot} + EtCF{=}CF_2 \longrightarrow C_2H_6 + CH_3\dot{C}HCF{=}CF_2$	-51

a) Quenching reactions (1a, 1b and 1c)

Reaction 1a has been well described already and requires no further discussion.

Quenching of triplet mercury by 1,1,2TFB to yield ethyl radicals in the manner illustrated by reaction 1b is slightly endothermic by 40 kJmol.$^{-1}$. This value is rather uncertain as the exact nature of the products of this primary reaction have not been elucidated. However, in view of the high positive heat of formation of ethyl radicals (+109 kJmol.$^{-1}$) it is unlikely that any reaction producing the radical is very exothermic.

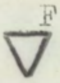
Reaction 1c, although appearing energetically favourable, has been discounted as a source of ethylene because of the absence of trifluoroethylene amongst the reaction products.

b) Reactions of oxygen atoms (2a, 2b, 2c and 2d)

All are considerably exothermic varying from -286 kJmol.$^{-1}$ for reaction 2d to -389 kJmol.$^{-1}$ for 2a. This is explained largely by the "driving force" for these reactions which is the highly reactive oxygen atom (heat of formation +248 kJmol.$^{-1}$). The absence of the epoxide $CH_3CH_2\underset{\diagdown \; O \; \diagup}{CF - CF_2}$ amongst the reaction products can probably be ascribed to this high exothermicity; the excess energy of the process must be retained by the epoxide molecule on formation. Necessarily, the high energy content of the molecule substantially reduces the lifetime. If the energy cannot be distributed adequately betweeen the available vibrational modes of the molecule and the lifetime is shorter than the time necessary to experience a collision, then fragmentation results. For this reason, high excess energy of the molecule can make pressure stabilisation difficult.

Comparison of reaction 2a and 2b reveals addition of oxygen atoms to 1,1,2 TFB is slightly more favourable for CF_2O formation than C_2H_5CFO by about 40 kJmol.$^{-1}$. However, it is difficult to believe that this small difference could be wholly responsible for the great predominance of reactions 2a over 2b. Evidently, other factors must play an important part in determining the main course of reaction. Support for the possible ~~variation~~ reaction of oxygen atoms with cis and trans 1 fluoropropene (2d) is provided by the high exothermicity of the reactions.

c) Reactions of CH_3CH_2CF: (3a, 3b, 3c, and 3d)

It can be seen that the exothermicities of the three carbene reactions considered in section 7.3, namely H atom shift, cyclisation and addition to the olefin, parallel well observed product yields from the three reactions. Exothermicities predict yields in the order $CH_3CH{=}CHF$ >  > addition product as was observed in this system.

Decomposition of the carbene to give ethylene (3c) would appear energetically unfavourable compared to the three other possible reactions of the carbene. For this reason, it appears unlikely that this reaction is significant as a source of ethylene.

d) Ethyl radical abstraction reactions (4a and 4b)

Both abstraction of a hydrogen atom and methyl group from 1,1,2 TFB by an ethyl radical are energetically feasible (both with ΔH of about -50 kJmol^{-1}). The results of the calculation support the view that propane is formed by reaction 4b.

7.9 CONCLUSIONS

It is believed that the mechanisms derived adequately describe the reaction of $O(^3P)$ with 1,1,2 TFB, both in the presence and absence of molecular oxygen. The mechanisms are illustrated diagrammatically in Figs.7.2 and 7.3 . Below is a summary of the main points of the reactions.

a) In the Absence of Oxygen (Fig.7.2)

The reaction proceeds almost entirely (greater than 90%) to yield ultimately, carbonyl fluoride and cis and trans 1 fluoropropene. The primary process is thought to be initial formation of an oxygen-containing biradical adduct, which decomposes rapidly to carbonyl fluoride and the carbene CH_3CH_2CF:. Predominant isomerisation of this carbene (by hydrogen atom shift) gives an overall 1 fluorpropene yield approximately equivalent to that of carbonyl fluoride. The cis/trans ratio of 1 fluoropropene shows a slight pressure dependence which has been explained by progressive removal of excess vibrational energy from a the carbene, with increasing pressure.

A notable feature of the reaction is the high yield of carbonyl fluoride which is characteristic of the reaction of those perfluoro-olefins with a terminal double bond (perfluoropropylene and tetrafluoroethylene). It has been seen that partially fluorinated olefins in which fluorine substitution is remote from the double bond give large yields of epoxide and aldehyde (as in the case of 2trifluoromethylpropene). This behaviour is similar to that of non-fluorinated olefins. The results of this work would lead one to anticipate that those partially fluorinated olefins with a <u>fully</u> fluorinated terminal double bond behave essentially as their perfluoro- counterparts. Absence of epoxide has been attributed to the high exothermicity of the addition process. It is possible that at high pressures (greater than those investigated in this study), the biradical adduct could be collisionally astabilised. If this is true, it is reasonable to suppose that epoxides and aldehyde yields would be considerably increased. This hypothesis can be broadened to predict that at sufficiently high pressures the fluorinated olefin systems assume the same characteristics as those exhibited by the non-fluorinated olefins, but as yet, remains to be verified.

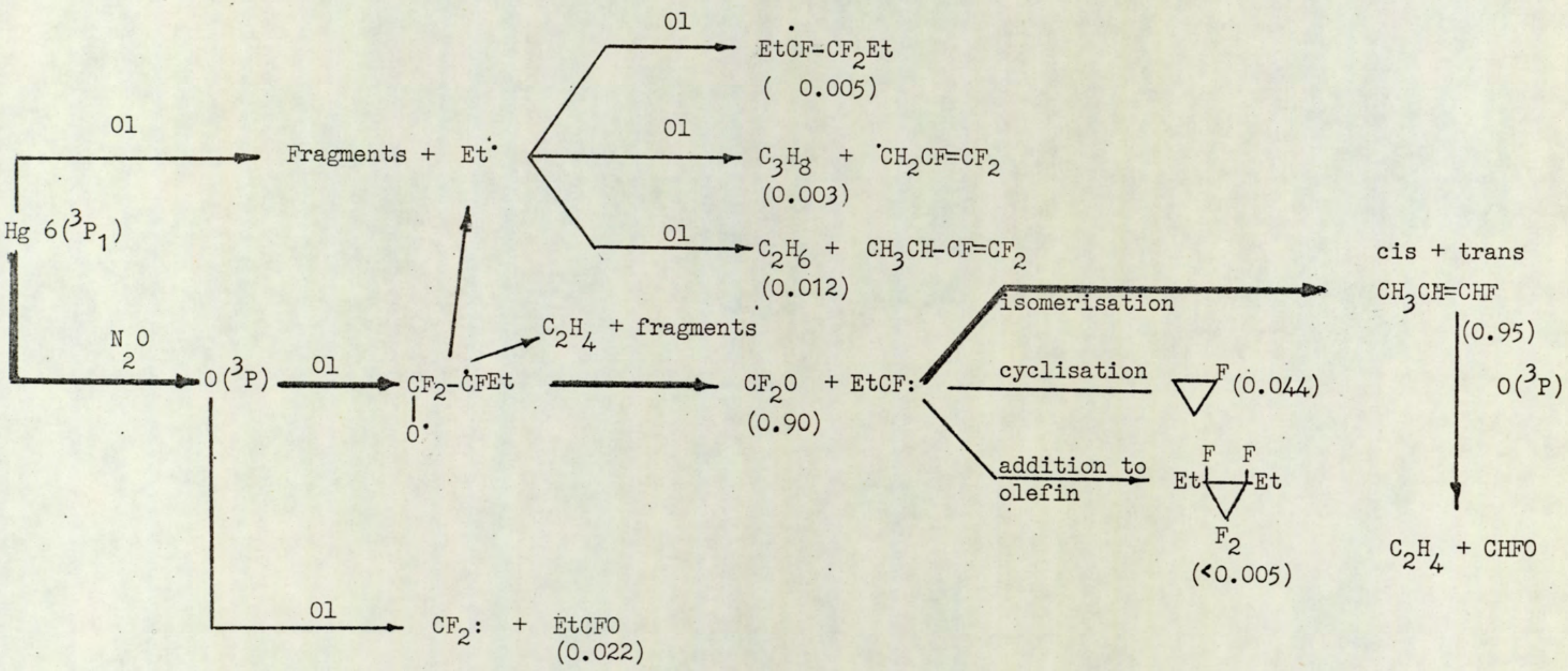
Minor product formation, whilst being relatively insignificant, is adequately explained by the reaction scheme.

b) <u>In the Presence of Oxygen (Fig. 7.3)</u>

Unchanged 1 fluoropropene yields in the presence of oxygen are not necessarily indicative of non-particpation of oxygen in the reaction scheme. Alternatively, this has been interpreted as reaction of the biradical adduct with oxygen in the manner illustrated in Fig.7.3. The scheme also explains increased yields of carbonyl and propionyl fluoride, observed when oxygen is added to the system.

Reaction o the <u>carbene</u> with oxygen, whilst satisfactorily explaining the unchanged 1 fluoropropene

FIG. 7.2 SUMMARY OF THE PROPOSED REACTION MECHANISM $O(^3P)$ + CF_2=CFEt IN THE ABSENCE OF OXYGEN

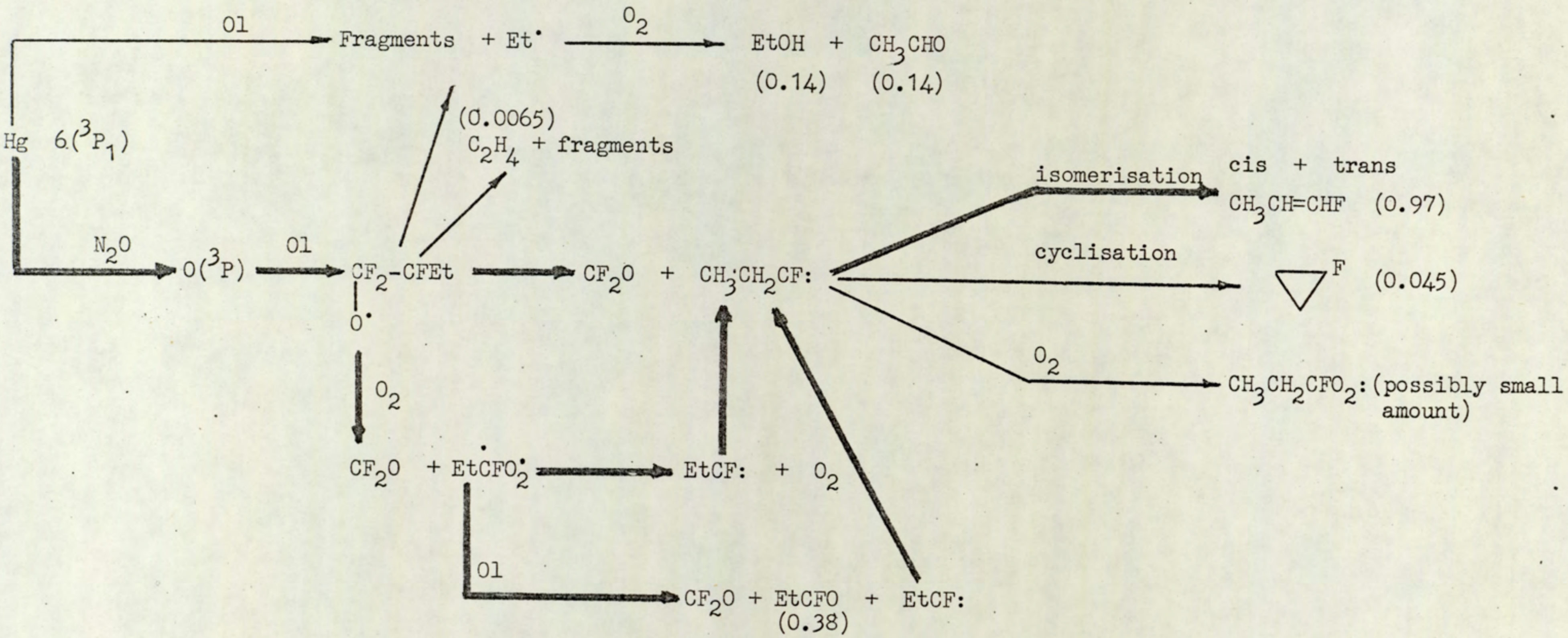


Heavy line represents the main course of the reaction.

The quantum yields of the products are indicated in brackets for a typical run at 250mm. Hg pressure at 23°C.

Ol represents CF_2=CFEt

FIG. 7.3 SUMMARY OF THE PROPOSED REACTION MECHANISM $O(^3P) + CF_2{=}CFC_2H_5$ IN THE PRESENCE OF OXYGEN.



The quantum yields of the products are enclosed in brackets. They represent those yields observed with $[O_2] = 4.5$mm.Hg.

Total CF_2O yield was 1.84, but has not been apportioned to the relevant reactions due to lack of information.

Ol represents $CF_2{=}CFEt$. Heavy lines represent the main course of reaction.

yield, predicts carbonyl and propionyl fluoride yields which are linearly dependant upon oxygen concentration, contrary to observation. Reaction is thought unlikely for this reason. On similar reasoning, schemes involving regeneration of oxygen atoms have also been discounted.

Satisfactory correlation of the preferred mechanism with observed product yields is tentative evidence of the existence of the biradical $C_2H_5\dot{C}F-CF_2O^{\cdot}$ and implies necessarily that it is sufficiently long-lived to react with an oxygen molecule. At first sight, this might appear contradictory to the ideas already advanced on lack of pressure stabilisation in this system. This can be explained by supposing that the biradical requires a multiple collision to be collisionally stabilised but need experience only a single collision to react with oxygen. The correlation is the only indication in the course of this work which directly supports the existence of a reactive intermediate prior to carbene formation.

Addition of oxygen provided valuable information on the origin of the minor products (ethane and propane) which are formed in the normal course of reaction (O_2 absent). Results were readily interpretable and provided evidence which could have proved difficult to obtain by alternative methods.

The major inconsistency between theory and results is the observed quantum yield of propionyl fluoride which is appreciably lower than predicted by the reaction scheme postulated. This has been attributed to error incurred in estimating the G.L.C. response factor of propionyl fluoride and/or a decomposition pathway for EtCFO which,as yet, remains uncertain.

In conclusion, it is appreciated that with relatively large errors possibly present in measured yields of carbonyl and propionyl fluoride, the finer detail of the proposed mechanism must be regarded as highly speculative. Further investigation, over a comprehensive range of olefin and oxygen concentrations, and accurate measurement of product yields would prove useful in this respect.

APPENDIX 1

a) MASS SPECTRAL DATA

All mass spectral data obtained using an A.E.I. MS 9 mass spectrometer.

All intensities are relative to the base peak of the spectrum (peak height = 100)

m/e	cis 1 fluoro-propene. rel.intensity	trans 1 fluoro-propene. rel. intensity	allyl fluoride rel.int.	fluoro-cyclo-propene rel.int.	probable frag-ment.
25	2	2	2	2	
26	4	4	10	6	
27	15	15	28	24	$C_2H_3^+$
28	2	8	0	20	(N_2^+)
29	2	0	0	2	
31	5	6	6	5	
32	2	2	2	2	
33	11	12	15	12	CH_2F^+
36	1	0	2	1	
37	3	4	8	6	
38	3	4	10	4	
39	27	30	55	40	$C_3H_3^+$
40	3	3	9	9	
41	2	2	8	7	
42	1	0	0	0	
43	4	0	0	1	C_2F^+
44	2	8	4	30	C_2FH^+, N_2O
45	2	2	2	6	$C_2FH_2^+$
55	1	0	0	0	C_3^+F
56	2	2	2	2	C_3H^+F
57	17	20	12	13	$C_3H_2^+F$
58	5	6	3	4	C_3H_3F
59	100	100	100	100	$C_3H_4^+F$
60	55	61	57	65	P
61	2	2	2	2	P + 1

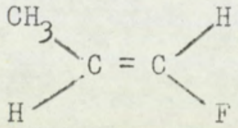
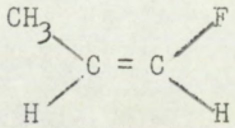
$\frac{m}{e}$	$C_2H_5CF=CF_2$ rel. int.	prob. fragment	$CH_2=CHCF=CF_2$ rel. int.	prob. fragment	C_2H_5F rel.int.	prob. fragment
15	4	CH_3^+	0		2	CH_3^+
25	0		2		2	$C2H^+$
26	0		3		15	$C_2H_2^+$
27	4		4		44	$C_2H_3^+$
28	10	$N_2{}^+$	0		8	$C_2H_4^+, N_2$
29	0		0		10	$C_2H_5^+$
31	11	CF^+	13	CF^+	2	
32	0		2		1	
33	3		2		35	CH_2F^+
37	3		5		0	
38	4		9	$C_3H_2^+$	0	
39	20	$C_3H_3^+$	53	$C_3H_3^+$	0	
40	2		3		0	
41	8		2		0	
44	2		3		6	C_2HF^+
45	8	$C_2FH_2^+$	3		8	$C_2H_2F^+$
46	1		0		10	$C_2H_3F^+$
47	0		0		100	$C_2H_4F^+$
48	0		0		9	$C_2H_5F^+$
49	0		2		0	
50	2		2		0	
51	15	CHF_2^+	8	CHF_2^+	0	
56	3		9		0	
57	11	$C_3H_2F^+$	53	$C_3H_2F^+$	0	
58	2	$C_3H_3F^+$	5		0	
59	24	$C_3H_4F^+$	5		0	
60	13	$C_3H_5F^+$	3		0	
64	4	$C_2F_2H_2^+$	21	$C_2F_2H_2^+$	0	
65	3	$C_2F_2H_3^+$	4		0	

$\frac{m}{e}$	$C_2H_5CF=CF_2$ rel. int.	prob. fragment	$CH_2=CHCF=CF_2$ rel. int.	prob. fragment	C_2H_5F rel.int.	prob. fragment
69	46	CF_3^+	4		0	
71	2		0		0	
75	9		12	$C_3F_2H^+$	0	
77	3		5		0	
82	8		12	$C_4F_2H^+$	0	
88	2		15	$C_4F_2H^+$	0	
89	5		5		0	
90	2		8		0	
93	0		3		0	
94	2		2		0	
95	100	$C_3F_3H_2^+$	20	$C_3F_3H_2^+$	0	
96	3		2		0	
106	0		5		0	
107	0		3		0	
108	0		100	$C_4F_3H_3^+$(P)	0	
109	3		8		0	
110	40	$C_4F_3H_5$(P)	9	$C_4F_3H_5^+$ (impurity)	0	
111	2	P + 1	0		0	

b) INFRA RED SPECTRAL DATA

Spectra were obtained using a Perkin Elmer 127 IR spectrometer, gases enclosed in the microcell previously described in Chapter 2. Intensities are classified as

vs: very strong s: strong m: medium w: weak.

trans 1 fluoropropene		cis 1 fluoropropene	
			
WAVELENGTH (cm.$^{-1}$)	INTENSITY	WAVELENGTH (cm.$^{-1}$)	INTENSITY
900	m	835	s
925	w	840	s
1080	m	845	m
1100	m	995	s
1120	s	1000	vs
1136	vs	1100	m
1640-1690	m	1125	m
2830	w	1225	m
2900	m	1235	m
2930	m	1245	m
2970	w	1340	w
		1360	w
		1640-1690	s
		2920	m
		2945	m
		3060	w

1,1,2 trifluorobutene-1

$CH_3CH_2CF{=}CF_2$

WAVELENGTH (cm.$^{-1}$)	INTENSITY
920	w
1030	m
1140	s
1235	m
1280	s
1290	s
1370	w
1430	m
1460	s
1800	m
2890	w
2920	w
2970	m

Allyl fluoride

$CH_2{=}CHCH_2F$

WAVELENGTH (cm.$^{-1}$)	INTENSITY
925	m
980	m
1020	s
1030	s
1100	m
1360	w
1415	m
1435	w

1,1,2 trifluoro-1,3 butadiene

$CH_2{=}CH.CF{=}CF_2$

WAVELENGTH (cm.$^{-1}$)	INTENSITY
780	w
840	m
900	s
910	s
60	m
970	s
1080	vs
1095	s
1140	m
1260	vs
1280	vs
1320	vs
1335	s
1415	s
1700-1770	s
1790	m
2590	w
2830	w
2900	w
2970	m
3020	w
3100	w

Carbonyl fluoride		Formyl fluoride	
CF_2O (using Perkin Elmer 225)		CHFO (using Perkin Elmer 457)	
WAVELENGTH(cm.$^{-1}$)	INTENSITY	WAVELENGTH (cm.$^{-1}$)	intensity
1022	m	1080	m
1927	s	1818	m
1942	s	1834	s
1956	s	1849	m
		2655	w
		2680	w
		2705	w
		2735	m
		2755	m
		2780	s
		2800	s
		28 0	s
		2845	s
		2870	s
		2910	m
		2930	m
		2945	s
		2963	s
		2980	s
		3000	s
		3020	m
		3035	w
		3045	w
		3060	w

APPENDIX 2

This appendix contains detailed quantative results of the series of runs investigating the reaction of oxygen atoms with the fluoroethylenes (summary in Chapter 4).

Key to tables overleaf.

A	represents	ETHYLENE $CH_2=CH_2$
B	"	VINYL FLUORIDE $CH_2=CHF$
C	"	1,1,DIFLUOROETHYLENE $CF_2=CH_2$
D	"	cis 1,2,DIFLUOROETHYLENE cis $CHF=CHF$
E	"	trans 1,2 DIFLUOROETHYLENE trans $CHF=$
F	"	TRIFLUOROETHYLENE $CF_2=CFH$
G	"	TETRAFLUOROETHYLENE $CF_2=CF_2$
*	"	a run with the reference olefin absent
$P_{ref.}$	"	pressure of reference olefin in a volume of 56.6ml.at 23°C.
$P_{ol.}$	"	pressure of olefin in a volume of 56.6 ml. at 23°C.
P_{N_2}	"	pressure of nitrogen in a volume of 2.22 ml. at 23°C.
P_{CO}	"	pressure of carbon monoxide in a volume of 2.22 ml. at 23°C.

APPENDIX 2

QUANTITATIVE RESULTS OF $O(^3P)$ + FLUOROETHYLENES

Run No.	P totalmm	Ol.	P REF	P Ol.	P N_2	P CO	Temp °C	Area epoxide	Area aldehyde	Ratio $\frac{\text{epox}}{\text{alde.}}$
101	7515	B"	169	0	116.1	2.0	22.2	6308	4290	1.97
102	606	B	158	0	220.7	n.k.	20	11872	7599	2.07
103	606	B	168	0	177.6	3.8	22.5	10000	6428	2.10
104	597	B*	0	140	181	0.2	20	-	-	-
105	595	B	149.1	154.0	211	19.5	24.9	6662	4568	1.948
106	610	B	148.0	22.0	187.6	21.2	23.6	5032	3547	1.925
107	605	B	139.2	301.0	191.6	26.3	23.8	4218	2985	1.932
108	596	B	158	0	196.6	3.9	23.0	11510	7498	2.02
109	634	B	155	0.	225.0	3.8	149	13555	9295	1.91
110	609	B	148	0	231.6	3.6	150	14320	9790	1.93
111	616	B	151.0	156.0	215.8	27.0	149	7055	5326	1.915
112	625	B	160.8	230.6	215.9	28.9	149	6085	4678	1.92
113	610	B	195.5	109.1	211.5	18.6	147	8665	6212	1.94
114	610	B	0	188	219.3	54.2	150	-	-	-
115	604	B	189	0	213.9	4.1	151	13095	8830	1.935
116	599	-	148	0	192.4	2.2	24.3	11075	7186	2.024
117	597	-	168	0	189.1	2.8	23.6	10970	7150	2.020
118	598	C*	0	159	179.6	25.2	23.0	-	-	-
119	599	C*	0	185	168	21.7	21.0	-	-	-
120	601	C	158.2	199.0	174.5	8.2	23.2	6870	4576	2.004
121	599	C	145.6	434.3	181.2	11.1	26.0	4788	3223	1.982
122	586	C	147.3	311.8	182.5	10.3	24.8	5730	3804	-
123	607	C	193	0	217.9	3.1	150	13045	8740	-
124	610	C	179.0	182.2	206.1	12.9	150	8445	5850	-

APPENDIX 2 (cont.)

Run	Area ratio $\frac{\text{epox.}}{\text{alde.}}$	Init. ratio $\frac{P_{ol}}{P_{ref}}$	conv. ref. %	conv. ol. %	$1/Q_E$	$1/Q_A$	%CO	Q_{CO}
101	1.46	0	2.68	0	0.0183	0.0270	1.72	-
102	1.56	0	5.23	0	0.0185	0.0290	1.68	-
103	1.56	0	4.15	0	0.0177	0.0276	2.14	-
104	-		0	-	-	-	22.82	22.82
105	1.46	1.033	3.22	1.95	0.0316	0.0461	9.24	8.256
106	1.42	1.500	2.49	1.53	0.0372	0.0528	11.30	10.450
107	1.41	2.162	2.22	1.43	0.0454	0.0641	13.73	13.031
108	1.54	0	5.12	0	0.0170	0.0262	1.98	-
109	1.46	0	5.62	0	0.0165	0.0242	1.69	-
110	1.46	0	6.21	0	0.0161	0.0236	1.55	-
111	1.32	1.033	3.08	2.55	0.0305	0.0405	12.51	11.598
112	1.30	1.434	2.50	1.88	0.0354	0.0461	13.39	12.596
113	1.396	0.558	2.87	2.37	0.0244	0.0340	8.79	7.681
114	-	-	-0	-	-	-	24.70	24.70
115	1.48_4	0	4.41	0	0.0163	0.0242	1.917	-
116	1.54_1	0	5.05	0	0.0173	0.0267	1.14	-
117	1.53_5	0	4.42	0	0.0172	0.0264	1.48	-
118	-		0	-	-	-	14.03	14.03
119	-		0	-	-	-	12.92	12.92
120	1.50_1	1.258	2.969	0.93	0.0254	0.0381	4.699	3.649
121	1.48_5	2.983	2.261	0.658	0.0378	0.0562	6.126	5.418
122	1.506	2.117	2.655	0.819	0.0318	0.0479	5.644	4.808
123	1.49_1	0	4.30	-	0.0167	0.0249	1.423	-
124	1.44_4	1.018	3.076	1.63	0.0244	0.0352	6.259	5.142

APPENDIX 2 (cont.)

Run	P total mm	Ol.	P_{REF}	$P_{OL.}$	P_{N_2}	P_{CO}	Temp °C	Area epoxide	Area aldehyde	Pk.ht ratio	Area ratio
125	611	C	149.3	320	200.9	16.3	150	5770	4102	-	1.407
126	587	C	165.2	486.0	188.8	19.9	150	4762	3472	-	1.370
127	587	C*	0	175.0	206.8	33.6	150	-	-	-	-
128	600	F*	0	160.0	220.5	9.0	23	-	-	-	-
129	596	F*	0	155	2329	4.6	24.8	-	-	-	-
130	595	F	178.2	183.0	189.4	2.4	26.2	5274	3554	-	1.484
131	580	F	193.0	414.8	181.3	3.0	25.5	3120	2285	2.05	1.365
132	598		172.5	105,5	178,9	3.1	25,5	6365	4200	-	1.515
133	590		186.0	0	189.9	2.0	25.5	11110	7224	2.011	1.5379
134	602	F	156.4	241.0	169.8	2.2	24.1	3714	2555	-	1.454
135	599		153	0	212.7	5.0	151	13165	8875	-	1.4833
136	621	F	169.3	166.2	210.8	6.2	150	6525	4376	-	1.491
137	601	F	155.8	241.3	207.8	7.4	152	4888	3285	-	1.493
138	601	F	166.0	99.2	206.8	5.7	150	7595	5094	-	1.496
141	597	A*	0	180	181.2	80.7	24.6	-	-	-	-
142	603	A	171.8	160.9	196.6	52.7	24.7	3812	2911	-	1.310
143	601	A	166.3	98.4	179.7	39.9	24.8	4662	3354	-	1.390
144	604	A	182.5	134.6	172.2	42.2	24.1	4092	2983	-	1.372
145	597		180	0	168.2	1.6	22.6	9805	6410	-	1.550
146	606	A*	0	178	209.0	95.3	148	-	-	-	-
147	603	A	172.8	167.1	200.0	67.8	150	5380	3597	-	1.496
148	601	A	178.9	105.2	204.3	55.2	149	6380	4536	-	1.407
149	597	A	170.7	136.1	194.8	61.2	150	5010	3574	-	1.402

APPENDIX 2 (cont.)

Run	Init. ratio $\frac{P_{ol.}}{P_{ref.}}$	Mean ratio $\frac{P_{ol.}}{P_{ref.}}$	conv. ref. %	conv. ol. %	$1/_{QE}$	$1/_{QA}$	%CO	Q_{CO}	$\%CH_4$
125	2.143	2.157	2.553	1.287	0.0348	0.0489	11.137	7.320	
126	2.942	2.955	1.929	1.070	0.0396	0.0543	10.54	9.834	
127			0	–	–	–	16.25	16.25	
128			0	–	–	–	4.1	4.1	
129			0	–	–	–	2.0	2.0	
130	1.027	1.0338	2.037	.7033	0.0359	0.0532	1.267	0.5198	
131	2.149	2.155	1.162	0.67	0.0581	0.0793	1.655	1.173	
132	.6115	0.6139	2.513	1.747	0.0281	0.0425	1.733	0.788	
133	0	0	4.035	0	0.0170	0.0262	1.05	–	
134	1.541	1.549	1.651	0.648	0.0457	0.0664	1.30	0.703	
135	0	0	5.53	0	0.0161	0.0239	2.35	2.35	
136	.9816	0.9765	2.47	3.50	0.0323	0.0481	2.941	2.112	
137	1.548	1.539	2.011	3.299	0.0425	0.0632	3.561	2.931	
138	.5975	0.5920	2.969	4.780	0.0268	0.0401	2.756	1.754	
141			0	–	–	–	44.37	44.37	10.8
142	.9365	0.9308	1.63	2.84	0.0515	0.0675	26.31	26.25	5.7
143	.5917	0.5872	1.99	3.47	0.0385	0.0535	22.20	21.48	6.3
144	.7375	0.7334	1.61	2.70	0.0420	0.0577	24.51	23.85	5.2
145	0	0	3.69	0	0.0171	0.0262	0.951	–	0
146			0	–	–	–	45.55	45.55	6.3
147	.9670	0.9600	1.99	3.42	0.0371	0.0556	33.9	33.18	3.5
148	.5880	0.5820	2.35	4.37	0.0320	0.0450	27.02	26.16	2.3
149	.7973	0.7398	1.94	3.78	0.0388	0.0545	31.42	30.71	2.9

APPENDIX 2 (cont.)

Run	P total mm	Ol.	$P_{ref.}$	$P_{ol.}$	P_{N_2}	P_{CO}	Temp °C	Area epoxide	Area aldehyde	Area ratio epox./alde.
150	598		180	0	202.9	4.2	150	12405	8475	1.464
151	600	A*	0	160	202.0	91.2	147	-	-	-
152	598	G*	0	173	197.9	1.6	145	-	-	-
153	598	G	187.8	166.6	149.2	0.3	21.2	2334	1565	1.492
154	592		196	0	156.0	1.0	22.2	8890	5862	1.520
155	598	G	184.0	97.0	173.0	0.8	23.3	4412	2938	1.501
156	598	G	181.8	138.0	161.8	0.6	23.4	2966	1988	1.492
157	610	G	196.2	207.6	188.7	1.3	149	3646	2408	1.514
158	593	G	188.0	96.6	200.8	1.6	149	5950	3968	1.499
159	591	G	178.5	65.2	191.6	1.9	152	6665	4482	1.487
160	598		195	0	190.6	2.9	150	11640	7970	1.460
161	598	A	188.2	58.0	189.7	35.6	150	8030	5696	1.415
162	604	A	181.8	149.5	179.8	59.4	149	4834	3348	1.444
163	597	A	177.1	63.7	216.2	39.5	26.5	7310	5168	1.414
164	593	G	193.8	56.5	169.0	1.0	26.7	5490	3664	1.498
165	593		192	0	171.4	2.6	26.7	10410	6870	1.515
166	595	D	0	135	173.7	4.0	25.5	-	-	-
167	597		140	0	175.5	2.1	26.0	10565	6915	1.528
168	593	E*	0	130	174.1	2.6	26.3	-	-	-
169	597	D	118.5	126.9	176.1	3.7	27.2	6535	4440	1.472
170	599	E	125.0	134.2	175.8	3.5	27.5	5023	3374	1.489
171	604	D	149.7	234.9	163.9	2.9	25.5	5184	3484	1.488
172	602	E	147.4	231.8	165.7	2.4	24.5	3806	2578	1.476
173	593	D	127.2	82.8	159.5	1.2	23.9	7035	4716	1.492
174	586	E	138.9	91.7	170.8	2.0	24.7	6190	4172	1.484

APPENDIX 2 (cont.)

Run	Init. ratio $\frac{P_{ol.}}{P_{ref.}}$	Mean ratio $\frac{P_{ol.}}{P_{ref.}}$	conv. ref. %	conv. oo. %	1/ QE	1/ QA	%CO	Q CO	%CH_4
150	0	0	4.46	0	0.0163	0.0239	2.07	-	-
151			0	-	-	-	45.15	45.15	6.3
152			0	-	-	-	0.8	-	-
153	0.8871	0.8943	0.85	0.76	0.0639	0.0953	0.20	-	-
154	0	0	3.09	0	0.0175	0.0266	0.64	-	-
155	0.527	0.5355	1.64	1.52	0.0403	0.0605	0.45	-	-
156	0.759	0.7654	1.12	0.55	0.0545	0.0813	0.37	-	-
157	1.0581	1.0602	1.18	0.79	0.0517	0.0783	0.69	-	-
158	0.5138	0.5188	2.02	0.08	0.0337	0.0506	0.80	-	-
159	0.3652	0.3659	2.40	0.96	0.0287	0.0427	0.99	-	-
160	0	-	3.86	0	0.0163	0.0239	1.52	-	-
161	0.3081	0.3048	2.81	4.96	0.0236	0.0334	18.77	17.61	1 8
162	0.8223	0.8155	1.73	3.36	0.0371	0.0537	33.204	32.47	3.7
163	0.3596	0.3554	2.91	5.20	0.0295	0.0418	18.270	17.34	10.3
164	0.2915	0.2991	1.94	-	0.0307	0.0461	0.59	-	-
165	0	0	3.52	0	0.0164	0.0249	1.52	-	-
166			0	-	-	-	2.30	-	-
167	0	0	4.89	0	0.0166	0.0253	1.20	-	-
168			0	-	-	-	1.49	-	-
169	1.0708	1.0759	3.68	2.71	0.0269	0.0396	2.10	1.145	-
170	1.0736	1.0643	2.64	4.34	0.0349	0.0521	1.99	1.259	-
171	1.5691	1.5780	2.27	1.14	0.0316	0.0470	1.77	0.9607	-
172	1.5725	1.5732	1.70	1.62	0.0435	0.0642	1.45	0.8599	-
173	0.6509	0.6670	3.62	1.23	0.0226	0.0338	0.752	-	-
174	0.6601	0.6660	2.93	1.18	0.0275	0.0409	1.17	-	-

APPENDIX 2 (cont.)

Run	P total mm.	Ol.	$P_{ref.}$	$P_{ol.}$	P_{N_2}	P_{CO}	Temp °C	Area epoxide	Area aldehyde	Area ratio $\frac{\text{epox.}}{\text{alde.}}$
175	603		120	0	173.0	2.6	24.0	10430	6870	1.520
176	605		120	0	205.1	3.4	154	13090	9015	1.452
177	602	D*	0	120	223.4	20.4	152	-	-	-
178	602	E*	0	120	208.8	15.0	152	-	-	--
179	602	D	138.3	132.6	196.2	8.8	149	7890	5320	1.483
180	602	E	123.5	134.9	195.2	8.3	150	5618	3880	1.448
181	596		115	00	198.7	3.3	151	12680	8600	1.474
182	603	D	123.1	73.8	194.3	7.3	151	8710	5868	1.484
183	597	E	129.0	75.3	186.2	9.1	151	7320	5014	1.460
184	604	D	135.3	252.9	183.5	12.9	149	5038	3457	1.457
185	602	E	130.8	245.7	182.2	10.9	151	3724	2616	1.4242
186	601	D	132.0	42.60	189.8	4.9	153	10035	6766	1.483
187	604	E	128.2	54.4	189.4	8.1	152	8510	5832	1.459

APPENDIX 2 (cont.)

Run	Init. ratio $\frac{P_{ol.}}{P_{ref.}}$	Mean ratio $\frac{P_{ol.}}{P_{ref.}}$	conv, ref. %	conv. ol. %	$^1/_{QE}$	$^1/_{QA}$	Q_{CO}
175	0	0	4.70	0	0.0166	0.0252	-
176	0	0	6.71	0	0.0156	0.0227	-
177			0	0	-	-	9.13
178			0	0	-	-	7.18
179	0.9587	0.9649	3.47	2.20	0.0248	0.0368	3.47
180	1.0923	1.0924	2.80	2.78	0.0347	0.0503	3.51
181	0	0	6.72	-	0.0156	0.0231	-
182	0.5995	0.6036	4.30	2.96	0.0223	0.0331	2.618
183	0.5837	0.5784	3.48	5.24	0.0254	0.0371	3.88
184	1.8691	1.8720	2.28	1.97	0.0364	0.0530	6.33
185	1.8784	1.8742	1.77	2.21	0.0489	0.0696	5.45
186	0.3227	0.3264	4.62	2.368	0.0189	0.0280	1.237
187	0.4243	0.4202	4.07	5.95	0.0222	0.0324	3.128

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