KINETICS OF SOME GAS PHASE REACTIONS OF HALOGENATED FREE RADICALS

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Kinetics of some gas phase reactions of halogenated free radicals

by Luc L.T. VERTOMMEN

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Kinetics of some gas phase reactions of halogenated free radicals.

Abstract from a thesis presented for the Degree of Doctor of Philosophy of the University of St. Andrews, by Luc L. Vertommen. October 1978.

The first two chapters of this thesis describe a study of the kinetics of the gas phase addition of perfluoroisopropyl and perfluoro-t-butyl radicals to various olefins. The radicals were produced by photolysing the corresponding perfluoroalkyl iodides.

Temperature variation data allowed determination of relative Arrhenius parameters. The results are compared with the data available for other simple radicals, and a comparison between the radicals of the series $CF_3^{\cdot}$, $CF_3CF_2^{\cdot}$, $(CF_3)_2CF^{\cdot}$ and $(CF_3)_3C^{\cdot}$, in particular, gives valuable information as to the relative importance of steric and other effects in free radical addition reactions.

Chapter 3 describes an attempt to determine the absolute rate constant for the recombination of perfluoroisopropyl radicals. The rotating sector method was used, but, due to a certain amount of thermal initiation and to a first order termination process as well as the more usual bimolecular disappearance of the radicals, the simple mathematical treatment, presented by Shepp, could not be applied to our system. A modified treatment was used and the rate constant was determined at 46°C. The result was taken as

evidence for an activation energy different from zero for the reaction.

Chapter 4 is a study of the orientation of the addition of monoiodomethyl radicals to various fluorinated olefins, at 150°C. Di-t-butyl peroxide was thermally decomposed and the methyl radicals produced initiated the free radical addition by abstracting iodine from diiodomethane. The results are compared with the data of some related radicals.

A mes parents,

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DECLARATION

I hereby declare that the work described in this thesis is a record of experiments carried out by me in the Chemistry Department of the University of St. Andrews, that it is my own composition and that it has not been previously submitted for a higher degree.

Luc L.T. Vertommen

CERTIFICATE

I certify that LUC LOUIS THEOPHILE VERTOMMEN, Licencie en Science, has spent 12 terms of research work under my direction and that he has fulfilled the conditions of the Resolution of the University Court, 1967, No. 1 and as such he is qualified to submit this thesis for the degree of Doctor of Philosophy.

Professor Lord Tedder

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I wish to express my deepest gratitude to Professor Lord Tedder and Dr. J.C. Walton for their continual encouragement and advice throughout the course of this work. I also thank Professor Lord Tedder and Professor Wyatt for the facilities provided during the period of this research.

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GENERAL INTRODUCTION.

The homolytic fission of a chemical bond produces free radicals and/or atoms. A radical may be defined as an electrically neutral polyatomic species with one unpaired electron. Radicals are usually generated by methods of primary homolysis (thermolysis, photolysis, radiolysis) or by induced homolysis (radical or electron transfer induced) of a weak bond.

Free radicals are known to be very reactive and this is particularly the case for small radicals containing only a few atoms. But, although most of them have only transient existence, several stable radicals (nitroxides, 2,2-diphenyl-1-picrylhydrazyl...) can be isolated. There are several factors controlling the stability (or persistency) of free radicals : (1) The first one is the ability of the groups attached to the radical centre to delocalize the unpaired electron. This results in an increase in the persistency by decreasing the spin density at the radical centre. (2) Steric effects can also influence their stability. Bulky radicals recombine more slowly. A good example is the persistency of the triphenylmethyl radical. Although the spin density at the radical centre is very similar to that of the benzyl radical, the triphenylmethyl radical is much more stable than the latter. This is due mainly to steric hindrance in the dimerization reaction. (3) Finally, the environment is also to be considered. For example, the lifetime of radicals in a solid matrix is much greater than it would be in solution, because of the slow rate of diffusion.

Free radicals commonly undergo five different types of reaction : fragmentation, transfer, addition, disproportionation and combination. The first three are chain carrying steps, whereas the last two are termination processes. Although this work is mainly concerned with the addition step, some knowledge of the nature and rate of the other reactions is essential.

In the gas phase, atom and radical combination reactions represent one of the simplest possible reactions. At moderate pressures, the rate of combination of simple radicals shows no temperature dependence and is in close accord with the predictions of the collision theory. The combination rates are much lower for atoms, the reason being that the newly formed molecule must get rid of the excess energy within one vibration period. For a diatomic molecule, this can only occur via collision with the walls of the reaction vessel or with another molecule.

Two radicals may, on collision, react to form, not a dimeric molecule, but two new molecules, one of which must be unsaturated. These disproportionation reactions are usually much less frequent than the combination ones, for primary radicals, but, with highly branched alkyl radicals, they can become more important.

The most common radical transfer reaction is that which involves hydrogen atom abstraction. A substantial amount of kinetic data is now available for these reactions. The pre-exponential rate factors are close to those predicted by the transition state theory ($\sim 10^{10}$ $1.mol^{-1}.sec^{-1}$ for atoms and $\sim 10^7$ l.mol^{-1}.sec^{-1} for simple alkyl radicals). Polar effects and the relative strengths of the bonds broken and formed play an important part in determining the rate. Transfer of other atoms, such as chlorine and bromine, has also received much attention.

Radical addition reactions to olefins have also been extensively investigated. In 1933, Kharasch and Mayo observed that the presence of peroxide or ultra-violet light caused a reversal in the orientation of addition of hydrogen bromide to unsymmetric olefins. This led to the importance of radical processes in organic chemistry.

Kharasch and co-workers[1] and Hey and Waters[2] simultaneously gave an explanation of the phenomenon. They established that the reaction was initiated by addition of a bromine atom but failed to explain the orientation of the radical addition. It was in 1940 that Mayo and Walling rationalized the observed orientation in terms of resonance stabilization of the intermediate radical[3]. Their hypothesis was that the point of attack was determined by the relative stabilities of the possible radical adducts. The stability of the radicals was specifically defined by Walling and Mayo in terms of heat of reaction. Unfortunately, by analogy with the ionic addition, most authors have attempted to assess this stability in terms of resonance theory. However, in terms of resonance theory, the resonance stabilization of the intermediate radical, in the addition to vinyl chloride, for example, can only be written as

$$BrCH_2-\dot{C}H-\overline{\underline{Cl}}| \longleftrightarrow BrCH_2-\overset{-}{\ddot{C}}H-\overset{+}{\dot{\underline{Cl}}}|$$

Since the second canonical form of the adduct radical involves separation of charge, the contribution due to the resonance stabilization of the electron to the total heat of formation of the adduct radical, will be very small compared with the contribution due to the formation of the new bond. This is already an indication of the inadequacy of the hypothesis, although it was in agreement with all the experimental data at the time.

The importance of polar effects was then investigated. Waters[4] suggested that free halogen atoms are electrophilic in character, and would therefore attack the point of highest electron density. This theory was analysed by Barton[5] who suggested that free radicals preferentially attack sites of electron density very different from that of the unsubstituted system.

Price[6] showed that the normal concepts of polarity could be used to explain the relative reactivities of monomers in radical copolymerization studies. These conclusions were considered by Mayo and Walling in a second review[7], in which they discuss the importance of both the polar and steric effects.

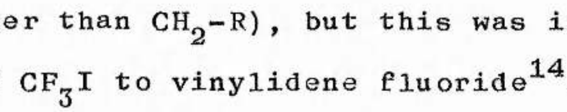
However, Haszeldine and his group[8-19,71,72] studied the addition of trifluoromethyl iodide to a number of olefins. Their results show that, although the polar effects influence the overall rate of addition, they do not explain the orientation of the attack. For each olefin $R-CH=CH_2$ (R = Me, Cl, F, CO_2Me, CF_3 or CN)[8-10], the attack is exclusively at the CH_2- group. In agreement with these observations, Henne and Nager[20] have shown that, in the free radical addition of

HBr, CF_3I and CCl_3Br to 1,1,1-trifluoropropene, the attack always takes place at the CH_2- end, and that additions are slower than to propene itself.

Most of Haszeldine's results could be explained in terms of steric interaction. It was difficult, however, on steric grounds alone, to account for the high specificity in the addition of CF_3I to vinyl fluoride[10], since fluorine is only slightly larger than hydrogen. Indeed, Haszeldine demonstrated that, in the addition of $CCl_3^{\cdot}$ and $CF_3^{\cdot}$ radicals to 1,1-difluoroprop-1-ene, the attack occurs in a direction contrary to that predicted on steric grounds[13].

It was also argued that a radical would attack the carbon with which it would form the stronger bond (CF_2-R is probably stronger than CH_2-R), but this was invalidated by the addition of CF_3I to vinylidene fluoride[14].

It was then postulated that the main factor influencing the orientation of radical addition was the relative stabilities of the intermediate radicals. The preferred reaction path is that requiring the smallest activation energy, which, in general, is the route from the reactants to the thermodynamically more stable adduct radical. Haszeldine[17] postulated that the radical stability decreases from tertiary to primary radicals



$$\geq C^{\cdot} \; > \; >CH^{\cdot} \; > \; -CH_2^{\cdot}$$

but that, by suitable choice of R and R', a secondary radical, RR'CH$^{\cdot}$, could be made more stable than a tertiary radical[18].

Most of this work was reviewed, in 1954, by Cadogan and Hey[21] who concluded that the approach to the problem had, so far, been empirical only and that no satisfactory theoretical interpretation of the experimental observations had been made.

Huang[22,23] studied the relative stabilizing influences of several substituents on free alkyl radicals. But the first kinetic data were obtained by Tedder and Walton[24]. They studied the gas phase addition of trichloromethyl radicals to fluorinated olefins and presented conclusive evidence to show that the rate and orientation of the addition did not fit the rationalization from resonance theory. They obtained a reasonable correlation between the measured activation energies and the atom localization energies, calculated by the Hückel method.

Undoubtedly, the most important compilation of results is that of Kerr and Parsonage[25] who made an extensive literature study up to 1971 and critically assessed all the kinetic data available at the time.

In 1973, Cadogan[26], in a review of radical chemistry, extended the resonance stabilization hypothesis by estimating adduct radical stability in terms of hyperconjugative delocalization.

Two years ago, in a review article, Tedder and Walton[27] underlined once more that the accepted resonance theory of reactivity in free radical addition to olefins is frequently inconsistent with experiment.They showed that the rate and orientation of these reactions are controlled by a series of factors comprising polar, steric and bond strength effects.

The kinetics of the addition process have been studied both in solution and in the gas phase. The great advantage of gas phase reactions is that a wide range of temperature can be studied and activation parameters can be determined. These parameters can be readily interpreted, using existing theories. Most theories of chemical kinetics deal with groups of isolated molecules and can therefore not be applied to reactions in solution, where the solvation effects play an important part.

Much work remains to be done in this field, before a complete understanding of the problem is reached. The more deeply we wish to understand the problem, the more sophisticated the theories we have to use and the broader the experimental basis we need. This is why this thesis is an attempt to provide more kinetic data in the field of free radical addition to olefins.

Chapter 1 of the thesis deals with the kinetics of the addition of perfluoroisopropyl radicals to fluoro-olefins.

Chapter 2 deals with the kinetics of the addition of perfluoro-t-butyl radicals to fluoro-olefins.

Chapter 3 is an attempt to measure the absolute rate constants for the recombination of $(CF_3)_2CF^\cdot$ radicals.

Chapter 4 is concerned with the orientation of the addition of iodomethyl radicals to fluorinated olefins.

CHAPTER 1:

THE ADDITION OF PERFLUOROISOPROPYL RADICALS TO OLEFINS.

Introduction

In 1973, Tedder and co-workers[73] reported the results of a study of the orientation of the gas phase addition of a series of perfluoroalkyl radicals ($CF_3^{\bullet}$, $C_2F_5^{\bullet}$, $n\text{-}C_3F_7^{\bullet}$, $n\text{-}C_4F_9^{\bullet}$, $n\text{-}C_7F_{15}^{\bullet}$, $n\text{-}C_8F_{17}^{\bullet}$, $i\text{-}C_3F_7^{\bullet}$) to vinyl fluoride, 1,1-difluoroethylene and trifluoroethylene. A comparison of the orientation ratios shows a substantial increase in selectivity in the series $CF_3^{\bullet}$, $CF_3CF_2^{\bullet}$, $(CF_3)_2CF^{\bullet}$, whereas the change is very small in the linear series $C_2F_5^{\bullet}$, $n\text{-}C_3F_7^{\bullet}$, $n\text{-}C_4F_9^{\bullet}$, $n\text{-}C_7F_{15}^{\bullet}$, $n\text{-}C_8F_{17}^{\bullet}$, where the steric hindrance at the carbon carrying the unpaired electron is virtually the same for each term. Since the effects can hardly be explained by electronic factors, the size and shape of the attacking radical appear to be important in the transition state. Hence, in order to determine the relative importance of steric and other effects, a study of the kinetics of the addition reaction for the series of radicals $CF_3^{\bullet}$, $C_2F_5^{\bullet}$, $i\text{-}C_3F_7^{\bullet}$ and $t\text{-}C_4F_9^{\bullet}$ seems to be very appropriate.

The addition of trifluoromethyl radicals to olefins has been thoroughly investigated. Szwarc and co-workers[59-63] were very active in this field. They studied the addition of $CF_3^{\bullet}$ radicals to various olefins, acetylenes and aromatics in both the liquid and the gas phases. The radicals were produced by photolysing hexafluoroazomethane and the reactions took place in the presence of isooctane[59,60] or 2,3-dimethylbutane[61-63]. The rate of addition (k_2) was measured relative to the rate of hydrogen abstraction from the alkane (k_1). The k_2/k_1 ratios observed in gas phase and liquid phase were very similar

$$(k_2/k_1)_l/(k_2/k_1)_g \sim 1.2 - 2$$

which demonstrates that the hydrocarbon solvent affects the addition and abstraction reactions to a similar extent. Nevertheless, the fact that the ratios were consistently slightly larger in solution was interpreted as being caused by a 20-50% decomposition of the adduct radical in the gas phase, due to the fact that the excess energy had not been released within one vibration period. The study of the reaction over a range of temperatures permitted the determination of relative Arrhenius parameters and it was noticed that replacement of a hydrogen by a methyl group or a chlorine at the addition site decreases the Arrhenius pre-exponential term by a factor of five, which is indicative of restriction of rotation of the $CF_3^{\cdot}$ in the transition state. A reasonable correlation was observed between the activation energies and the ionization potentials for a series of methyl substituted olefins[63]. Szwarc also gave evidence for the strongly electrophilic character of the trifluoromethyl radicals[59]. A secondary deuterium effect study[60] led him to conclude that the incipient R-C bond (R = CF_3 or CH_3) is relatively long and that the configuration around the reactive centre remains unaltered (i.e.planar) in the transition state.

Haszeldine and co-workers made a comprehensive study of the addition of $CF_3^{\cdot}$ radicals to unsymmetrical alkenes[8-19]. The olefins and an excess of trifluoromethyl iodide were placed in a sealed tube so that the reactions, initiated either photochemically or thermally, occurred in both the gas and liquid phases. The results have been discussed in the general introduction of the thesis.

Sangster and Thynne[28] measured the rate of addition of a series of radicals ($CF_3^{\cdot}$, $CCl_3^{\cdot}$, $CH_3^{\cdot}$, n-$C_3H_7^{\cdot}$, n-$C_3F_7^{\cdot}$, $CF_3CH_2CH_2^{\cdot}$) to ethylene relative to their rate of hydrogen abstraction from hydrogen sulfide. Arrhenius parameters were available for the abstraction reactions, so that the addition step results could be put on an absolute scale. $CF_3^{\cdot}$ was shown to be by far the most reactive species. The large difference in reactivity is almost entirely due to variations in the activation energy term. For $CCl_3^{\cdot}$, however, the A factor is two orders of magnitude lower than that of $CF_3^{\cdot}$, which can be explained by steric effect.

Braslawsky, Casas and Cifuentes[64] obtained relative parameters for the $CF_3^{\cdot}$ addition to 1,1-difluoroethylene. The radicals were produced by photolysing trifluoromethyl iodide. Mercury was present in the system to trap the iodine atoms.

Tedder and co-workers[29,30] studied the kinetics of the gas phase addition of trifluoromethyl radicals to fluoro-olefins and propene. Relative Arrhenius parameters were found and absolute rate parameters were determined by comparing the rate of addition to ethylene with the rate of combination of the radicals. The same authors studied the kinetics of the addition of $CF_3^{\cdot}$ radicals to a series of vinyl monomers[65].

Only a few people have studied the addition of perfluoroethyl radicals to olefins. Banus, Emeleus and Haszeldine[67] were amongst the first to observe that the thermolysis of pentafluoroethyl iodide, at 100°C, gave $C_2F_5^{\cdot}$ radicals and that, in the presence of an excess of ethylene, polymers of general formula $C_2F_5(CH_2CH_2)_nI$ were obtained. Haszeldine[68] observed a similar reaction in the presence of tetrafluoroethylene; the products were polymers of general formula $C_2F_5(CF_2CF_2)_nI$.

Haszeldine and Steele[17] showed that the addition of pentafluoroethyl radicals to 1,1-difluoroethylene occurs mainly at the CH_2- end (over 90%). That observation was confirmed by Chambers and his group[69].

No kinetic studies were reported for the addition of $C_2F_5^{\cdot}$ to olefins, until very recently. El Soueni, Tedder and Walton[66] obtained relative Arrhenius parameters for the gas phase addition of pentafluoroethyl radicals to fluorinated olefins. The results show that the $C_2F_5^{\cdot}$ radicals are more selective than the $CF_3^{\cdot}$ radicals and that the difference in selectivity can be attributed mainly to changes in the activation energy term.

Chambers and co-workers[69] reported that the addition of perfluoroisopropyl radicals to 1,1-difluoroethylene gave the adduct resulting from the reaction at the CH_2- end only. By increasing the proportions of the olefin, they obtained polymers of general formula $(CF_3)_2CF(CH_2CF_2)_nI$. The radicals were produced by thermolysis of the perfluoroisopropyl iodide. $(CF_3)_2CFI$ was shown to be the most efficient chain transfer agent in the series CF_3I, C_2F_5I, n-C_3F_7I, i-C_3F_7I.

Haszeldine and his group[70] studied the thermal and photochemical addition of $(CF_3)_2CFI$ to vinyl fluoride, trifluoroethylene and hexafluoropropene. They showed that the addition occurs mainly at the least substituted end for the first two olefins and that perfluoroisopropyl radicals are more selective than trifluoromethyl radicals. It was also found that $(CF_3)_2CF^{\cdot}$ radicals did not add to hexafluoropropene under various conditions.

In 1977, Tedder and his group[74] reported the results of a kinetic study of the addition of perfluoroisopropyl radicals to various fluorinated alkenes (this work is described in chapter 1 of this thesis).

No data were available in the literature for the addition of perfluoro-t-butyl radicals to olefins, when this work was started.

Experimental

1. Material

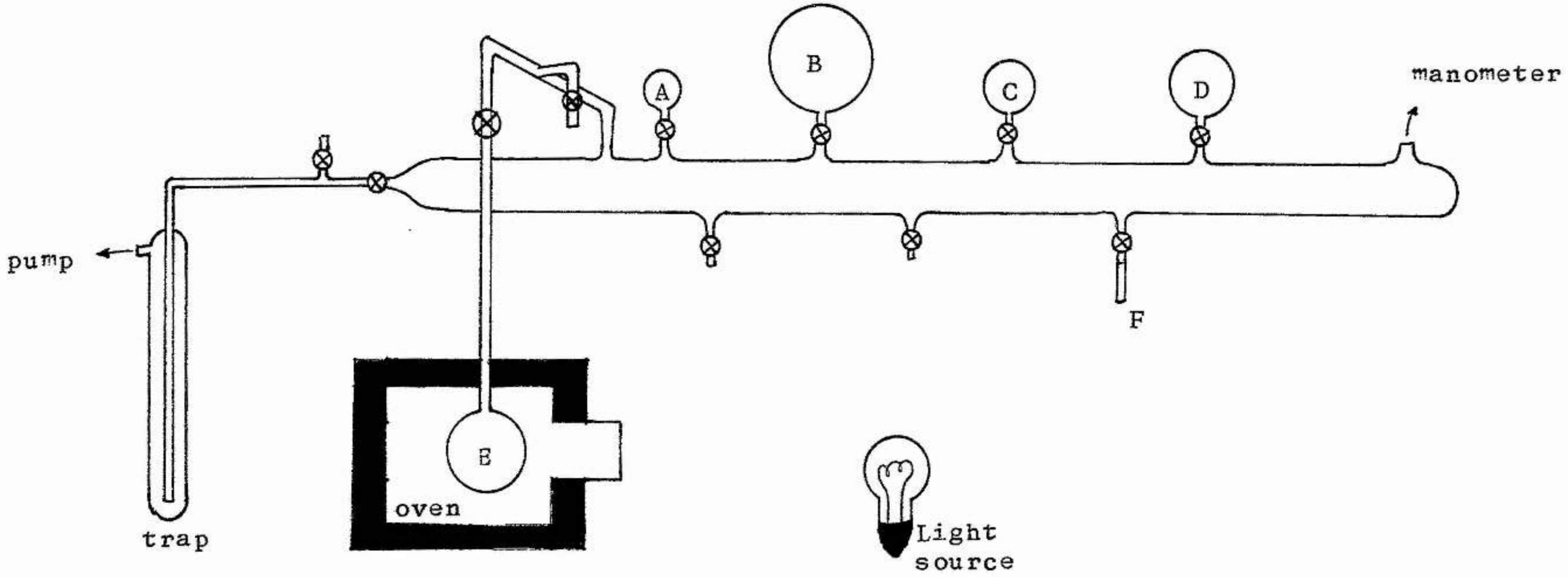
Commercial 2-iodoheptafluoropropane (Bristol Organics Ltd) was degassed and trap to trap distilled to eliminate water. Only the middle fraction was used for the reactions.

Commercial ethylene (BOC medical anaesthetic grade), vinyl fluoride (Matheson), 1,1-difluoroethylene (Matheson), trifluoroethylene (Peninsular Chem. Research), tetrafluoroethylene (ICI), propene (MacFarlane-Robson), 1,1,1-trifluoropropene (Peninsular Chem. Research) and hexafluoropropene (Bristol Organics Ltd) were dried and trap to trap distilled and degassed before use.

2. Apparatus

The experiment was performed in a spherical pyrex reaction vessel (E) of capacity 305 ml, connected to a conventional pyrex glass vacuum line. The vacuum was maintained at a pressure of 10^{-3} to 10^{-5} torr by means of an Edwards silicone oil diffusion pump, backed by a NGN PSR 1 rotary piston pump. The reactant pressures were measured using a calibrated spiral guage and volumes were measured into storage bulbs on the line, namely bulbs A, B, C and D of capacity 144 ml, 2,308 ml, 215 ml and 309 ml respectively.

The 2-iodoheptafluoropropane was stored in a pyrex tube (F) closed by a greaseless tap. The tube was kept in the dark and remained connected to the line all


A
B
C
D
manometer
pump
F
E
oven
trap
Light source

the time.

The furnace comprised an electrically heated hot plate inside a well insulated aluminium cylinder fitted with an asbestos lid. It had a window at one side, which allowed irradiation of the system for measured lengths of time. The temperature, measured by a mercury in glass thermometer, could be maintained to $\pm 2^{\circ}C$ using a 0-250 Volt "variac" transformer. Photolitic reactions were initiated with either a 25, 60, 100, or 150 Watt visible lamp or a Hanovia U.V.S. 220 medium pressure mercury arc (U.V.).

3. Method

The pressure of 2-iodoheptafluoropropane was measured directly into the reaction vessel (100 torr). Known amounts of the appropriate alkene (s) were distilled into the vessel which was then isolated from the rest of the line by a greaseless tap and the furnace, at the required temperature, was put around it. The mixture was irradiated for various lengths of time and, after reaction, it was distilled into a greaseless tube and analysed immediately.

4. Analysis

Quantitative analysis was achieved using a Griffin and George gas density balance chromatograph fitted with 15 ft columns of 10% embaphase silicone oil, 15% tritolylphosphate on chromosorb G or squalene. The carrier gas was nitrogen. The peak areas were measured with a Dupont 310 curve resolver (for vinyl fluoride) or a planometer. The response of a gas density balance detector is proportional to the concentration of a compound and to the difference between its molecular weight and the molecular weight of the carrier gas

$$A = k \frac{Q}{M} (M-m)$$

where Q is the weight of a compound of molecular weight M, A is the area of the peak, m is the molecular weight of the carrier gas and k is a constant depending on the detector. The concentration is given by

$$\frac{Q}{M} = \frac{k'A}{M-m}$$

It is easy to see that relative concentrations would be readily obtained from the areas under the peaks. If $\underline{E}'$ is a fluorinated olefin and $\underline{E}$ is ethylene, we have

$$\frac{[(CF_3)_2CF-\underline{E}'-I]}{[(CF_3)_2CF-\underline{E}-I]} = \frac{A_1}{A_2} \times \frac{M_2-28}{M_1-28}$$

where A_1 is the area of the peak for the fluorinated olefin adduct, A_2 is the area of the peak for the ethylene adduct, M_1 and M_2 are their respective molecular weight and 28 is the molecular weight of the carrier gas.

5. Identification

A. Vinyl fluoride

A preliminary experiment was carried out to identify the reaction products in which heptafluoro-2-iodopropane (1.6×10^{-3} moles), vinyl fluoride (2.3×10^{-4} moles) and ethylene (7.75×10^{-5} moles) were irradiated in the reaction vessel for 30 minutes, using a medium pressure mercury arc. Gas chromatography indicated the presence of four products: $(CF_3)_2CFCF(CF_3)_2$; $(CF_3)_2CFCH_2CH_2I$; $(CF_3)_2CFCH_2CHFI$ and $(CF_3)_2CFCHFCH_2I$, eluted in that order on a 6' tritolylphosphate column. Each of the products gave a parent ion in the mass spectrum together with the expected fragmentation ions. The two adducts of vinyl fluoride, $(CF_3)_2CFCH_2CHFI$ and $(CF_3)_2CFCHFCH_2I$, were distinguished by the presence of the ion $CHFI^+$ (m/e = 159) in the spectrum of the former adduct and its absence in the spectrum of the latter adduct, while the ion CH_2I^+ (m/e = 141) was present in the spectrum of the latter product, but not the former.

A-1:- $(CF_3)_2CFCF(CF_3)_2$

m/e	rel. Abundance	Assignment
319	42.4	$C_6F_{13}^+$
250	6	$C_5F_{10}^{\cdot+}$
231	36.4	$C_5F_9^+$
181	100	$C_4F_7^+$
169	42.4	$C_3F_7^+$
150	21.2	$C_3F_6^+$
143	6	$C_4F_5^+$
131	54.5	$C_3F_5^+$
119	27.3	$C_2F_5^+$
112	9.1	$C_3F_4^+$
100	27.3	$C_2F_4^+$
93	39.4	$C_3F_3^+$
69	>100	CF_3^+
50	18.2	CF_2^+
31	57.5	CF^+

A-2:- $(CF_3)_2CFCH_2CH_2I$

m/e	rel. Abundance	Assignment
324	100	$C_5H_4F_7I^+$
197	25.9	$C_5H_4F_7{}^+$
177	46.5	$C_5H_3F_6{}^+$
157	10.3	$C_5H_2F_5{}^+$
155	48.3	$C_5F_5{}^+$
145	5.2	$C_4H_2F_5{}^+$
141	17.2	CH_2I^+
128	24.1	HI^+
127	34.5	I^+
114	17.2	$C_3H_2F_4{}^+$
109	8.6	$C_4H_4F_3{}^+$
100	5.2	$C_2F_4{}^+$
95	10.3	$C_3H_2F_3{}^+$
89	6.9	$C_4H_3F_2{}^+$
77	36.2	$C_3H_3F_2{}^+$
75	6.9	$C_3HF_2{}^+$
69	72.4	$CF_3{}^+$
65	8.6	$C_2H_3F_2{}^+$
64	5.2	$C_2H_2F_2{}^+$
59	10.3	$C_3H_4F^+$
57	10.3	$C_3H_2F^+$
51	27.6	$CHF_2{}^+$
47	48.3	$C_2H_4F^+$
39	10.3	$C_3H_3{}^+$
33	10.3	CH_2F^+

A-2 (cont)

m/e	rel. Abundance	Assignment
31	10.3	CF^+
27	41.4	$C_2H_3^+$
26	6.5	$C_2H_2^+$
19	24	F^+

A-3:- $(CF_3)_2CFCH_2CHFI$

m/e	rel. Abundance	Assignment
342	7.8	$C_5H_3F_8I^+$
216	5.9	$C_4H_3F_2I^+$
215	100	$C_5H_3F_8^+$
195	15.7	C_4HFI^+
176	9.8	$C_5H_2F_6^+$
175	13.7	$C_5HF_6^+$
173	5.9	$C_2H_3FI^+$
159	7.8	$CHFI^+$
145	33.3	$C_4H_2F_4^+$
140	9.8	CHI^+
128	7.8	HI^+
127	29.4	I^+
108	8.8	$C_4H_3F_3^+$
107	7.8	$C_4H_2F_3^+$
106	6.8	$C_4HF_3^+$
95	31.4	$C_3H_2F_3^+$
81	5.7	$C_2F_3^+$
77	13.7	$C_3H_3F_2^+$

A-3 (cont)

m/e	rel. Abundance	Assignment
75	8.8	$C_3HF_2^+$
69	54.9	CF_3^+
65	9.8	$C_2H_3F_2^+$
57	7.8	$C_3H_2F^+$
51	76.5	CHF_2^+
46	15.7	$C_2H_3F^+$
45	7.8	$C_2H_2F^+$
33	5.9	CH_2F^+
31	11.8	CF^+
27	5.9	$C_2H_3^+$
19	37.3	F^+

A-4:- $(CF_3)_2CFCHFCH_2I$

m/e	rel. Abundance	Assignment
342	23	$C_5H_3F_8I^+$
173	9	$C_2H_3FI^+$
153	5	$C_3H_3F_6^+$
141	7.5	CH_2I^+
128	5	HI^+
127	10	I^+
77	8	$C_3H_3F_2^+$
69	25	CF_3^+
65	38	$C_2H_3F_2^+$
51	9	CHF_2^+
46	8	$C_2H_3F^+$

A-4 (cont)

m/e	rel. Abundance	Assignment
45	7.5	$C_2H_2F^+$
44	7	C_2HF^+
31	5	CF^+
27	5	$C_2H_3{}^+$
19	100	F^+

B. 1,1-Difluoroethylene

In a preliminary experiment heptafluoro-2-iodopropane (8.1×10^{-4} moles) and 1,1-difluoroethylene (4.13×10^{-4} moles) were irradiated together for 30 minutes at 214°C using a medium pressure mercury arc. The gas chromatogram, using a silicone oil column, showed three product peaks, which were identified by their mass spectra. The first product peak was that of $(CF_3)_2CFCF(CF_3)_2$; the second $(CF_3)_2CFCH_2CF_2I$ and the third $(CF_3)_2CFCF_2CH_2I$. All three gave their parent ions in the mass spectrum; the second product gave an ion m/e = 177 (CF_2I^+) not present in the spectrum of the third product which in turn gave an ion m/e = 141 (CH_2I^+) not present in the spectrum of the second product.

B-1:- $(CF_3)_2CFCH_2CF_2I$

m/e	rel. Abundance	Assignment
360	0.25	$C_5H_2F_9I^+$
233	100	$C_5H_2F_9{}^+$
214	14.5	$C_4HF_2I^+$
195	10.6	C_4HFI^+
177	18.6	CF_2I^+
163	16	$C_4HF_6{}^+$
145	17.3	$C_4HF_6I^{++}$
132	8	$C_3HF_5{}^+$
127	26.6	I^+
113	18.6	$C_3HF_4{}^+$
100	5.3	$C_2F_4{}^+$
95	12	$C_3H_2F_3{}^+$
75	9.3	$C_3HF_2{}^+$
69	98.6	$CF_3{}^+$
64	25.3	$C_2H_2F_2{}^+$

B-2:- $(CF_3)_2CFCF_2CH_2I$

m/e	rel. Abundance	Assignment
360	52.3	$C_5H_2F_9I^+$
233	5.5	$C_5H_2F_9{}^+$
191	42.8	$C_2H_2F_2I^+$
190	5.5	$C_2HF_2I^+$
164	5.5	C_3HI^+
141	28.5	CH_2I^+
128	7.9	HI^+

B-2 (cont)

m/e	rel. Abundance	Assignment
127	42.8	I^+
113	15.8	$C_3HF_4^+$
100	6.3	$C_2F_4^+$
95	26.9	$C_3H_2F_3^+$
83	33.3	$C_2H_2F_3^+$
80	31.7	C_5HF^+
69	77.7	CF_3^+
64	100	$C_2H_2F_2^+$

C. Trifluoroethylene

In a preliminary experiment heptafluoro-2-iodopropane (8.1×10^{-4} moles) and trifluoroethylene (4.13×10^{-4} moles) were irradiated by a medium pressure mercury lamp at 122°C for 45 minutes. Three products were observed on the g.l.c. trace: $(CF_3)_2CFCF(CF_3)_2$; $(CF_3)_2CFCHFCF_2I$ and $(CF_3)_2CFCF_2CHFI$ eluted in this order on a 12' silicone oil column. Each component gave the expected parent ion in its mass spectrum, and the ion m/e = 159 ($CHFI^+$) was present in the spectrum of the third product but absent in the spectrum of the second product, while exactly the opposite was true of the ion m/e = 177 (CF_2I^+).

C-1:- $(CF_3)_2CFCHFCF_2I$

m/e	rel. Abundance	Assignment
378	0.08	$C_5HF_{10}I^+$
251	32.7	$C_5HF_{10}{}^+$
213	3.6	$C_5HF_8{}^+$
208	3.4	$C_2F_3I^+$
177	10.9	CF_2I^+
163	12.7	$C_4HF_6{}^+$
127	30.9	I^+
113	18.7	$C_3HF_4{}^+$
101	5.9	$C_2HF_4{}^+$
93	7.3	$C_3F_3{}^+$
82	20.2	$C_2HF_3{}^+$
75	5.7	$C_3HF_2{}^+$
69	100	$CF_3{}^+$
51	21.8	$CHF_2{}^+$

C-2:- $(CF_3)_2CFCF_2CHFI$

m/e	rel. Abundance	Assignment
378	4.9	$C_5HF_{10}I^+$
251	23.2	$C_5HF_{10}{}^+$
208	9.7	$C_2F_3I^+$
163	13.4	$C_4HF_6{}^+$
159	8.5	$CHFI^+$
128	4.9	HI^+
127	64.6	I^+

C-2 (cont)

m/e	rel. Abundance	Assignment
113	13.4	$C_3HF_4^+$
101	32.9	$C_2HF_4^+$
82	28	$C_2HF_3^+$
69	100	CF_3^+
64	13.4	HI^{++}
63	6.1	$C_2HF_2^+$
51	42.7	CHF_2^+

D. Tetrafluoroethylene

In a preliminary experiment, heptafluoro-2-iodopropane (1.6 x 10^{-3} moles), 1,1-difluoroethylene (7.75 x 10^{-5} moles) and tetrafluoroethylene (5.75 x 10^{-4} moles) were irradiated by a medium pressure mercury lamp for 45 minutes at 190°C. Five product peaks were observed on the chromatogram. The 15' column used was packed with squalene. The products were $(CF_3)_2CFCF(CF_3)_2$; $(CF_3)_2CFCF_2CF_2I$; $(CF_3)_2CFCH_2CF_2I$; $(CF_3)_2CF(CF_2)_4I$ and $(CF_3)_2CFCH_2(CF_2)_3I$. Each component was identified from its molecular ion and characteristic fragment ions in the mass spectra. The cross-telomer was identified as the product of addition to difluoroethylene first, because of the presence of a signal for $C_5H_2F_9^+$ (m/e = 233) in the spectrum. If the addition was to the tetrafluoroethylene first, no fragment containing only 5 carbons could contain two hydrogens and as many as nine fluorines without extensive rearrangement.

D-1:- $(CF_3)_2CFCF_2CF_2I$

m/e	rel. Abundance	Assignment
396	6	$C_5F_{11}I^+$
269	23.1	$C_5F_{11}^+$
227	7.3	$C_2F_4I^+$
181	7.3	$C_4F_7^+$
177	11.3	CF_2I^+
131	8	$C_3F_5^+$
127	16.3	I^+
119	13.8	$C_2F_5^+$
100	10	$C_2F_4^+$
93	3.2	$C_3F_3^+$
69	100	CF_3^+

D-2:- $(CF_3)_2CF(CF_2)_4I$

m/e	rel. Abundance	Assignment
496	1.4	$C_7F_{15}I^+$
369	8.7	$C_7F_{15}^+$
219	4.8	C_6FI^+
181	5.3	$C_4F_7^+$
177	12	CF_2I^+
131	12	$C_3F_5^+$
127	18.8	I^+
119	7.7	$C_2F_5^+$
100	8.2	$C_2F_4^+$
69	100	CF_3^+

D-3:- $(CF_3)_2CFCH_2(CF_2)_3I$

m/e	rel. Abundance	Assignment
460	1.5	$C_7H_2F_{13}I^+$
333	13.8	$C_7H_2F_{13}{}^+$
283	7.7	$C_5H_2F_9{}^+$
177	21.5	CF_2I^+
169	9.2	$C_3F_7{}^+$
145	10.7	$C_4H_2F_5{}^+$
127	9.2	I^+
119	6.1	$C_2F_5{}^+$
113	6.1	$C_3HF_4{}^+$
100	7.7	$C_2F_4{}^+$
95	10.7	$C_3H_2F_3{}^+$
69	100	$CF_3{}^+$

E. Propene

In the preparative run, heptafluoro-2-iodopropane (1.6×10^{-3} moles) and propene (4.15×10^{-4} moles) were irradiated for 2 hours at 140°C using a medium pressure mercury arc. Three products were observed on the g.l.c. trace, using a 12' silicone oil column; $(CF_3)_2CFCF(CF_3)_2$, $(CF_3)_2CFCH_2CH(CH_3)I$ and $(CF_3)_2CFCH(CH_3)CH_2I$. Each component showed the expected parent ion in the mass spectra and component 2 showed a strong ion at m/e = 155 ($C_2H_4I^+$) which was weak in the spectrum of component 3, while component 3 showed a strong ion at 141 (CH_2I^+) which was weak in the spectrum of component 2. The order of elution was also the same as that of the analogous CF_3I adducts.

E-1:- **$(CF_3)_2CFCH_2CH(CH_3)I$**

m/e	rel. Abundance	Assignment
338	4.6	$C_6H_6F_7I^+$
211	100	$C_6H_6F_7^+$
192	6	$C_6H_6F_6^+$
171	21.3	$C_6H_4F_5^+$
169	6	$C_3F_7^+$ & $C_6H_2F_5^+$
151	7.4	$C_6H_3F_4^+$
145	19.9	$C_4H_2F_5^+$
141	6.9	CH_2I^+
128	8.8	HI^+
127	23.1	I^+
121	8.3	$C_5H_4F_3^+$
101	6.5	$C_2HF_4^+$ & $C_5H_3F_2^+$
95	8.8	$C_3H_2F_3^+$
77	15.7	$C_3H_3F_2^+$
69	26	CF_3^+
65	14.3	$C_2H_3F_2^+$
61	7.9	$C_3H_6F^+$
59	26.8	$C_3H_4F^+$
51	11.1	CHF_2^+ & $C_4H_3^+$
47	12	$C_2H_4F^+$

E-2:- $(CF_3)_2CFCH(CH_3)CH_2I$

m/e	rel. Abundance	Assignment
338	14.3	$C_6H_6F_7I^+$
211	100	$C_6H_6F_7^+$
192	14.3	$C_6H_6F_6^+$
171	35.7	$C_6H_4F_5^+$
169	28.6	$C_6H_2F_5^+$ & $C_3F_7^+$
151	21.5	$C_6H_3F_4^+$
145	28.6	$C_4H_2F_5^+$
141	21.5	CH_2I^+
128	35.7	HI^+
127	42.8	I^+
101	14.3	$C_2HF_4^+$ & $C_5H_3F_2^+$
95	21.5	$C_3H_2F_3^+$ & $C_6H_4F^+$
77	35.7	$C_3H_3F_2^+$
69	64.2	CF_3^+
65	50	$C_2H_3F_2^+$
61	28.6	$C_3H_6F^+$
59	50	$C_3H_4F^+$
51	28.6	CHF_2^+ & $C_4H_3^+$
47	21.5	$C_2H_4F^+$

F. 1,1,1-Trifluoropropene

In the preliminary experiment, heptafluoro-2-iodopropane (8.1×10^{-4} moles) and 1,1,1-trifluoropropene (2.89×10^{-4} moles) were photolysed by a medium pressure mercury lamp for 10 hours at 170°C. Three product peaks were observed on the g.l.c. trace obtained from elution on a 12' silicone oil column: $(CF_3)_2CFCF(CF_3)_2$, $(CF_3)_2CFCH_2CH(CF_3)I$ and $(CF_3)_2CFCH(CF_3)CH_2I$. The first two compounds gave the expected parent ion in their mass spectra, and the ion at m/e = 141 (CH_2I^+) was absent in the spectrum of peak 2. The third compound was produced in insufficient quantity for mass spectral analysis, but its identity was attested by the similarity of its relative retention time to that of the corresponding adduct from CF_3I.

F-1:- $(CF_3)_2CFCH_2CH(CF_3)I$

m/e	rel. Abundance	Assignment
392	90.5	$C_6H_3F_{10}I^+$
265	9.5	$C_6H_3F_{10}^+$
246	6.7	$C_6H_3F_9^+$
245	31.1	$C_6H_2F_9^+$
227	5.4	$C_6H_3F_8^+$
223	10.8	$C_3H_3F_3I^+$
209	8.1	$C_2HF_3I^+$
177	8.1	$C_5H_3F_6^+$
145	13.5	$C_4H_2F_5^+$
128	97.2	HI^+
127	68.4	I^+
126	5.4	$C_4H_2F_4^+$
115	8.1	$C_4HF_4^+$
113	18.9	$C_3HF_4^+$
100	5.4	$C_2F_4^+$
95	27	$C_3H_2F_3^+$

F-1 (cont)

m/e	rel. Abundance	Assignment
82	9.5	$C_2HF_3^+$ & $C_5H_3F^+$
77	90.5	$C_3H_3F_2^+$
75	13.5	$C_3HF_2^+$
69	100	CF_3^+

6. Details of Kinetic Experiments

A. Competitive addition of $(CF_3)_2CFI$ to ethylene and vinyl fluoride

Because of the relatively very small amount of reverse adduct, $(CF_3)_2CFCHFCH_2I$, formed, it was not possible, at low temperatures, to limit the consumption of ethylene to 5% or less (necessary so as not to invalidate kinetic studies) and also measure accurately the three adducts in competitive experiments. Two series of photolyses were therefore carried out. In the first low conversion series, ethylene and vinyl fluoride were present. In the second series, ethylene was excluded and the percentage conversion was increased allowing analysis of both adducts of vinyl fluoride.

a) Runs with ethylene

Heptafluoro-2-iodopropane (1.6×10^{-3} moles) was photolysed in the presence of ethylene (7.75×10^{-5} moles) and vinyl fluoride (2.32×10^{-4} moles) using a tungsten lamp or a medium pressure mercury arc. The temperature was varied in the range 24-170°C. The peak areas were measured relative to that of the normal adduct of vinyl fluoride, which was set equal to 100. The term "normal adduct" refers to the product of addition to the least substituted end of an unsymmetrical olefin; the term "reverse adduct" refers to the product of addition to the most substituted end of that olefin.

let a_1 = the relative area of $(CF_3)_2CFCH_2CH_2I$
a_2 = the relative area of $(CF_3)_2CFCH_2CHFI$
a_3 = the relative area of $(CF_3)_2CFCHFCH_2I$

Temp. 170°C time 10 min
Lamp 60 W

	a_1	a_2	a_3
	110	100	1.8
	112	100	1.8
	112	100	1.8
	110.5	100	1.6
mean	111.1	100	1.75

Temp. 148°C time 45 min
Lamp 60 W

	a_1	a_2	a_3
	122	100	1.4
	122	100	1.5
	122	100	1.5
	121	100	1.6
mean	121.8	100	1.5

Temp. 129°C time 35 min
Lamp 60 W

	a_1	a_2	a_3
	130	100	1.25
	134	100	1.3
	128	100	1.2
	131	100	1.2
mean	130.7	100	1.25

Temp. 110°C time 45 min
Lamp 60 W

	a_1	a_2	a_3
	140	100	-
	140	100	-
	138	100	1
	136	100	1
	134	100	1.1
mean	137.6	100	1.03

Temp 88°C time 95 min
Lamp 60 W

	a_1	a_2	a_3
	155	100	-
	156	100	-
	158	100	-
	165	100	-
mean	158.5	100	-

Temp 72°C time 150 min
Lamp 150 W

	a_1	a_2	a_3
	162	100	-
	164	100	-
	165	100	-
	166	100	-
mean	164.2	100	-

Temp. 44°C time 5 min
Lamp U.V.

	a_1	a_2	a_3
	162	100	-
	165	100	-
	162.4	100	-
	163	100	-
mean	163.1	100	-

Temp. 24°C time 15 min
Lamp U.V.

	a_1	a_2	a_3
	170	100	-
	172	100	-
	172	100	-
	172	100	-
mean	171.5	100	-

The relative rates of formation of the observed products at the various temperatures are shown in table 1-1.

b) Runs without ethylene

Heptafluoro-2-iodopropane (1.6×10^{-3} moles) was photolysed in the presence of vinyl fluoride (2.32×10^{-4} moles) at different temperatures using a medium pressure mercury lamp. The temperature was varied in a range 37-200°C and peak areas were measured relative to that of the normal adduct which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCH_2CHFI$

a_2 = the relative area of $(CF_3)_2CFCHFCH_2I$

Temp. 200°C time 10 min

	a_1	a_2
	100	2.3
	100	2.25
	100	2.3
mean	100	2.25

Temp. 190°C time 35 min

	a_1	a_2
	100	1.9
	100	1.9
	100	1.9
	100	2
mean	100	1.9

Temp. 150°C time 60 min

	a_1	a_2
	100	1.6
	100	1.5
	100	1.4
	100	1.5
mean	100	1.5

Temp. 90°C time 60 min

	a_1	a_2
	100	0.85
	100	0.85
	100	0.85
	100	0.8
	100	0.85
mean	100	0.85

Temp. 37°C time 90 min

	a_1	a_2
	100	0.45
	100	0.48
	100	0.48
	100	0.5
mean	100	0.48

Temp. 152°C time 60 min

	a_1	a_2
	100	1.4
	100	1.6
	100	1.5
	100	1.4
	100	1.5
mean	100	1.5

The relative rates of formation of the observed products at the various temperatures are shown in table 1-1. In all the tables, subscript i refers to initial concentrations and subscript f to final concentrations.

Table 1-1. The addition of $(CF_3)_2CFI$ to vinyl fluoride and ethylene

	reactants	products	
Temperature °C	$\frac{[CHF{=}CH_2]_i}{[CH_2{=}CH_2]_i}$	$\frac{[(CF_3)_2CFCH_2CH_2I]_f}{[(CF_3)_2CFCH_2CHFI]_f}$	$\frac{[(CF_3)_2CFCHFCH_2I]_f}{[(CF_3)_2CFCH_2CHFI]_f}$
200	-	-	0.023
190	-	-	0.019
170	2.987	1.18	0.017(5)
152	-	-	0.015
150	-	-	0.015
148	2.987	1.29	0.015
129	2.987	1.39	0.012(5)
110	2.987	1.46	0.010
90	-	-	0.009(5)
88	2.987	1.68	-
72	2.987	1.74	-
44	2.987	1.73	-
37	-	-	0.0047(5)
24	2.987	1.82	-

A least squares plot of log $([(CF_3)_2CFCHFCH_2I)]_f/[(CF_3)_2CFCH_2CHFI]_f)$ against 10^3 K/T gave an intercept of -0.42 ± 0.02 and a gradient of -0.6 ± 0.05. Similarily a least squares plot of log $([(CF_3)_2CFCH_2CHFI]_f \times [CH_2{=}CH_2]_i/[(CF_3)_2CFCH_2CH_2I]_f \times [CHF{=}CH_2]_i)$ against 10^3 K/T gave a straight line with an intercept of -0.158 ± 0.026 and a gradient of -0.183 ± 0.072.

B. Competitive addition of $(CF_3)_2CFI$ to ethylene and 1,1-difluoroethylene

a) Runs with ethylene

In a series of low conversion runs, heptafluoro-2-iodopropane (1.63×10^{-3} moles) was photolysed over a range of temperatures (52-174°C), in presence of 1,1-difluoroethylene (2.32×10^{-4} moles) and ethylene (7.75×10^{-5} moles). The light source was a tungsten lamp. Reaction times were adjusted to ensure the conversion of the olefins did not exceed 5%. The peak areas were measured relative to that of the normal difluoroethylene adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCH_2CH_2I$

a_2 = the relative area of $(CF_3)_2CFCH_2CF_2I$

Temp. 174°C time 4 min
Lamp 25 W

	a_1	a_2
	248	100
	247	100
	254	100
	254	100
mean	250.8	100

Temp. 148°C time 15 min
Lamp 60 W

	a_1	a_2
	267	100
	267	100
	267	100
	263	100
mean	266	100

Temp. 117°C time 30 min
Lamp 60 W

	a_1	a_2
	305	100
	327	100
	315	100
	300	100
mean	311.8	100

Temp. 109°C time 45 min
Lamp 60 W

	a_1	a_2
	330	100
	340	100
	330	100
	350	100
mean	337.5	100

Temp. 89°C time 90 min
Lamp 60 W

	a_1	a_2
	362	100
	355	100
	352	100
	355	100
mean	356	100

Temp. 73°C time 220 min
Lamp 150 W

	a_1	a_2
	364	100
	350	100
	373	100
	363	100
mean	362.5	100

Temp. 52°C time 270 min
Lamp 150 W

	a_1	a_2
	428	100
	420	100
	425	100
mean	424.3	100

The relative rates of formation of these two products are shown in table 1-2.

b) Runs without ethylene

In a series of high conversion runs, heptafluoro-2-iodopropane (1.63 x 10^{-3} moles) and 1,1-difluoroethylene

(4.13×10^{-4} moles) were photolysed over a range of temperatures, using a medium pressure mercury arc. The temperature was varied in the range 116-232°C. The peak areas were measured relative to that of the normal adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCH_2CF_2I$
a_2 = the relative area of $(CF_3)_2CFCF_2CH_2I$

Temp. 232°C time 60 min

	a_1	a_2
	100	0.194
	100	0.1935
	100	0.1934
	100	0.1987
mean	100	0.1949

Temp. 214°C time 45 min

	a_1	a_2
	100	0.165
	100	0.171
	100	0.168
	100	0.158
mean	100	0.166

Temp. 193°C time 80 min

	a_1	a_2
	100	0.13
	100	0.13
	100	0.12
	100	0.133
mean	100	0.128

Temp. 178°C time 60 min

	a_1	a_2
	100	0.1025
	100	0.11
	100	0.11
mean	100	0.1075

Temp. 150°C time 120 min

	a_1	a_2
	100	0.083
	100	0.0815
	100	0.076
	100	0.077
mean	100	0.079

Temp. 130°C time 150 min

	a_1	a_2
	100	0.0606
	100	0.0573
	100	0.0577
	100	0.0600
mean	100	0.0589

Temp. 116°C time 180 min

	a_1	a_2
	100	0.0447
	100	0.0434
	100	0.0431
	100	0.0442
mean	100	0.0439

The relative rates of formation of the observed products are shown in table 1-2.

Table 1-2 The addition of $(CF_3)_2CFI$ to 1,1-difluoroethylene and ethylene

Temperature °C	reactants	products	
	$\frac{[CH_2=CF_2]_i}{[CH_2=CH_2]_i}$	$\frac{[(CF_3)_2CFCH_2CH_2I]_f}{[(CF_3)_2CFCH_2CF_2I]_f}$	$\frac{[(CF_3)_2CFCF_2CH_2I]_f}{[(CF_3)_2CFCH_2CF_2I]_f}$
232	-	-	0.00195
214	-	-	0.00166
193	-	-	0.00128
178	-	-	0.00108
174	2.987	2.812	-
150	-	-	0.00079
148	2.987	2.982	-
130	-	-	0.000589
117	2.987	3.495	-
116	-	-	0.000439
109	2.987	3.78	-
89	2.987	3.99	-
73	2.987	4.06	-
52	2.987	4.76	-

A least squares plot of log $([(CF_3)_2CFCF_2CH_2I]_f / [(CF_3)_2CFCH_2CF_2I]_f)$ against 10^3 K/T gave a line with a gradient of -1.07 ± 0.06 and an intercept of -0.586 ± 0.026. A similar plot of log $([(CF_3)_2CFCH_2CF_2I]_f \times [CH_2{=}CH_2]_i / [(CF_3)_2CFCH_2CH_2I]_f \times [CH_2{=}CF_2]_i)$ gave a line with a gradient 0.273 ± 0.06 and an intercept -0.32 ± 0.02.

C. Competitive addition of $(CF_3)_2CFI$ to ethylene and trifluoroethylene

a) Runs with ethylene

In a first series of experiments, heptafluoro-2-iodopropane (1.6×10^{-3} moles) was photolysed at different temperatures by means of a tungsten lamp in the presence of trifluoroethylene (5.79×10^{-4} moles) and ethylene (7.75×10^{-5} moles). The temperature was varied in the range 72-150°C. Peak areas were measured relative to that of the normal adduct of trifluoroethylene, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCH_2CH_2I$
a_2 = the relative area of $(CF_3)_2CFCHFCF_2I$
a_3 = the relative area of $(CF_3)_2CFCF_2CHFI$

Temp. 150°C time 10 min
Lamp 25 W

	a_1	a_2	a_3
	1335	100	9.8
	1330	100	10
	1305	100	10.6
	1275	100	8.9
mean	1311.3	100	9.8

Temp. 141°C time 10 min
Lamp 25 W

	a_1	a_2	a_3
	1700	100	-
	1700	100	-
	1715	100	-
	1720	100	-
mean	1708.8	100	-

Temp. 127°C time 30 min
Lamp 25 W

	a_1	a_2	a_3
	2023	100	-
	2028	100	-
	2105	100	-
	2050	100	-
mean	2051.5	100	-

Temp. 118°C time 30 min
Lamp 60 W

	a_1	a_2	a_3
	1810	100	-
	1910	100	-
	1980	100	-
mean	1900	100	-

Temp. 106°C time 40 min
Lamp 100 W

	a_1	a_2	a_3
	2323	100	-
	2290	100	-
	2312	100	-
	2200	100	-
mean	2281.3	100	-

Temp. 97°C time 45 min
Lamp 25 W

	a_1	a_2	a_3
	2210	100	-
	2350	100	-
	2360	100	-
	2320	100	-
mean	2310	100	-

Temp. 92°C time 90 min
Lamp 100 W

	a_1	a_2	a_3
	2550	100	-
	2710	100	-
	2630	100	-
	2580	100	-
mean	2618	100	-

Temp. 82°C time 135 min
Lamp 150 W

	a_1	a_2	a_3
	2824	100	-
	2778	100	-
	2696	100	-
	2680	100	-
mean	2744.5	100	-

Temp. 72°C time 180 min
Lamp 150 W

	a_1	a_2	a_3
	3167	100	-
	3143	100	-
	3179	100	-
mean	3163	100	-

The relative rates of formation of the observed products are shown in table 1-3.

b) Runs without ethylene

In a second series of experiments, heptafluoro-2-iodopropane (1.6×10^{-3} moles) was photolysed at different temperatures by means of a medium pressure mercury lamp, in the presence of trifluoroethylene (4.13×10^{-3} moles). The temperature range was between 74 and 231°C. Peak areas were measured relative to the normal adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCHFCF_2I$
a_2 = the relative area of $(CF_3)_2CFCF_2CHFI$

Temp. 231°C time 4 min

	a_1	a_2
	100	13.06
	100	12.7
	100	12.0
mean	100	12.59

Temp. 187°C time 5 min

	a_1	a_2
	100	11.0
	100	10.6
	100	10.0
	100	12.0
mean	100	10.9

Temp. 152°C time 20 min

	a_1	a_2
	100	9.4
	100	10.2
	100	9.0
	100	10.0
mean	100	9.65

Temp. 122°C time 45 min

	a_1	a_2
	100	8.6
	100	8.33
	100	8.57
mean	100	8.5

Temp. 102°C time 17 min

	a_1	a_2
	100	7.6
	100	7.62
	100	7.93
	100	8.0
mean	100	7.79

Temp. 82°C time 150 min

	a_1	a_2
	100	6.6
	100	6.9
	100	6.67
mean	100	6.72

Temp. 74°C time 150 min

	a_1	a_2
	100	6.98
	100	6.94
	100	6.67
mean	100	6.86

The relative rates of formation of these products are shown in table 1-3

Table 1-3 The addition of $(CF_3)_2CFI$ to ethylene and trifluoroethylene

Temperature °C	reactants	products	
	$\frac{[CHF{=}CF_2]_i}{[CH_2{=}CH_2]_i}$	$\frac{[(CF_3)_2CFCH_2CH_2I]_f}{[(CF_3)_2CFCHFCF_2I]_f}$	$\frac{[(CF_3)_2CFCF_2CHFI]_f}{[(CF_3)_2CFCHFCF_2I]_f}$
231	-	-	0.126
187	-	-	0.109
152	-	-	0.0965
150	7.465	15.5	0.0982
141	7.465	20.2	-
127	7.465	24.2	-
122	-	-	0.085
118	7.465	22.5	-
106	7.465	27.0	-
102	-	-	0.078
97	7.465	27.3	-
92	7.465	30.9	-
82	7.465	32.45	-
82	-	-	0.067
74	-	-	0.0686
72	7.465	37.4	-

A least squares plot of log $([(CF_3)_2CFCF_2CHFI]_f / [(CF_3)_2CFCHFCF_2I]_f)$ against 10^3 K/T gave a line with intercept -0.29 ± 0.01 and gradient -0.31 ± 0.03. A similar line for log $([(CF_3)_2CFCHFCF_2I]_f / [(CF_3)_2CFCH_2CH_2I]_f \times [CH_2{=}CH_2]_i / [CHF{=}CF_2]_i)$ against 10^3 K/T had an intercept of -0.67 ± 0.06 and a gradient of -0.61 ± 0.17.

D. Competitive addition of $(CF_3)_2CFI$ to tetrafluoroethylene and 1,1-difluoroethylene

Because of the important difference in reactivity between tetrafluoroethylene and ethylene, the competitive runs were carried out using 1,1-difluoroethylene instead of ethylene. In a series of experiments, heptafluoro-2-iodopropane (1.6×10^{-3} moles) was photolysed at different temperatures by a tungsten lamp or a medium pressure mercury lamp in the presence of tetrafluoroethylene (5.79×10^{-4} moles) and 1,1-difluoroethylene (7.75×10^{-5} moles). The reaction times were adjusted so that the conversion of the minor reactant did not exceed 5%. The temperature was varied in the range 52-190°C. Peak areas were measured relative to that of the tetrafluoroethylene adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCH_2CF_2I$
a_2 = the relative area of $(CF_3)_2CFCF_2CF_2I$
a_3 = the relative area of $(CF_3)_2CFCH_2(CF_2)_3I$
a_4 = the relative area of $(CF_3)_2CF(CF_2)_4I$

Temp. 190°C time 30 min
Lamp 100 W

a_1	a_2	a_3	a_4	
148	100	21.6	16.2	
150	100	21.3	16.4	
154	100	21.2	16.3	
148	100	22.3	16.2	
150	100	21.6	16.2	mean

Temp. 148°C time 60 min
Lamp 100 W

a_1	a_2	a_3	a_4	
213	100	50	40	
210	100	45	40	
211.5	100	47	40	
211.5	100	47.3	40	mean

Temp. 146°C time 30 min
Lamp 100 W

a_1	a_2	a_3	a_4	
225	100	40	31	
217	100	33	36	
233	100	-	33.5	
225	100	36.5	33.5	mean

Temp. 125°C time 30 min
Lamp U.V.

a_1	a_2	a_3	a_4	
210	100	-	-	
205	100	-	-	
215	100	17	11	
210	100	16	14	
210	100	16.5	12.5	mean

Temp. 108°C time 30 min
Lamp U.V.

a_1	a_2	a_3	a_4	
250	100	-	16	
241	100	31	17	
235	100	33	16	
242	100	32	16.3	mean

Temp. 94°C time 90 min
Lamp U.V.

a_1	a_2	a_3	a_4	
230	100	15.5	14.6	
230	100	15.5	14.4	
230	100	-	14.8	
230	100	15.5	14.6	mean

Temp. 82°C time 90 min
Lamp U.V.

a_1	a_2	a_3	a_4	
300	100	-	13	
292	100	12	12.5	
285	100	12.5	12.5	
292.3	100	12.3	12.7	mean

Temp. 80°C time 90 min
Lamp U.V.

a_1	a_2	a_3	a_4
241.5	100	24.5	22
267	100	23	-
260	100	24	16
256	100	-	19
256.1	100	23.8	19

Temp. 60°C time 300 min
Lamp U.V.

a_1	a_2	a_3	a_4	
291	100	-	-	
293	100	-	-	
290	100	-	-	
291.3	100	-	-	mean

Temp. 52°C time 240 min
Lamp U.V.

a_1	a_2	a_3	a_4	
248	100	-	-	
263	100	-	-	
256	100	-	-	
255.7	100	-	-	mean

Table 1-4 The addition of $(CF_3)_2CFI$ to 1,1-difluoroethylene and tetrafluoroethylene

Temperature °C	$\frac{[CF_2=CF_2]_i}{[CH_2=CF_2]_i}$	$\frac{[(CF_3)_2CFCH_2CF_2I]_f}{[(CF_3)_2CFCF_2CF_2I]_f}$	$\frac{[(CF_3)_2CF(CF_2)_4I]_f}{[(CF_3)_2CFCF_2CF_2I]_f}$	$\frac{[(CF_3)_2CFCH_2(CF_2)_3I]_f}{[(CF_3)_2CFCF_2CF_2I]_f}$
190	7.465	1.66	0.127	0.184
148	7.465	2.35	0.315	0.403
146	7.465	2.49	0.315	0.263
125	7.465	2.32	0.098	0.140
108	7.465	2.68	0.128	0.272
94	7.465	2.55	0.115	0.132
82	7.465	3.24	0.1	0.104
80	7.465	2.84	0.149	0.203
60	7.465	3.23	–	–
52	7.465	2.83	–	–

The relative rates of formation of the four products are shown in table 1-4.

A least squares plot of log $([(CF_3)_2CFCF_2CF_2I]_f + [(CF_3)_2CF(CF_2)_4I]_f / [(CF_3)_2CFCH_2CF_2I]_f + [(CF_3)_2CFCH_2(CF_2)_3I]_f \times [CH_2{=}CF_2]_i / [CF_2{=}CF_2]_i$ against $10^3\ {}^K/T$ gave a straight line with an intercept -0.545 ± 0.042 and a gradient -0.271 ± 0.111.

B. Competitive addition of $(CF_3)_2CFI$ to propene and 1,1-difluoroethylene

As for tetrafluoroethylene, 1,1-difluoroethylene was used as a reference, instead of ethylene.

a) Runs with 1,1-difluoroethylene

In a first series of experiments, heptafluoro-2-iodopropane (1.6×10^{-3} moles) was photolysed at a series of temperatures with propene (7.75×10^{-5} moles) and 1,1-difluoroethylene (3.32×10^{-4} moles). The temperature was varied in the range 70-184°C. The light source was a tungsten lamp and the reaction times were adjusted to help the consumption of the minor reactant below 5%. Peak areas were measured relative to that of the propene normal adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCH_2CF_2I$

a_2 = the relative area of $(CF_3)_2CFCH_2CH(CH_3)I$

Temp. 184°C time 10 min
Lamp 25 W

	a_1	a_2
	28.6	100
	23.5	100
	24.4	100
mean	23.83	100

Temp. 155°C time 35 min
Lamp 25 W

	a_1	a_2
	16.7	100
	15.7	100
	16.5	100
mean	16.3	100

Temp. 141°C time 30 min
Lamp 25 W

	a_1	a_2
	17.4	100
	17.4	100
	16.7	100
mean	17.17	100

Temp. 125°C time 35 min
Lamp 60 W

	a_1	a_2
	12.7	100
	13.2	100
	13.3	100
mean	13.07	100

Temp. 108°C time 30 min
Lamp 100 W

	a_1	a_2
	10.0	100
	9.4	100
	10.5	100
mean	9.97	100

Temp. 90°C time 55 min
Lamp 100 W

	a_1	a_2
	10.7	100
	11.4	100
	10.0	100
mean	10.7	100

Temp. 78°C time 60 min
Lamp 150 W

	a_1	a_2
	8.83	100
	9.27	100
	9.63	100
mean	9.24	100

Temp. 70°C time 60 min
Lamp 100 W

	a_1	a_2
	6.14	100
	6.76	100
	7.10	100
mean	6.67	100

The relative rates of formation of the observed adducts are shown in Table 1-5.

b) Runs without 1,1-difluoroethylene

In a series of high conversion experiments, heptafluoro-2-iodopropane (1.6×10^{-3} moles) was photolysed with propene (4.13×10^{-4} moles) at various temperatures using a medium pressure mercury lamp. The temperature was varied in the range 74-178°C. Peak areas were measured relative to that of the normal adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCH_2CH(CH_3)I$

a_2 = the relative area of $(CF_3)_2CFCH(CH_3)CH_2I$

Temp. 178°C time 60 min

	a_1	a_2
	100	1.159
	100	1.202
	100	1.176
mean	100	1.179

Temp. 162°C time 45 min

	a_1	a_2
	100	1.044
	100	1.036
	100	1.050
mean	100	1.043

Temp. 140°C time 120 min

	a_1	a_2
	100	0.928
	100	0.915
	100	0.918
mean	100	0.920

Temp. 124°C time 90 min

	a_1	a_2
	100	0.818
	100	0.822
	100	0.826
mean	100	0.822

Table 1-5. Addition of heptafluoro-2-iodopropane to propene and 1,1-difluoroethylene

Temperature °C	reactants	products	
	$\frac{[CH_2=CH-CH_3]_i}{[CH_2=CF_2]_i}$	$\frac{[(CF_3)_2CFCH_2CF_2I]_f}{[(CF_3)_2CFCH_2CH(CH_3)I]_f}$	$\frac{[(CF_3)_2CFCH(CH_3)CH_2I]_f}{[(CF_3)_2CFCH_2CH(CH_3)I]_f}$
184	0.233	0.223	-
178	-	-	0.01179
162	-	-	0.01043
155	0.233	0.152	-
141	0.233	0.160	-
140	-	-	0.00920
125	0.233	0.122	-
124	-	-	0.00822
108	0.233	0.093	-
105	-	-	0.00694
90	0.233	0.1	-
78	0.233	0.086	-
74	-	-	0.00512
70	0.233	0.062	-

Temp. 105°C time 90 min

	a_1	a_2
	100	0.712
	100	0.675
	100	0.694
mean	100	0.694

Temp. 74°C time 90 min

	a_1	a_2
	100	0.515
	100	0.495
	100	0.525
mean	100	0.512

The relative rates of formation of the observed products are shown in Table 1-5.

A least squares plot of log $([(CF_3)_2CFCH(CH_3)CH_2I]_f / [(CF_3)_2CFCH_2CH(CH_3)I]_f)$ against 10^3 K/T gave a line of gradient -0.54 ± 0.02 and intercept -0.74 ± 0.01. A least squares plot of log $([(CF_3)_2CFCH_2CH(CH_3)I]_f / [(CF_3)_2CFCH_2CF_2I]_f \times [CH_2{=}CF_2]_i / [CH_3{-}CH{=}CH_2]_i)$ against 10^3 K/T gave a line of gradient $+0.66 \pm 0.05$ and intercept -0.13 ± 0.04.

F. Competitive addition of $(CF_3)_2CFI$ to 1,1,1-trifluoropropene and 1,1-difluoroethylene

As for tetrafluoroethylene and propene, 1,1-difluoroethylene was the reference.

a) Runs with difluoroethylene

In a first series of experiments, heptafluoro-2-iodopropane (1.6×10^{-3} moles) was photolysed at various temperatures, in the presence of 1,1,1-trifluoropropene (3.47×10^{-4} or 2.32×10^{-4} moles) and 1,1-difluoroethylene (7.75×10^{-5} moles) using a medium pressure mercury lamp. The temperature was varied over the range 73-204°C. The reaction times were adjusted to keep the consumption of

1,1-difluoroethylene below 5%. Peak areas were measured relative to the normal adduct of 1,1,1-trifluoropropene, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCH_2CF_2I$
a_2 = the relative area of $(CF_3)_2CFCH_2CH(CF_3)I$

Temp. 204°C time 5 min

	a_1	a_2
	49.0	100
	56.0	100
	53.0	100
mean	52.67	100

Temp. 168°C time 10 min

	a_1	a_2
	60.0	100
	54.6	100
	56.0	100
mean	56.87	100

Temp. 143°C time 20 min

	a_1	a_2
	37.0	100
	36.7	100
	35.4	100
mean	36.37	100

Temp. 125°C time 30 min

	a_1	a_2
	60.7	100
	59.0	100
	57.0	100
mean	58.9	100

Temp. 104°C time 30 min

	a_1	a_2
	64.4	100
	60.0	100
	62.7	100
mean	62.36	100

Temp. 87°C time 30 min

	a_1	a_2
	67.0	100
	61.7	100
	61.0	100
mean	63.23	100

Temp. 73°C time 45 min

	a_1	a_2
	44.7	100
	42.6	100
	42.7	100
mean	43.33	100

The relative rates of formation of the observed products are shown in Table 1-6.

b) Runs without 1,1-difluoroethylene

In a series of high conversion experiments, heptafluoro-2-iodopropane (1.6×10^{-3} moles) was photolysed at various temperatures, in the presence of 1,1,1-trifluoropropene (2.89×10^{-4} moles), by means of a medium pressure mercury lamp. The temperature was varied in the range 75-170°C. Peak areas were measured relative to that of the normal adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCH_2CH(CF_3)I$
a_2 = the relative area of $(CF_3)_2CFCH(CF_3)CH_2I$

Temp. 170°C time 300 min

	a_1	a_2
	100	0.142
	100	0.145
	100	0.130
mean	100	0.139

Temp. 150°C time 180 min

	a_1	a_2
	100	0.114
	100	0.100
	100	0.108
mean	100	0.107

Table 1-6. Addition of $(CF_3)_2CFI$ to 1,1,1-trifluoropropene and 1,1-difluoroethylene

Temperature °C	reactants	products	
	$\frac{[CF_3-CH=CH_2]_i}{[CH_2=CF_2]_i}$	$\frac{[(CF_3)_2CFCH_2CF_2I]_f}{[(CF_3)_2CFCH_2CH(CF_3)I]_f}$	$\frac{[(CF_3)_2CFCH(CF_3)CH_2I]_f}{[(CF_3)_2CFCH_2CH(CF_3)I]_f}$
204	2.987	0.577	-
170	-	-	0.00139
168	2.987	0.624	-
150	-	-	0.00107
143	4.479	0.398	-
127	-	-	0.000777
125	2.987	0.646	-
105	-	-	0.000545
104	2.987	0.684	-
92	-	-	0.000443
87	2.987	0.693	-
75	-	-	0.000346
73	4.479	0.475	-

Temp. 127°C time 360 min

	a_1	a_2
	100	0.0720
	100	0.0820
	100	0.0790
mean	100	0.0777

Temp 105°C time 465 min

	a_1	a_2
	100	0.0555
	100	0.0512
	100	0.0569
mean	100	0.0545

Temp. 92°C time 600 min

	a_1	a_2
	100	0.0480
	100	0.0422
	100	0.0427
mean	100	0.0443

Temp. 75°C time 510 min

	a_1	a_2
	100	0.0310
	100	0.0323
	100	0.0370
	100	0.0380
mean	100	0.0346

The relative rates of formation of these adducts are shown in Table 1-6.

A least squares plot of log ($[(CF_3)_2CFCH(CF_3)CH_2I]_f / [(CF_3)_2CFCH_2CH(CF_3)I]_f$) against 10^3 K/T gave a line of gradient -0.993 ± 0.062 and an intercept -0.62 ± 0.02. A similar plot of log ($[(CF_3)_2CFCH_2CH(CF_3)I]_f / [(CF_3)_2CFCH_2CF_2I]_f \times [CH_2{=}CF_2]_i / [CF_3{-}CH{=}CH_2]_i$) against 10^3 K/T gave a line of gradient -0.116 ± 0.04 and intercept 0.005 ± 0.01.

G. Attempted addition of $(CF_3)_2CFI$ to hexafluoropropene

In an attempt to add perfluoroisopropyl radicals to hexafluoropropene, heptafluoro-2-iodopropane (8×10^{-4} moles) was irradiated with hexafluoropropene (1.5×10^{-4} and 3×10^{-4} moles) at 140°C and 288°C, for 24 hours. Several experiments were carried out under these conditions and both a 150 watt tungsten lamp and a medium pressure mercury lamp were tried. No adduct was ever detected in any of the experiments.

The results of this chapter will be discussed at the end of chapter 2, along with the results of the kinetic study of the addition of $(CF_3)_3C^\cdot$ radicals to olefins.

CHAPTER 2:

THE ADDITION OF PERFLUORO-t-BUTYL RADICALS TO OLEFINS.

Experimental

1. Material

Nonafluoro-2-methyl-2-iodopropane was a gift from Dr. D.C. England and the Central Research Department of E.I. Du Pont de Nemours and Company. It was used as received.

As in part 1, the olefins (ethylene, vinyl fluoride, 1,1-difluoroethylene, trifluoroethylene, tetrafluoroethylene, propene and hexafluoropropene) were dried and trap to trap distilled and degassed before use.

2. Apparatus and Procedure

The apparatus and procedure were as described in part 1, with the following modification:

a) Owing to the involatility of the perfluoro-t-butyl iodide, its pressure was measured into the largest storage bulb on the line, namely bulb B, and distilled into the reaction vessel together with the other reactants.

b) After reaction, reactants and products were distilled into a greaseless tube and a few drops of methylene chloride were added to dissolve the solid mixture.

3. Analysis and Identification of Products

Methods of analysis and identification were as in Chapter 1, the only difference being that analysis was on a 15 ft, squalene column. The same column was used in coupled g.l.c.-m.s. studies.

The spectra of the adducts from competitive addition of $(CF_3)_3Cl$ to ethylene and various olefins are shown below.

A. Vinyl fluoride

A preliminary experiment was carried out to identify the reaction products, in which nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles), vinyl fluoride (2.32×10^{-4} moles) and ethylene (7.75×10^{-5} moles) were photolysed together, at 140°C, for one hour, using a medium pressure mercury lamp. Gas chromatography indicated the presence of three adducts: $(CF_3)_3CCH_2CHFI$, $(CF_3)_3CCH_2CH_2I$ and $(CF_3)_3CCHFCH_2I$, eluted in that order. Each of the adducts gave the expected parent ion in the mass spectrum, together with the expected fragmentation ions.

The two adducts of vinyl fluoride, $(CF_3)_3CCH_2CHFI$ and $(CF_3)_3CCHFCH_2I$, were distinguished by the presence of the ion $CHFI^+$ (m/e = 159) in the spectrum of the former adduct and absent in the spectrum of the latter adduct, while the ion CH_2I^+ (m/e = 141) was present in the spectrum of the latter adduct, but not the former.

A-1:- $(CF_3)_3CCH_2CHFI$

m/e	rel. Abundance	Assignment
392	3.6	$C_6H_3F_{10}I^+$
265	85.4	$C_6H_3F_{10}^+$
246	15	$C_6H_3F_9^+$
225	8.7	$C_6HF_8^+$
196	15	$C_5H_3F_7^+$

A-1(cont)

m/e	rel. Abundance	Assignment
181	25	$C_4F_7^+$
173	42.5	$C_2H_3FI^+$
159	5	$CHFI^+$
157	15	$C_5H_2F_5^+$
145	10	$C_4H_2F_5^+$
137	5	$C_5HF_4^+$
128	12.5	HI^+
127	40	I^+
113	10	$C_3HF_4^+$
95	7.5	$C_3H_2F_3^+$
93	10	$C_3F_3^+$
75	10	$C_3HF_2^+$
69	100	CF_3^+
65	25	$C_2H_3F_2^+$
64	10	$C_2H_2F_2^+$
51	27.5	CHF_2^+
50	37.5	CF_2^+

A-2:- $(CF_3)_3CCH_2CH_2I$

m/e	rel. Abundance	Assignment
374	20	$C_6H_4F_9I^+$
247	13.3	$C_6H_4F_9^+$
228	5.3	$C_6H_4F_8^+$
208	9.3	$C_6H_3F_7^+$ & $C_2F_3I^+$

A-2(cont)

m/e	rel. Abundance	Assignment
181	9.3	$C_4F_7^+$
155	33.3	$C_2H_4I^+$ & $C_5F_5^+$
141	8	CH_2I^+
139	6.7	$C_5H_3F_4^+$
128	22.7	HI^+
127	26.7	I^+
95	6.7	$C_3H_2F_3^+$
93	6.7	$C_3F_3^+$
69	100	CF_3^+
75	10.7	$C_3HF_2^+$
47	> 100	$C_2H_4F^+$

A-3:- $(CF_3)_3CCHFCH_2I$

m/e	rel. Abundance	Assignment
392	25	$C_6H_3F_{10}I^+$
365	6.2	$C_6H_3F_{10}$
208	20.8	$C_6H_3F_7^+$ & $C_2F_3I^+$
181	12.5	$C_4F_7^+$
173	29.1	$C_2H_3FI^+$
153	8.3	$C_2H_2I^+$
141	12.5	CH_2I^+
128	33.3	HI^+
127	37.5	I^+
95	6.2	$C_3H_2F_3^+$
93	8.3	$C_3F_3^+$

A-3(cont)

m/e	rel. Abundance	Assignment
69	100	CF_3^+
65	91.7	$C_2H_3F_2^+$

B. 1,1-Difluoroethylene

In a preliminary experiment, nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) and 1,1-difluoroethylene (2.32×10^{-4} moles) were irradiated together for 30 minutes at 150°C using a medium pressure mercury arc. The g.l.c. trace, obtained after passing the mixture on a squalene column, showed only one adduct, which was identified by the parent ion in its mass spectrum, and the presence of an ion m/e = 177 (CF_2I^+). The ion m/e = 141 (CH_2I^+) was absent.

B-1:- $(CF_3)_3CCH_2CF_2I$

m/e	rel. Abundance	Assignment
410	0	$C_6H_2F_{11}I^+$
283	42.9	$C_6H_2F_{11}^+$
200	5.7	$C_4F_8^+$
195	5.7	$C_5H_2F_7^+$
191	7.1	$C_2H_2F_2I^+$
181	8.6	$C_4F_7^+$
177	22.9	CF_2I^+
145	7.1	$C_4H_2F_5^+$

B-1(cont)

m/e	rel. Abundance	Assignment
128	7.1	HI^+
127	14.3	I^+
113	7.1	$C_3HF_4^+$
93	5.7	$C_3F_3^+$
69	100	CF_3^+
64	35.7	$C_2H_2F_2^+$

C. Trifluoroethylene

In a preliminary experiment, nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) was irradiated in the presence of trifluoroethylene (2.32×10^{-4} moles) for 30 minutes, at 200°C. The light source was a medium pressure mercury lamp. Two adducts were observed on the g.l.c. trace: $(CF_3)_3CCHFCF_2I$ and $(CF_3)_3CCF_2CHFI$. Each component gave the expected parent ion in its mass spectrum and the ion m/e = 159 ($CHFI^+$) was present in the spectrum of the latter but absent in the spectrum of the former, while exactly the opposite was true of the ion m/e = 177 (CF_2I^+).

C-1:- $(CF_3)_3CCHFCF_2I$

m/e	rel. Abundance	Assignment
428	0.05	$C_6HF_{12}I^+$
301	100	$C_6HF_{12}^+$

C-1(cont)

m/e	rel. Abundance	Assignment
213	33.3	$C_5HF_8^+$
209	72.2	$C_2HF_3I^+$
181	27.7	$C_4F_7^+$
177	38.9	CF_2I^+
163	27.7	$C_4HF_6^+$
128	16.7	HI^+
127	55.5	I^+
113	16.7	$C_3HF_4^+$
101	33.3	$C_2HF_4^+$
93	22.2	$C_3F_3^+$
82	83.3	$C_2HF_3^+$
75	22.2	$C_3HF_2^+$
69	$>$100	CF_3^+
63	16.7	$C_2HF_2^+$
51	72.2	CHF_2^+

C-2:- $(CF_3)_3CCF_2CHFI$

m/e	rel. Abundance	Assignment
428	22.7	$C_6HF_{12}I^+$
301	36.3	$C_6HF_{12}^+$
209	61.3	$C_2HF_3I^+$
181	43.2	$C_4F_7^+$
163	11.4	$C_4HF_6^+$
159	22.7	$CHFI^+$

C-2(cont)

m/e	rel. Abundance	Assignment
128	22.7	HI^+
127	45.5	I^+
113	6.8	$C_3HF_4^+$
101	100	$C_2HF_4^+$
93	11.4	$C_3F_3^+$
82	54.5	$C_2HF_3^+$
75	9.1	$C_3HF_2^+$
69	> 100	CF_3^+
63	11.4	$C_2HF_2^+$
51	40.1	CHF_2^+

D. Tetrafluoroethylene

In a preliminary experiment, nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles), trifluoroethylene (7.75×10^{-5} moles) and tetrafluoroethylene (2.32×10^{-4} moles) were irradiated by a medium pressure mercury lamp for 30 minutes at 200°C. Five addition products were observed on the chromatogram: $(CF_3)_3C(CF_2)_2I$; $(CF_3)_3CCHFCF_2I$; $(CF_3)_3CCF_2CHFI$; $(CF_3)_3C(CF_2)_4I$ and $(CF_3)_3CCHF(CF_2)_3I$. These products were eluted in that order on a squalene column. Each component was identified from its molecular ion and characteristic fragment ions in the mass spectra. The cross-telomer was identified as the product of addition to trifluoroethylene first because of the presence of a signal for $C_6HF_{12}^+$ (m/e = 301) in the spectrum. If the addition was to the tetrafluoroethylene first, no fragment containing 6 carbons could contain one hydrogen and as many as twelve fluorines without extensive rearrangement.

D-1:- $(CF_3)_3C(CF_2)_2I$

m/e	rel. Abundance	Assignment
446	2.7	$C_6F_{13}I^+$
319	41.1	$C_6F_{13}^+$
231	16.4	$C_5F_9^+$
227	68.5	$C_2F_4I^+$
181	33.0	$C_4F_7^+$
177	23.2	CF_2I^+
127	41.1	I^+
119	53.4	$C_2F_5^+$
100	41.1	$C_2F_4^+$
93	13.7	$C_3F_3^+$
81	8.2	$C_2F_3^+$
74	5.5	$C_3F_2^+$
69	100	CF_3^+
50	9.6	CF_2^+

D-2:- **$(CF_3)_3C(CF_2)_4I$**

m/e	rel. Abundance	Assignment
546	0	$C_8F_{17}I^+$
419	4.1	$C_8F_{17}^+$
270	2.7	$C_4F_5I^+$
220	9.6	$C_3F_3I^+$
181	17.8	$C_4F_7^+$
177	10.9	CF_2I^+
131	8.2	$C_3F_5^+$
127	17.8	I^+
119	5.4	$C_2F_5^+$
100	5.4	$C_2F_4^+$
69	100	CF_3^+

D-3:- **$(CF_3)_3CCHF(CF_2)_3I$**

m/e	rel. Abundance	Assignment
528	0	$C_8HF_{16}I^+$
401	9.7	$C_8HF_{16}^+$
301	4.2	$C_6HF_{12}^+$
227	2.8	$C_2F_4I^+$
201	19.4	$C_4HF_8^+$
181	11.1	$C_4F_7^+$
177	34.7	CF_2I^+
163	8.3	$C_4HF_6^+$
131	6.9	$C_3F_5^+$
127	25	I^+
119	6.9	$C_2F_5^+$

D-3(cont)

m/e	rel. Abundance	Assignment
113	8.3	$C_3HF_4^+$
101	8.3	$C_2HF_4^+$
100	11.1	$C_2F_4^+$
69	100	CF_3^+
51	37.5	CHF_2^+

E. Propene

In the preparative run, nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) and propene (2.32×10^{-4} moles) were irradiated for 2 hours at 150°C, using a medium pressure mercury lamp. Two adducts were observed on the g.l.c. trace: $(CF_3)_3CCH_2CH(CH_3)I$ and $(CF_3)_3CCH(CH_3)CH_2I$. The former was identified by its mass spectrum. It showed the expected parent ion and fragmentation ions, and there was no ion at m/e = 141 (CH_2I^+). The latter could not be identified by mass spectrometry because of its very small concentration in the mixture, but its identity was attested by the similarity of its relative retention time to that of the corresponding adduct from CF_3I and $(CF_3)_2CFI$.

E-1:- $(CF_3)_3CCH_2CH(CH_3)I$

m/e	rel. Abundance	Assignment
388	0.05	$C_7H_6F_9I^+$
261	100	$C_7H_6F_9^+$

E-1(cont)

m/e	rel. Abundance	Assignment
220	19.1	$C_3F_3I^+$
180	22.1	$C_5H_6F_6^+$
168	26.1	$C_6HF_5^+$
151	8.8	$C_3HF_6^+$
145	44.1	$C_4H_2F_5^+$
128	13.2	HI^+
127	48.5	I^+
113	5.8	$C_3HF_4^+$
101	5.8	$C_2HF_4^+$
93	10.3	$C_3F_3^+$
77	7.4	$C_3H_3F_2^+$
75	8.8	$C_3HF_2^+$
69	98.5	CF_3^+
65	23.5	$C_2H_3F_2^+$
61	48.5	$C_3H_6F^+$
59	26.5	$C_3H_4F^+$
47	30.9	$C_2H_4F^+$
41	97.1	$C_3H_5^+$
39	61.8	$C_3H_3^+$

4. Details of Kinetic Experiments

A. Competitive addition of $(CF_3)_3CI$ to ethylene and vinyl fluoride.

Because of the smaller amount of reverse adduct formed (c.f. the reactions of $(CF_3)_2CFI$), it was not possible to limit the consumption of ethylene to 5% or less and also measure accurately the three adducts in competitive experiments. Two series of photolyses were therefore carried out. In the first low conversion series, ethylene was present; in the second high conversion series, it was excluded and both adducts of vinyl fluoride could be analysed quantitatively.

a) Runs with ethylene

Nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) was photolysed in the presence of ethylene (7.75×10^{-5} moles) and vinyl fluoride (2.32×10^{-4} moles) using a tungsten lamp. The temperature was varied in the range 36-151°C. The peak areas were measured relative to that of the normal adduct of vinyl fluoride, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_3CCH_2CH_2I$

a_2 = the relative area of $(CF_3)_3CCH_2CHFI$

Temp $151^{o}C$ time 3 min
Lamp 25 W

	a_1	a_2
	150.0	100
	146.0	100
	148.0	100
mean	148	100

Temp. $137^{o}C$ time 15 min
Lamp 25 W

	a_1	a_2
	147.0	100
	147.0	100
	142.0	100
mean	145.3	100

Temp. $102^{o}C$ time 30 min
Lamp 60 W

	a_1	a_2
	138.5	100
	144.0	100
	140.0	100
mean	140.8	100

Temp. $89^{o}C$ time 30 min
Lamp 100 W

	a_1	a_2
	162.5	100
	166.0	100
	161.0	100
mean	163.2	100

Temp. $72^{o}C$ time 30 min
Lamp 100 W

	a_1	a_2
	200.0	100
	201.0	100
	197.0	100
mean	199.3	100

Temp. $58^{o}C$ time 45 min
Lamp 150 W

	a_1	a_2
	175.7	100
	186.0	100
	188.0	100
mean	183.2	100

Temp. $36^{o}C$ time 35 min
Lamp 100 W

	a_1	a_2
	209.4	100
	220.0	100
	236.0	100
mean	221.8	100

The relative rate of formation of the observed adducts are shown in table 2-1.

b) Runs without ethylene

Nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) was photolysed in the presence of vinyl fluoride (2.32×10^{-4} moles) at different temperatures using a medium pressure mercury lamp. The temperature was varied in the range 76-163°C and peak areas were measured relative to that of the normal adduct which was set equal to 100.

let a_1 = the relative area of $(CF_3)_3CCH_2CHFI$

a_2 = the relative area of $(CF_3)_3CCHFCH_2I$

Temp. 163°C time 120 min

	a_1	a_2
	100	0.534
	100	0.541
	100	0.548
mean	100	0.541

Temp. 142°C time 150 min

	a_1	a_2
	100	0.423
	100	0.430
	100	-
mean	100	0.426

Temp. 140°C time 120 min

	a_1	a_2
	100	0.405
	100	0.386
	100	0.427
mean	100	0.406

Temp. 123°C time 120 min

	a_1	a_2
	100	0.346
	100	0.367
	100	0.372
mean	100	0.362

Temp. 107°C time 120 min

	a_1	a_2
	100	0.299
	100	0.340
	100	0.278
mean	100	0.305

Temp. 94°C time 120 min

	a_1	a_2
	100	0.268
	100	0.279
	100	0.272
mean	100	0.273

Temp. 72°C time 120 min

	a_1	a_2
	100	0.176
	100	0.179
	100	0.194
mean	100	0.183

The relative rates of formation of these observed adducts are shown in Table 2-1

A least squares plot of log $\left(\left[(CF_3)_3CCHFCH_2I\right]_f / \left[(CF_3)_3CCH_2CHFI\right]_f\right)$ against 10^3 K/T gave a line with a gradient of -0.73 ± 0.09 and an intercept of -0.602 ± 0.04. A similar plot of log $\left(\left[(CF_3)_3CCH_2CHFI\right]_f / \left[(CF_3)_3CCH_2CH_2I\right]_f \times \left[CH_2{=}CH_2\right]_i / \left[CH_2{=}CHF\right]_i\right)$ against 10^3 K/T gave a line with a gradient of -0.215 ± 0.13 and an intercept of -0.129 ± 0.04.

Table 2-1: Addition of $(CF_3)_3CI$ to ethylene and vinyl fluoride

subscript i refers to initial concentrations; subscript f refers to final concentrations.

Temperature °C	reactants	products	
	$\frac{[CH_2=CHF]_i}{[CH_2=CH_2]_i}$	$\frac{[(CF_3)_3CCH_2CH_2I]_f}{[(CF_3)_3CCH_2CHFI]_f}$	$\frac{[(CF_3)_3CCHFCH_2I]_f}{[(CF_3)_3CCH_2CHFI]_f}$
163	-	-	0.00541
151	2.987	1.557	-
142	-	-	0.00426
140	-	-	0.00406
137	2.987	1.529	-
123	-	-	0.00362
107	-	-	0.00305
102	2.987	1.482	-
94	-	-	0.00273
89	2.987	1.717	-
72	-	-	0.00183
72	2.987	2.097	-
58	2.987	1.927	-
36	2.987	2.333	-

B. Competitive addition of $(CF_3)_3CI$ to ethylene and 1,1-difluoroethylene

a) Runs with ethylene

In a series of low conversion runs, nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) was photolysed over a range of temperature 48-152°C, in the presence of 1,1-difluoroethylene (2.32×10^{-4} moles) and ethylene (7.75×10^{-5} moles). The light source was a tungsten lamp. Reaction times were adjusted to ensure that the conversion of the olefins did not exceed 5%. The peak areas were measured relative to that of the normal difluoroethylene adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_3CCH_2CH_2I$

a_2 = the relative area of $(CF_3)_3CCH_2CF_2I$

Temp. 152°C time 30 min
Lamp 25 W

	a_1	a_2
	188.5	100
	195.0	100
	195.0	100
	192.6	100
mean	192.8	100

Temp. 132°C time 25 min
Lamp 60 W

	a_1	a_2
	197.8	100
	198.7	100
	198.3	100
mean	198.3	100

Temp. 115°C time 20 min
Lamp 60 W

	a_1	a_2
	217.4	100
	220.0	100
	220.0	100
mean	219.1	100

Temp. 100°C time 30 min
Lamp 60 W

	a_1	a_2
	225.0	100
	228.6	100
	236.8	100
mean	230.1	100

Temp. 88°C time 60 min
Lamp 150 W

	a_1	a_2
	216.7	100
	216.7	100
	216.2	100
mean	216.5	100

Temp. 68°C time 50 min
Lamp 150 W

	a_1	a_2
	243.2	100
	258.9	100
	-	100
mean	251.1	100

Temp. 60°C time 45 min
Lamp 150 W

	a_1	a_2
	291.0	100
	300.0	100
	300.0	100
mean	297.0	100

Temp. 48°C time 130 min
Lamp 60 W

	a_1	a_2
	285	100
	285	100
	287.5	100
mean	285.8	100

The relative rates of formation of these two adducts are shown in table 2-2

b) Runs without ethylene

In an attempt to study the orientation ratios, nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) was photolysed in the presence of 1,1-difluoroethylene (2.32×10^{-4} moles) for 24 hours, using a medium pressure mercury lamp. The photolysis was tried at 150°C and 200°C. No reverse adduct could be detected (not even using a more sensitive flame ionization detector). Therefore, we can estimate that the ratio $[(CF_3)_3CCF_2CH_2I]_f / [(CF_3)_3CCH_2CF_2I]_f$ was, in both cases, smaller than 0.0001.

Table 2-2: Addition of $(CF_3)_3CI$ to ethylene and 1,1-difluoroethylene.

	reactants	products	
Temperature °C	$\frac{[CH_2=CF_2]_i}{[CH_2=CH_2]_i}$	$\frac{[(CF_3)_3CCH_2CH_2I]_f}{[(CF_3)_3CCH_2CF_2I]_f}$	$\frac{[(CF_3)_3CCF_2CH_2I]_f}{[(CF_3)_3CCH_2CF_2I]_f}$
200	-	-	$<10^{-4}$
152	2.987	2.128	-
150	-	-	$<10^{-4}$
132	2.987	2.189	-
115	2.987	2.419	-
100	2.987	2.540	-
88	2.987	2.391	-
68	2.987	2.772	-
60	2.987	3.279	-
48	2.987	3.156	-

A least squares plot of log $([(CF_3)_3CCH_2CF_2I]_f/[(CF_3)_3CCH_2CH_2I]_f \times [CH_2=CH_2]_i/[CH_2=CF_2]_i)$ against 10^3 K/T gave a line with a gradient of -0.243 ± 0.1 and an intercept of -0.222 ± 0.04.

C. Competitive addition of $(CF_3)_3CI$ to ethylene and trifluoroethylene

a) Runs with ethylene

In a first series of experiments, nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) was photolysed at different temperatures in the presence of trifluoroethylene (3.47×10^{-4} moles) and ethylene (7.75×10^{-5} moles), by means of a tungsten lamp. The temperature was varied in the range 58-159°C. Peak areas were measured relative to that of the normal adduct of trifluoroethylene which was set equal to 100.

let a_1 = the relative area of $(CF_3)_3CCH_2CH_2I$

a_2 = the relative area of $(CF_3)_2CCHFCF_2I$

Temp. 159°C time 9 min
Lamp 25 W

	a_1	a_2
	3050	100
	2910	100
	2930	100
mean	2963	100

Temp. 141°C time 30 min
Lamp 25 W

	a_1	a_2
	3790	100
	3920	100
	3770	100
mean	3827	100

Temp. 97°C time 15 min
Lamp 100 W

	a_1	a_2
	6230	100
	6860	100
	6880	100
mean	6657	100

Temp. 91°C time 20 min
Lamp 25 W

	a_1	a_2
	5946	100
	5943	100
	5831	100
mean	5907	100

Temp. 76°C time 40 min
Lamp 100 W

	a_1	a_2
	7610	100
	7390	100
	7140	100
mean	7380	100

Temp. 58°C time 120 min
Lamp 100 W

	a_1	a_2
	10000	100
	8550	100
	8100	100
mean	8883	100

The relative rates of formation of the observed products are shown in table 2-3.

b) Runs without ethylene

In a second series of experiments, nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) was photolysed at different temperatures by means of a medium pressure mercury lamp in the presence of trifluoroethylene (2.32×10^{-4} moles). The temperature range was between 78 and 190°C. Peak areas were measured relative to that of the normal adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_3CCHFCF_2I$

a_2 = the relative area of $(CF_3)_3CCF_2CHFI$

Temp. 190°C time 90 min

	a_1	a_2
	100	2.48
	100	2.36
	100	–
mean	100	2.42

Temp. 178°C time 75 min

	a_1	a_2
	100	2.61
	100	2.59
	100	2.61
mean	100	2.603

Temp. 140°C time 90 min

	a_1	a_2
	100	1.89
	100	1.83
	100	1.86
mean	100	1.86

Temp. 109°C time 150 min

	a_1	a_2
	100	1.485
	100	1.40
	100	1.41
mean	100	1.432

Temp. 96°C time 120 min

	a_1	a_2
	100	1.16
	100	1.20
	100	1.25
mean	100	1.203

Temp. 78°C time 120 min

	a_1	a_2
	100	1.05
	100	1.10
	100	1.20
mean	100	1.167

The relative rates of formation of the observed adducts are shown in table 2-3

Table 2-3: Addition of $(CF_3)_3CI$ to ethylene and trifluoroethylene

Temperature °C	reactants	products	
	$\frac{[CHF=CF_2]_i}{[CH_2=CH_2]_i}$	$\frac{[(CF_3)_3CCH_2CH_2I]_f}{[(CF_3)_3CCHFCF_2I]_f}$	$\frac{[(CF_3)_3CCF_2CHFI]_f}{[(CF_3)_3CCHFCF_2I]_f}$
190	-	-	0.0242
178	-	-	0.0260
159	4.479	34.26	-
141	4.479	44.24	-
140	-	-	0.0186
109	-	-	0.0143
97	4.479	76.96	-
96	-	-	0.0120
91	4.479	68.29	-
78	-	-	0.0117
76	4.479	85.32	-
58	4.479	102.69	-

A least squares plot of log $([(CF_3)_3CCF_2CHFI]_f/[(CF_3)_3CCHFCF_2I]_f)$ against $10^3\,K/T$ gave a line with intercept -0.44 ± 0.05 and gradient -0.534 ± 0.1. A similar line for log $([(CF_3)_3CCHFCF_2I]_f/[(CF_3)_3CCH_2CH_2I]_f \times [CH_2{=}CH_2]_i/[CHF{=}CF_2]_i)$ against $10^3\,K/T$ had an intercept of -0.683 ± 0.06 and a gradient of -0.663 ± 0.15.

D. Competitive addition of $(CF_3)_3CI$ to tetrafluoroethylene and trifluoroethylene

Because of the large difference in reactivity between tetrafluoroethylene and ethylene, the competitive runs were carried out using trifluoroethylene instead of ethylene. In a series of experiments at various temperatures, nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) was photolysed by a tungsten lamp or a medium pressure mercury arc in the presence of tetrafluoroethylene (2.32×10^{-4} moles) and trifluoroethylene (1.55×10^{-4} moles). The reaction times were adjusted so that the conversion of the olefins did not exceed 5%. The temperature was varied in the range 53-170°C. Peak areas were measured relative to that of the tetrafluoroethylene adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_3CCHFCF_2I$
a_2 = the relative area of $(CF_3)_3CCF_2CF_2I$
a_3 = the relative area of $(CF_3)_3CCHF(CF_2)_3I$
a_4 = the relative area of $(CF_3)_3C(CF_2)_4I$

Because of the time required for the g.l.c. analysis, only two g.l.c. traces were taken for each reaction mixture, so that the analysis could be achieved the same day as the experiment.

Temp. 170°C time 20 min
Lamp 60 W

	a_1	a_2	a_3	a_4
	500	100	34	9
	494	100	37	10
mean	497	100	35.5	9.5

Temp. 156°C time 20 min
Lamp 60W

	a_1	a_2	a_3	a_4
	600	100	-	-
	600	100	-	-
mean	600	100	-	-

Temp. 140°C time 10 min
Lamp 150 W

	a_1	a_2	a_3	a_4
	520	100	110	36
	510	100	75	30
mean	515	100	92.5	33

Temp. 128°C time 30 min
Lamp 150 W

	a_1	a_2	a_3	a_4
	675	100	135	37
	679	100	139	41
mean	677	100	137	39

Temp. 109°C time 45 min
Lamp 150 W

	a_1	a_2	a_3	a_4
	607	100	123	33
	610	100	122	35
mean	608.5	100	122.5	34

Temp. 94°C time 35 min
Lamp 150 W

	a_1	a_2	a_3	a_4
	752	100	139	37
	730	100	129	31
mean	741	100	134	33

Table 2-4: Addition of $(CF_3)_3CI$ to tetrafluoroethylene and trifluoroethylene

Temperature °C	reactants	products		
	$\frac{[CF_2{=}CF_2]_i}{[CHF{=}CF_2]_i}$	$\frac{[(CF_3)_3CCHFCF_2I]_f}{[(CF_3)_3CCF_2CF_2I]_f}$	$\frac{[(CF_3)_3CCHF(CF_2)_3I]_f}{[(CF_3)_3CCF_2CF_2I]_f}$	$\frac{[(CF_3)_3C(CF_2)_4I]_f}{[(CF_3)_3CCF_2CF_2I]_f}$
170	1.493	5.194	0.297	0.077
156	1.493	6.27	-	-
140	1.493	5.382	0.769	0.266
128	1.493	7.075	1.145	0.315
109	1.493	6.359	1.024	0.274
94	1.493	7.743	1.120	0.266
82	1.493	8.245	0.840	0.222
63	1.493	7.331	-	-
53	1.493	8.172	0.226	0.077

Temp. 82°C time 240 min
Lamp 150 W

	a_1	a_2	a_3	a_4
	783	100	92	27
	795	100	109	28
mean	789	100	100.5	27.5

Temp. 63°C time 60 min
Lamp U.V.

	a_1	a_2	a_3	a_4
	700	100	-	-
	703	100	-	-
mean	701.5	100	-	-

Temp. 53°C time 60 min
Lamp U.V.

	a_1	a_2	a_3	a_4
	764	100	29	11
	800	100	25	8
mean	782	100	27	9.5

The relative rates of formation of these adducts are shown in table 2-4.

A least squares plot of log $([(CF_3)_3C(CF_2)_2I]_f + [(CF_3)_3C(CF_2)_4I]_f / [(CF_3)_3CCHFCF_2I]_f + [(CF_3)_3CCHF(CF_2)_3I]_f \times [CHF{=}CF_2]_i / [CF_2{=}CF_2]_i)$ against $10^3\ K/T$ gave a straight line with an intercept -0.377 ± 0.05 and a gradient of -0.225 ± 0.14.

B. Addition of $(CF_3)_3CI$ to propene

Two experiments were carried out to determine the orientation ratio for the addition of perfluoro-t-butyl radicals to propene. Nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) was photolysed at 163°C in the presence of propene (4.13×10^{-4} moles). The light source was a 150 W tungsten lamp. Peak areas were measured relative to that of the normal adduct, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_3CCH_2CH(CH_3)I$

a_2 = the relative area of $(CF_3)_3CCH(CH_3)CH_2I$

run 1

	a_1	a_2
	100	0.230
	100	0.220
	100	0.219
mean	100	0.223

run 2

	a_1	a_2
	100	0.26
	100	0.19
	100	0.25
mean	100	0.233

The average ratio $\frac{[(CF_3)_3CCH(CH_3)CH_2I]_f}{[(CF_3)_3CCH_2CH(CH_3)I]_f}$ is 0.00228

F. Addition of $(CF_3)_3CI$ to hexafluoropropene

In an attempt to add $(CF_3)_3C\cdot$ radicals to hexafluoropropene, nonafluoro-2-methyl-2-iodopropane (6.21×10^{-4} moles) was irradiated with hexafluoropropene (4.13×10^{-4} moles) at 163°C, for 15 hours. As in the analogous reaction with $(CF_3)_2CFI$, no adduct was detected at all.

Discussion.

The mechanism of the photochemical addition of perfluoroalkyl iodides to olefins has been well established. The photolysis of perfluoroiodoalkanes produces perfluoroalkyl radicals ($R^{\cdot}$) and iodine atoms. If B represents an unsymmetrical olefin, the reaction sequence, for both the perfluoro isopropyl iodide and the perfluoro-t-butyl iodide, may be written :

$$RI \xrightarrow{h\nu} R^{\cdot} + I^{\cdot} \tag{1}$$

$$R^{\cdot} + B \longrightarrow RB^{\cdot} \tag{2}$$

$$R^{\cdot} + B \longrightarrow RB'^{\cdot} \tag{2'}$$

$$RB^{\cdot} + RI \longrightarrow RBI + R^{\cdot} \tag{3}$$

$$RB'^{\cdot} + RI \longrightarrow RB'I + R^{\cdot} \tag{3'}$$

$$R^{\cdot} + R^{\cdot} \longrightarrow R\text{-}R \tag{4}$$

$$R^{\cdot} + I^{\cdot} \longrightarrow RI \tag{5}$$

$$I^{\cdot} + I^{\cdot} + M \longrightarrow I_2 + M \tag{6}$$

where $RB^{\cdot}$ and RBI are products derived from the addition to the least substituted end of the olefin and $RB'^{\cdot}$ and RB'I are products derived from addition to the most substituted end of the same olefin.

Iodine atoms may also add to the olefin, but this reaction is known to be reversible

$$I^{\cdot} + B \rightleftharpoons IB^{\cdot} \tag{7}$$

$$I^{\cdot} + B \rightleftharpoons IB'^{\cdot} \tag{7'}$$

and, since no di-iodo product was detected in any of the experiments, it may reasonably be assumed that the equilibrium lies well to the left.

The radicals produced in the initiation step (1) may be thermally excited, but, since the chains are long, as measured by the ratio of the yields of dimer (R-R) and adduct (RBI), the effects of the excited radicals on the overall kinetics can be neglected.

It can be shown that

$$k_2'/k_2 = \text{Orientation ratio (Or)} = \frac{[RB'I]_f}{[RBI]_f}$$

In a similar way, in competition runs with another olefin (B_o) used as a reference, it can be shown that

$$k_2/k_{2o} = \frac{[RBI]_f}{[RB_oI]_f} \times \frac{[B_o]_i}{[B]_i}$$

(subscript f = final; i = initial)

where k_{2o} is the rate constant for the addition to the reference olefin and RB_oI is the product resulting from that reaction. However, it is necessary to maintain the yield of products low enough to be able to assume that the ratio $[B_o]/[B]$ remains constant throughout the experiment.

In the case of the addition to tetrafluoroethylene, some telomerization reactions occurred and the following reactions have to be added to the reaction sequence :

$$R(CF_2)_2^{\cdot} + C_2F_4 \longrightarrow R(CF_2)_4^{\cdot} \qquad (8)$$

$$RB_o^{\cdot} + C_2F_4 \longrightarrow RB_o(CF_2)_2^{\cdot} \qquad (9)$$

$$R(CF_2)_4^{\cdot} + RI \longrightarrow R(CF_2)_4I + R^{\cdot} \qquad (10)$$

$$RB_o(CF_2)_2^{\cdot} + RI \longrightarrow RB_o(CF_2)_2I + R^{\cdot} \qquad (11)$$

In the addition of $(CF_3)_2CFI$ to tetrafluoroethylene, E_o represents 1,1-difluoroethylene, whereas in the reactions with $(CF_3)_3CI$, it represents trifluoroethylene. In such systems, all telomers derived from the same adduct radical must be added to the appropriate adduct to obtain the relative rate constants for addition to a particular site. Hence, for tetrafluoroethylene, the rate constants' ratios become

$$k_2/k_{2o} = \frac{[R(CF_2)_2I]_f + [R(CF_2)_4I]_f}{[RE_oI]_f + [RE_o(CF_2)_2I]_f} \times \frac{[E_o]_i}{[C_2F_4]_i}$$

The orientation ratios found for the addition of perfluoroisopropyl iodide to vinyl fluoride and trifluoroethylene are in good agreement with the results of Haszeldine and co-workers[70]. In their work, they report $Or_{(CH_2=CHF)}$ to be 0.01 for the photolytic reaction at 30°C and 0.03 for the thermal reaction at 200°C. In this work, we find an orientation ratio for vinyl fluoride of 0.004 at 30°C and of 0.02 at 200°C. For trifluoroethylene, the Manchester group obtained orientation ratios of 0.04 for the photochemical initiation at 30°C and of 0.15 for the thermal initiation at 190°C, compared to our results 0.05 at 30°C and 0.11 at 190°C. Considering that the work of Haszeldine et al. was performed in sealed tubes and that their experiments were carried out to high conversion (nearly 100%), the agreement is very satisfactory.

The orientation ratios also compare very well with those obtained by Tedder and co-workers[73]. Table 2-5 shows the orientation ratios for the addition of various perfluoroalkyl radicals to vinyl fluoride, 1,1-difluoroethylene and trifluoroethylene. The data show clearly that the successive replacement of fluorine atoms in the trifluoromethyl radical by CF_3- groups causes a substantial increase in selectivity, in contrast to the straight chain radicals, all of which show approximately the same selectivity as pentafluoroethyl radicals.

Table 2-5 : Orientation ratios for the addition of perfluoroalkyl radicals to $CH_2=CHF$, $CH_2=CF_2$ and $CHF=CF_2$.

radical	Or (150°C)			reference
	$CH_2=CHF$	$CH_2=CF_2$	$CHF=CF_2$	
$CF_3^{\cdot}$	0.09	0.03	0.5	29,30
$CF_3CF_2^{\cdot}$	0.06	0.01	0.38	66
$(CF_3)_2CF^{\cdot}$	0.014	0.0009	0.1	this work
$(CF_3)_3C^{\cdot}$	0.0046	0.0001*	0.02	this work
$CF_3(CF_2)_2^{\cdot}$	0.05	0.009	0.25	73
$CF_3(CF_2)_3^{\cdot}$	0.05	0.007	0.24	73
$CF_3(CF_2)_6^{\cdot}$	0.05	0.007	0.23	73
$CF_3(CF_2)_7^{\cdot}$	0.04	0.006	0.22	73

* Upper limit

The study, over a range of temperatures, of the competitive addition, either between two different olefins or between both ends of an unsymmetrical olefin, allows determination of relative Arrhenius parameters. Table 2-6 compares the rate constant ratios at 164°C (437K) and the

Table 2-6 : The Arrhenius parameters for the addition of branched perfluoroalkyl radicals to substituted olefins[29,30,66,74]. (subscript e refers to ethylene)

Olefin	k_2/k_{2e} (437 K) **				E_2-E_{2e} (Kcal.mol^{-1})				A_2/A_{2e}**			
	$CF_3^{\cdot}$	$C_2F_5^{\cdot}$	$i-C_3F_7^{\cdot}$	$t-C_4F_9^{\cdot}$	$CF_3^{\cdot}$	$C_2F_5^{\cdot}$	$i-C_3F_7^{\cdot}$	$t-C_4F_9^{\cdot}$	$CF_3^{\cdot}$	$C_2F_5^{\cdot}$	$i-C_3F_7^{\cdot}$	$t-C_4F_9^{\cdot}$
$\overset{*}{C}H_2CHF$	0.49	0.59	0.53	0.48	0.5	0.6	0.83	0.98	0.9	1.2	1.4	1.48
$\overset{*}{C}H_2CF_2$	0.15	0.17	0.23	0.33	1.2	1.2	1.24	1.11	0.6	0.6	1.0	1.20
$\overset{*}{C}H_2CHCF_3$	0.4	---	0.13	---	0.2	---	1.77	---	0.5	---	1.0	---
$\overset{*}{C}H_2CHCH_3$	2.3	---	5.5	---	-0.9	---	-1.77	---	0.9	---	0.7	---
$\overset{*}{C}HFCH_2$	0.056	0.036	0.0089	0.0026	1.9	2.5	3.55	4.33	0.5	0.7	0.5	0.37
$\overset{*}{C}HFCF_2$	0.031	0.031	0.017	0.013	1.9	1.2	2.8	3.03	0.3	0.1	0.4	0.41
$\overset{*}{C}F_2CH_2$	0.006	0.002	0.0002	---	3.2	3.7	6.13	---	0.2	0.2	0.3	---
$\overset{*}{C}F_2CHF$	0.016	0.012	0.0017	0.0003	2.7	3.3	4.2	5.47	0.4	0.4	0.2	0.15
$\overset{*}{C}F_2CF_2$	0.12	0.067	0.008	0.0008	1.7	1.5	2.47	4.06	0.8	0.4	0.14	0.09
$CH_3\overset{*}{C}HCH_2$	0.20	---	0.059	---	0.89	---	0.68	---	0.4	---	0.1	---
$CF_3\overset{*}{C}HCH_2$	0.008	---	0.0002	---	2.9	---	6.3	---	0.2	---	0.2	---

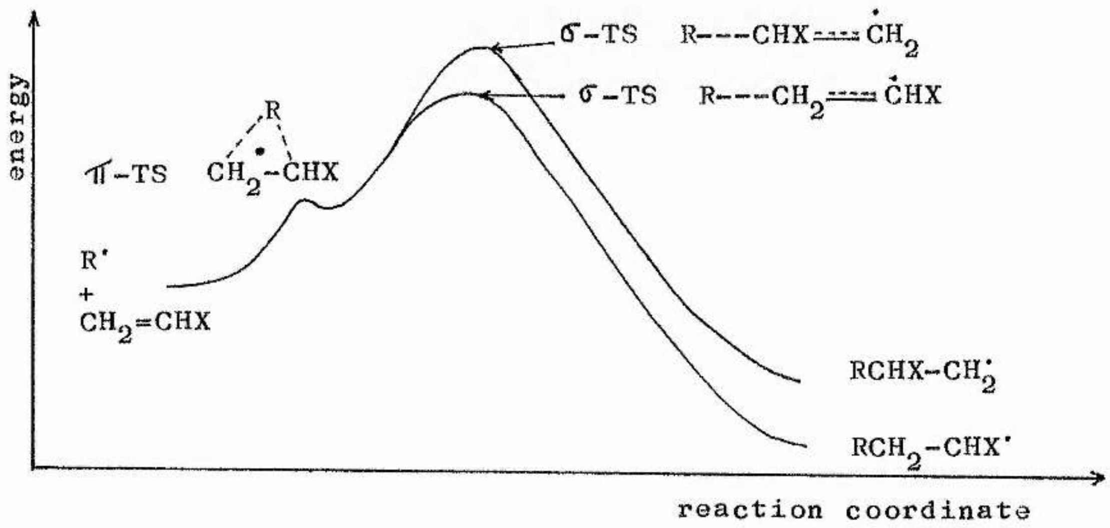
* site of attack

** corrected for both ends when necessary relative parameters for the addition of trifluoromethyl, pentafluoroethyl, perfluoroisopropyl and perfluoro-t-butyl radicals to each site of various olefins. The rate of addition to ethylene is taken as standard.

The orientation of the additions, depicted in table 2-6, is consistent with the predictions of the Walling and Mayo theory in its simplest form, which relates the orientation to the relative resonance stabilization of the adduct radicals. However, by examining the relative rates of addition between different olefins, it becomes apparent that this picture no longer gives the correct predictions. Indeed, the rate of addition to the CH_2- end of ethylene, vinyl fluoride and 1,1-difluoroethylene decreases although the odd electron in the adduct radical is situated at sites where increasing delocalization is possible. Also, the rate of addition decreases and the activation energy increases rapidly for addition to the CH_2-, CHF-, and CF_2- ends of those olefins respectively, although, in each case, the odd electron is situated on a CH_2- group. Substituents on the carbon atom where the new bond is formed have a far greater influence than substituents on the carbon where the odd electron is situated in the adduct radical. This is in direct contradiction with the Walling and Mayo theory, in its simplest form.

Two possible transition states have been proposed for the addition of small radicals to mono-olefins : a π-transition state, in which the attacking radical is associated with the double bond (three electrons delocalized over three carbons), and a σ-transition state, in which the radical is associated with one of the carbon atoms adjacent to the double bond (two electrons delocalized over two carbons). The fact that the orientation ratios vary with temperature means that the σ-complex represent the top of the potential energy pass. Correlation of the data with atom rather than bond properties is therefore appropriate.

Figure 2-1 : Potential energy diagram for small radicals addition reactions.



Further evidence for the σ-transition state is the fact that the relative activation energies ($\Delta E_2 = E_2 - E_{2e}$) correlate with the localization energies (L_μ) calculated from the simple Hückel m.o. theory. The correlation can be improved by adding an extra term calculated from the net atom charge (δQ_μ) at the site in question.

$$\Delta E_2 = A(L_\mu + B\delta Q_\mu)$$

The extra term is to allow for polar contributions to the transition state in the attack by an electrophilic species. Tedder et al.[105] found 0.5 to be the best value for B. The final correlation for the addition of $CF_3^\cdot$, $i\text{-}C_3F_7^\cdot$, $t\text{-}C_4F_9^\cdot$ radicals to fluoro-olefins is shown in figure 2-2 and the data are in table 2-7.

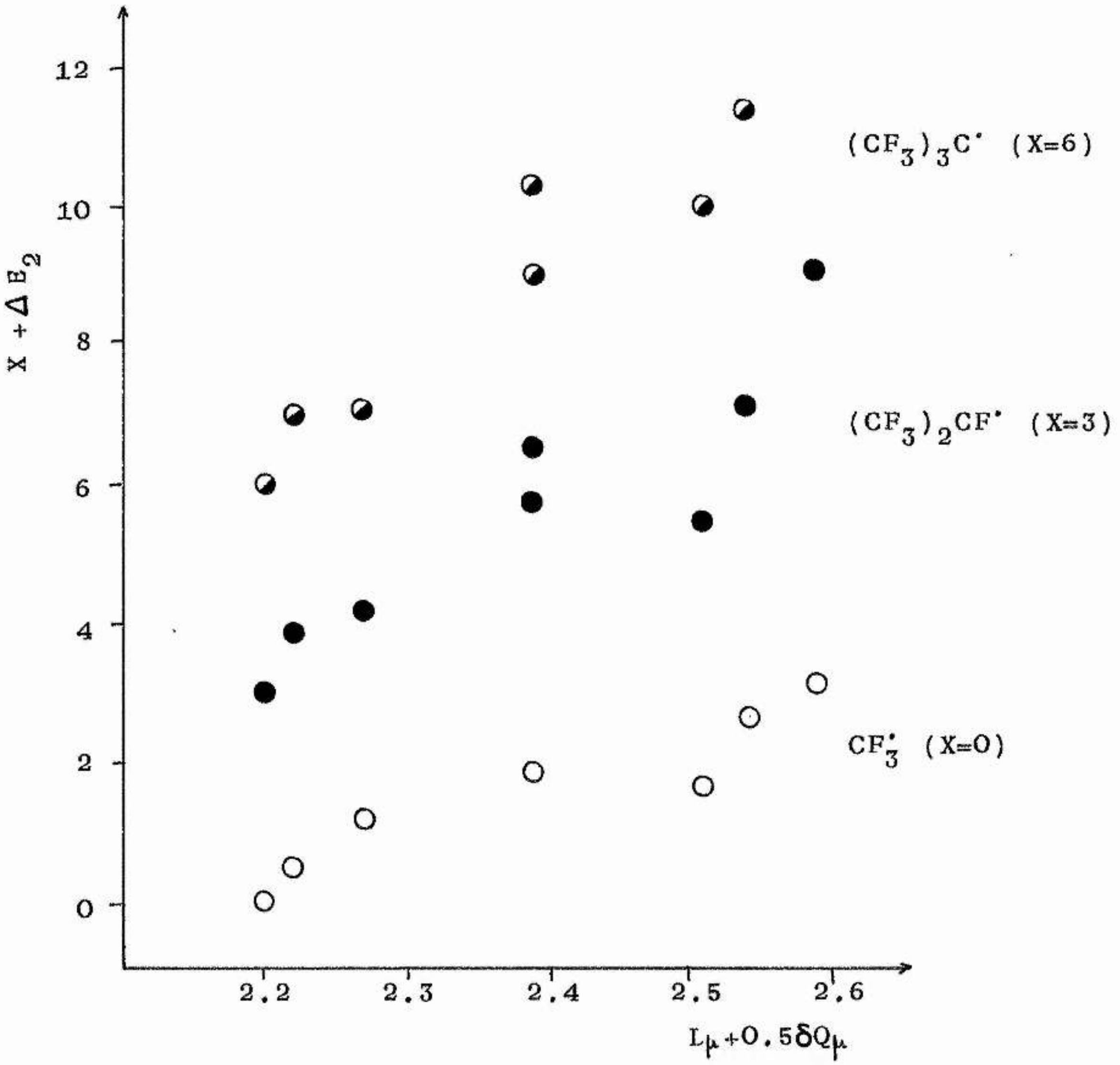
Table 2-7 : Data for the correlation between ΔE_2 and localization energies.

olefin	$L\mu$	$\delta Q\mu$	$L\mu+0.5\delta Q\mu$	E_2-E_{2e}		
				$CF_3^\cdot$	$i\text{-}C_3F_7^\cdot$	$t\text{-}C_4F_9^\cdot$
$\overset{*}{C}H_2CH_2$	2.20	0.00	2.20	0.0	0.0	0.0
$\overset{*}{C}H_2CHF$	2.15	+0.13	2.22	0.5	0.83	0.98
$\overset{*}{C}H_2CF_2$	2.13	+0.25	2.27	1.20	1.24	1.11
$\overset{*}{C}HFCF_2$	2.31	+0.17	2.39	1.9	2.8	3.02
$\overset{*}{C}HFCH_2$	2.43	-0.07	2.39	1.9	3.55	4.33
$\overset{*}{C}F_2CH_2$	2.66	-0.13	2.59	3.2	6.13	---
$\overset{*}{C}F_2CHF$	2.55	-0.02	2.54	2.7	4.2	5.46
$\overset{*}{C}F_2CF_2$	2.49	+0.05	2.51	1.7	2.5	4.08

*site of attack

The values of the Hückel parameters used are $\alpha_C=10\beta_o$; $\alpha_F=12.73\beta_o$; $\beta_{FC}=0.908\beta_o$. It is interesting to notice that each of the plots, in figure 2-2, splits into three other lines, for the addition to the CH_2-, CHF- and CF_2- ends respectively.

Figure 2-2 : Correlation between ΔB_2 and localization energy (data in table 2-7)



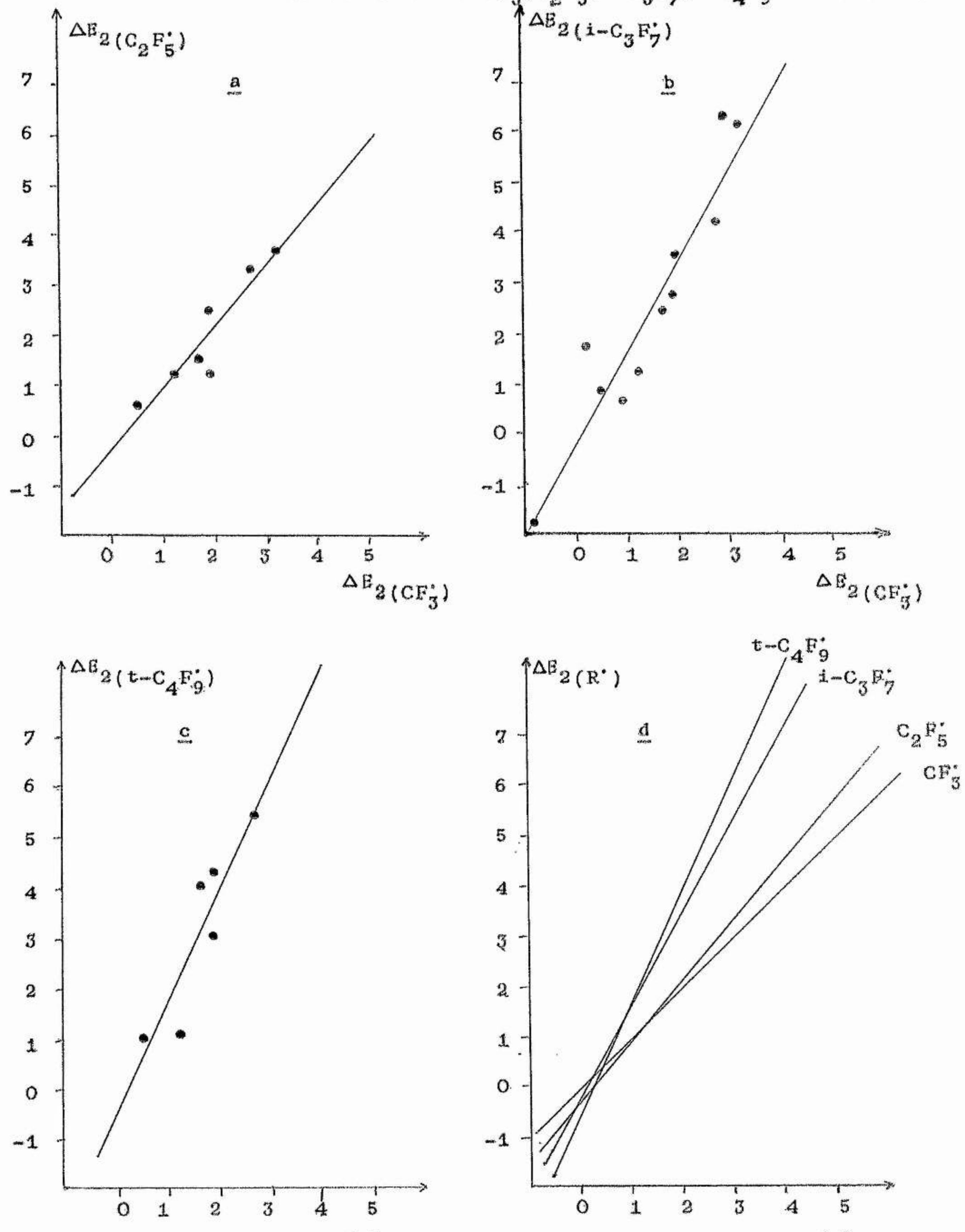
A very striking feature of table 2-6 is the small variation in the ratios of the pre-exponential terms compared with the very large variation in the ratios of the rate constants at 437 K, for each radical. However, by far the most important feature of the table is that, although the four radicals follow a very similar pattern, the selectivity of the addition increases noticeably from $CF_3^{\cdot}$ to $(CF_3)_3C^{\cdot}$. It is clear that this increase in selectivity is mainly due to the activation energy term. There is some indication that the pre-exponential term becomes smaller when the radicals attack a CF_2-, CF_3CH- or CH_3CH- site, but the maximum variation in the A_2/A_{2e} ratios is only just over a power of ten, compared to more than three powers of ten for the ratios of the rate constants. The ratios of the A factors appear to be scattered. This may be due to small errors in the slopes of the Arrhenius plots (a small change in slope can have a big effect on the intercept of a straight line). It is significant, however, that the activation energies show very regular and consistent trends.

The similar behaviour of the four radicals is illustrated by figure 2-3, where the relative activation energies for $C_2F_5^{\cdot}$, i-$C_3F_7^{\cdot}$ and t-$C_4F_9^{\cdot}$ radicals are plotted against the relative activation energies for $CF_3^{\cdot}$ radicals. A"least squares" calculation gives the value of the slope and of the correlation coefficient for each plot.(table 2-8)

Table 2-8 : Slope and correlation coefficient for each of the plots shown in figure 2-3.

radical	slope	corr.coeff.	fig.2-3
$C_2F_5^{\cdot}$	1.215	0.93	a
i-$C_3F_7^{\cdot}$	1.840	0.95	b
t-$C_4F_9^{\cdot}$	2.232	0.91	c

Figure 2-3 : Comparison of the relative activation energies for the addition of $CF_3^{\cdot}$, $C_2F_5^{\cdot}$, $i-C_3F_7^{\cdot}$, $t-C_4F_9^{\cdot}$ to olefins.



The equivalent plot for $CF_3^{\bullet}$ radicals would, of course, give a straight line of slope 1.0 and correlation coefficient 1.0. The"least squares" lines obtained (figure $2\text{-}3_d$) show the increase in selectivity from trifluoromethyl to perfluoro-t-butyl radicals.

Only small differences in polar effects are expected between the four radicals, since the Hammett σ-values for CF_3-, C_2F_5-, $(CF_3)_2CF$- and $(CF_3)_3C$- groups are similar[110]. Therefore, at first sight, the most likely explanation for the increase in selectivity would be based on steric grounds. However, in 1964, Andreades[100] determined the acid dissociation constants of the corresponding perfluoroalkyl hydrides and he found that they increased by twenty orders of magnitude from fluoroform to tris(trifluoromethyl)methane. The results were interpreted in terms of stabilization of the fluorocarbanion by fluorine hyperconjugation. Holtz[101] re-evaluated the data and showed that inductive effects are primarily responsible for the difference in reactivity and that fluorine hyperconjugation has, at the best, only a secondary influence in determining the reactivity of fluorinated molecules. He determined Taft σ^* constants for α- and β-fluorine substituents and obtained a good correlation between the pK_a values and the sum of the σ^* constants.

Figure 2-4 shows a plot of the logarithm of the orientation ratio for the addition of each of the four radicals to fluorinated olefins against the pK_a values of the corresponding perfluoroalkyl hydrides.

Figure 2-4: Correlation between log Or for the addition of $CF_3^{\cdot}$, $C_2F_5^{\cdot}$, i-$C_3F_7^{\cdot}$, t-$C_4F_9^{\cdot}$ to CH_2CHF ○, CH_2CF_2 ◒, $CHFCF_2$ ◑ and CF_2CF_2 ●, and the pK_a values of the corresponding perfluoroalkylhydrides.

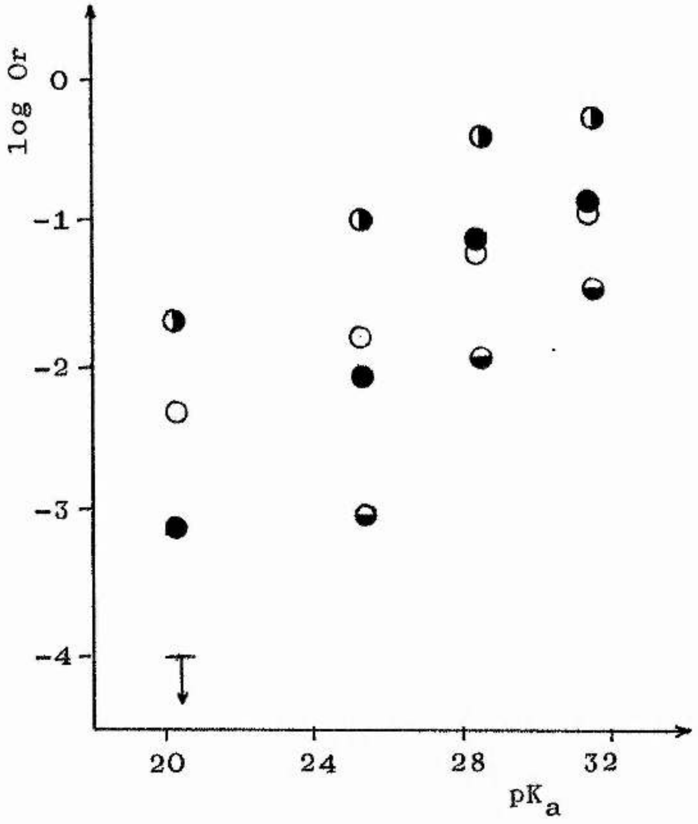


Table 2-9 : data used in figure 2-4.

Radical	log Or (437 K)				pK_a
	CH_2=CHF	CH_2=CF_2	CHF=CF_2	CF_2=CF_2 *	
$CF_3^{\cdot}$	-0.94	-1.44	-0.29	-0.92	31.41
$C_2F_5^{\cdot}$	-1.22	-1.89	-0.41	-1.17	28.50
i-$C_3F_7^{\cdot}$	-1.78	-3.0	-1.0	-2.10	25.22
t-$C_4F_9^{\cdot}$	-2.28	-4.0**	-1.67	-3.10	20.29

* log $(k_{2(C_2F_4)}/k_{2e})$

** Upper limit

Since Holtz has shown that there is a direct relation between the pK_a's and the Taft inductive parameters, the orientation ratios also correlate with the sum of the σ^* constants.

Holtz suggested that fluoroalkyl carbanions with α-fluorines are destabilized by p-p lone pair repulsion. Since fluoroalkyl radicals contain a single electron in the orbital which contains two electrons in the anion, a similar repulsion, and hence destabilization, could be expected.

Epiotis and co-workers[102] came to a similar conclusion in a m.o. interpretation of the properties of monohalogenomethyl radicals. They found that, for constant energy separation between the interacting orbitals (the half-filled orbital of the carbon and the $2p_z$ orbital of the halogen), stabilization reaches a maximum at a particular value of the overlap. An increase or decrease of the overlap at that point would decrease the stability of the radical.

Although figure 2-4 shows that there is a good correlation between the acidity and the logarithm of the orientation ratio, it would be wrong to conclude that polarity is the only governing factor in radical addition reactions.

Epiotis et al.[102] came to the conclusion that, for constant overlap, the smaller the energy separation between the interacting orbitals, the greater the stabilization of the radical. For halogenomethyl radicals, the energy of the singly occupied carbon orbital tends to approach the energy of the halogen atom lone pair, upon pyramidalization (the energy of a sp^3 orbital is 3.25 eV lower than that of a p_z orbital). Hence, pyramidalization stabilizes radicals with α-halogens and particularly α-fluorines. In other words, the non-bonded electron repulsion, as well as increasing the energy of the unpaired electron, also bends the three bonds joined to the trivalent carbon out of plane. Thus, trifluoromethyl is the least electronegative, but also the most pyramidal (3 α-fluorines), while perfluoro-t-butyl is the most electronegative and the most planar in the series. ESR studies have confirmed this[103].

If classical steric hindrance is involved, one would expect to be able to correlate the size and shape of the attacking radicals to the rate of addition. Tedder and Walton[104] showed that there was a significant correlation between the attacking radical diameter, given in table 2-10, and the logarithm of the orientation ratios for addition to vinyl fluoride, 1,1-difluoroethylene and trifluoroethylene (figure 2-5). The diameters (d_c) of the radicals were estimated from the covalent atomic radii, by finding the smallest circle, perpendicular to the three-fold axis, which could contain the three substituents attached to the radical centre. All the radicals were considered as pyramidal and regular tetrahedral bond angles were assumed. Only atoms α- and β- to the radical centre were taken into account. The pyramidal shape is justified since those radicals which are planar or nearly planar would become pyramidal in the transition state of an addition reaction. $(CF_3)_2CF^{\cdot}$ and $(CF_3)_3C^{\cdot}$ conform to the correlation, as shown in figure 2-5.

Figure 2-5.

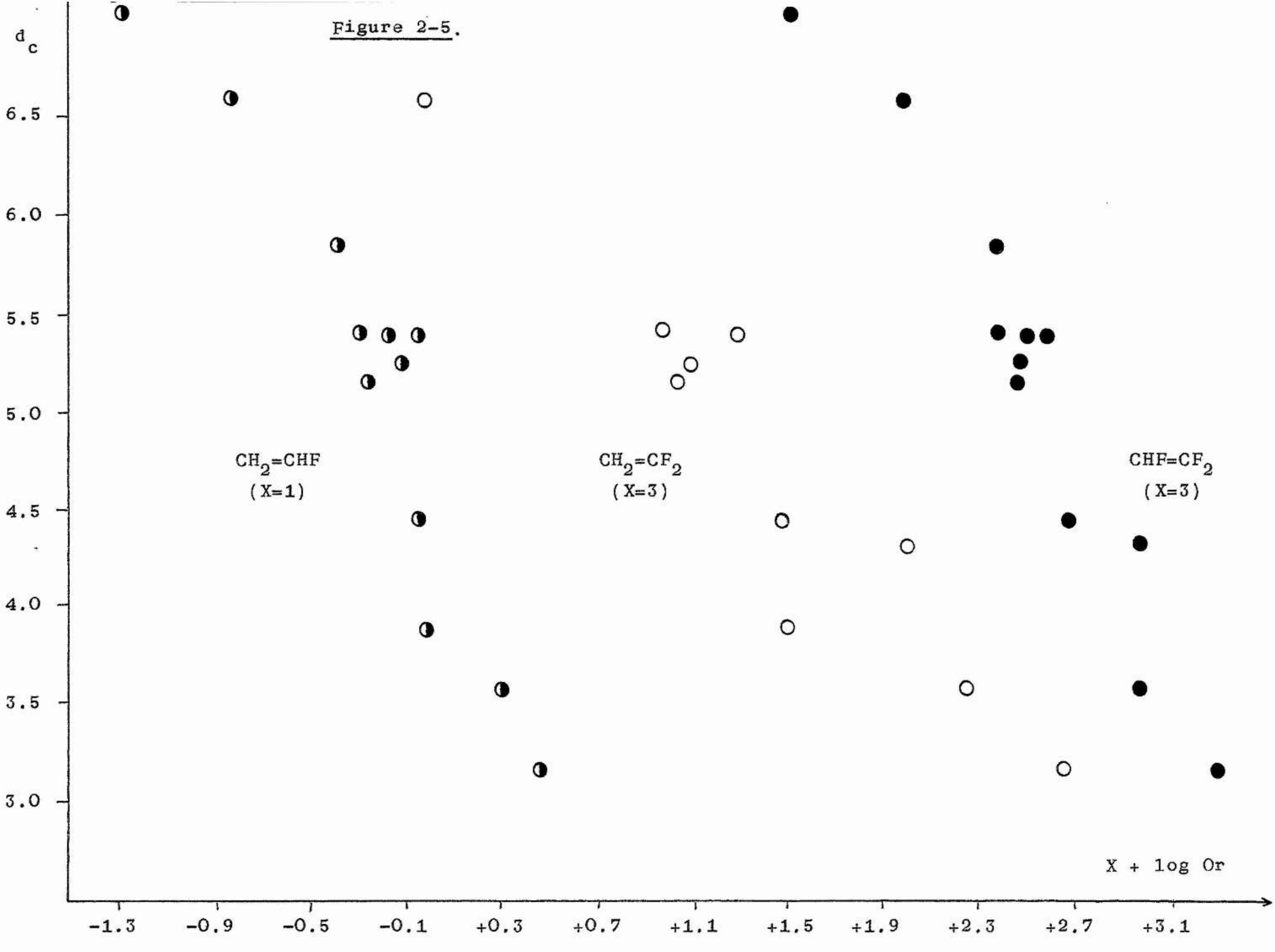

d_c
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
$CH_2=CHF$ (X=1)
$CH_2=CF_2$ (X=3)
$CHF=CF_2$ (X=3)
X + log Or
-1.3
-0.9
-0.5
-0.1
+0.3
+0.7
+1.1
+1.5
+1.9
+2.3
+2.7
+3.1

Table 2-10 : Data for the correlation between d_c and the logarirhm of the orientation ratio.

Radical	$d_c(A^o)$	log Or (150°C)		
		$CH_2{=}CHF$	$CH_2{=}CF_2$	$CHF{=}CF_2$
$CH_2F^{\cdot}$	3.16	-0.54	-0.35	+0.31
$CHF_2^{\cdot}$	3.63	-0.72	-0.75	-0.02
$CF_3^{\cdot}$	3.92	-1.03	-1.49	-0.30
$CH_2I^{\cdot}$	4.32	---	-0.98	-0.04
$CF_2Br^{\cdot}$	4.45	-1.05	-1.54	-0.33
$CF_3CF_2^{\cdot}$	5.16	-1.30	-1.96	-0.54
$CCl_3^{\cdot}$	5.26	-1.16	-1.92	-0.54
$CFBr_2^{\cdot}$	5.41	-1.07	-1.72	-0.44
$CHBr_2^{\cdot}$	5.41	-1.20	---	-0.51
$CF_3(CF_2)_2^{\cdot}$	5.42	-1.30	-2.05	-0.60
$CBr_3^{\cdot}$	5.84	-1.40	---	-0.62
$(CF_3)_2CF^{\cdot}$	6.62	-1.85	-3.05	-1.02
$(CF_3)_3C^{\cdot}$	7.06	-2.23	---	-1.70

We then tried to correlate d_c directly with the orientation ratios, for the series $CF_3^{\cdot}$, $C_2F_5^{\cdot}$, $n\text{-}C_3F_7^{\cdot}$, $i\text{-}C_3F_7^{\cdot}$, $t\text{-}C_4F_9^{\cdot}$ (data in table 2-11). The very satisfactory correlation is shown in figure 2-6.

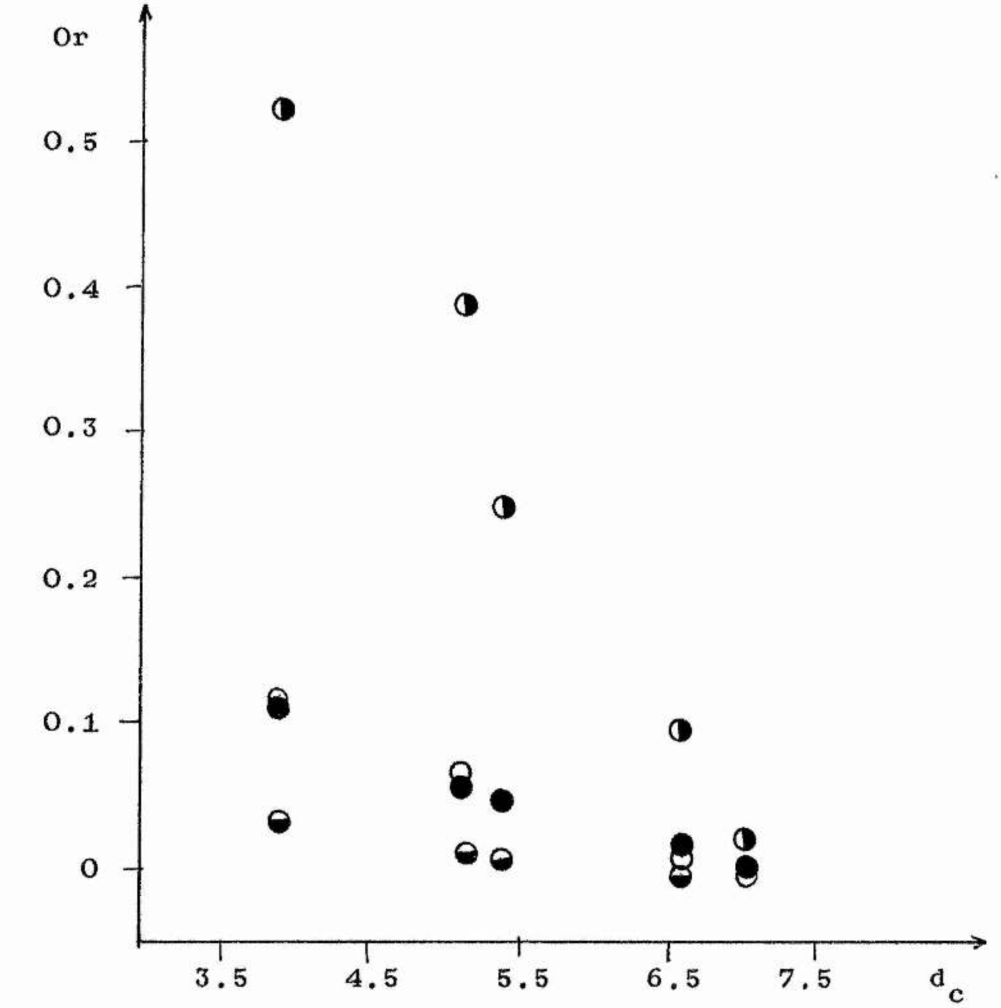
Figure 2-4 seems to show that the addition of perfluoroalkyl radicals to olefins is governed by polar effects, while figure 2-6 seems to show that it is governed by steric effects. That, surely, is a sign that both the effects are important and that it is very difficult to

Table 2-11 : Data for the correlation between d_c and Or (437 K)

Radical	d_c (A°)	Or (437 K)			
		$CH_2{=}CHF$	$CH_2{=}CF_2$	$CHF{=}CF_2$	$CF_2{=}CF_2$*
$CF_3^{\cdot}$	3.92	0.114	0.037	0.52	0.12
$C_2F_5^{\cdot}$	5.16	0.061	0.013	0.39	0.067
$n\text{-}C_3F_7^{\cdot}$	5.42	0.05	0.009	0.25	---
$i\text{-}C_3F_7^{\cdot}$	6.62	0.017	0.001	0.1	0.008
$t\text{-}C_4F_9^{\cdot}$	7.06	0.0052	---	0.021	0.0008

*$\log(k_{2(C_2F_4)}/k_{2e})$

Figure 2-6 : Correlation between d_c and Or for the addition of $CF_3^{\cdot}$, $C_2F_5^{\cdot}$, $n\text{-}C_3F_7^{\cdot}$, $i\text{-}C_3F_7^{\cdot}$ and $t\text{-}C_4F_9^{\cdot}$ to CH_2CHF ●, CH_2CF_2 ◒, $CHFCF_2$ ◑ and CF_2CF_2 ○.



separate them. An interesting feature of the present results is that, although the difference in selectivity between the four radicals ($CF_3^\cdot$, $C_2F_5^\cdot$, $i\text{-}C_3F_7^\cdot$, $t\text{-}C_4F_9^\cdot$) can be attributed partly to steric factors which lead to substantial differences in activation energy, this steric compression has a negligible effect on the pre-exponential term.

CHAPTER 3:

THE RATE OF RECOMBINATION OF PERFLUOROISOPROPYL RADICALS.

Introduction

In chapter I, relative rates of addition of perfluoro-isopropyl radicals to various olefins were measured. In order to find absolute rate constants for the addition reactions, it is necessary to know the rate of recombination of the radicals (k_4). This data is not available in the literature and it was therefore decided to measure k_4 in the gas phase.

Methods of determining the absolute rate of radical recombination

In one of the first attempts to determine a radical recombination rate, Miller and Steacie measured the rate of recombination of methyl radicals relative to their rate of reaction with nitric oxide[45]. This result was used by Durham and Steacie to calculate the rate constant of the recombination reaction as 1.1×10^9 l. mol^{-1} sec^{-1} by combining it with their measurements of the rate of reaction of methyl radicals with nitric oxide[46]. In principle, this method of comparing the rate of an unknown reaction with that of a known reaction is of wide applicability, but the accuracy of the final result is dependent on the accuracy of the known reaction rate. In the case of methyl, the obtained value was more than a power of ten lower than the accepted value of k_4

Lossing, Ingold, and Tickner have measured the rate of methyl radical recombination with the aid of a mass spectrometer[32,33,34]. Methyl radicals were produced in the thermal decomposition of mercury-dimethyl at 850-975°C. The furnace was placed just above a pin-hole leak into the ionization chamber of the mass-spectrometer. The peak occurring at the mass number of the free radical (m/e=15) included relatively large contributions from fragments formed by electron impact from the stable molecules present ($Hg(CH_3)_2$, CH_4, C_2H_6 and other possible products). Contributions from these molecules can be calculated from their mass spectra measured under corresponding conditions and subtracted from the total peak height. Since the contribution from methyl radicals is itself very small, errors in the result can arise if the contribution from any product is neglected. The result obtained by this method is also rather low.

Moseley and Robb studied the mercury-photosensitized decomposition of acetone[35]. They determined the absolute rate constants of methyl recombination by measuring the small change in pressure caused by the heat of reaction. This could be done with a manometer with a sensitivity of 10^{-4} torr and a response time of less than 10^{-3} sec. From the rate of heat production they calculated k_4 to be 3.8×10^{10} l. $mol^{-1}sec^{-1}$ at room temperature.

More recently, Hiatt and Benson developed a technique based on the rapidly established vapour phase equilibrium $R^{\cdot} + R'I \rightleftharpoons RI + R'^{\cdot}$ [47-50]. This equilibrium provides a buffer system for radicals $R^{\cdot}$ and $R'^{\cdot}$ whose R-I bond energies are not too different. If the recombination rate constant of one of the radicals and the value of the equilibrium constant ($K_{RR'}$) are known, the second recombination rate constant can be measured. The accuracy of the final result depends on the accuracy of the known rate constant and of the equilibrium constant. The latter has to be calculated from thermochemical data, which can lead to a fair amount of uncertainty. The method has been applied to the following pairs of radicals: methyl-ethyl, methyl-trifluoromethyl, methyl-isopropyl and ethyl-isopropyl. The obtained values ($k_{4(C_2H_5^{\cdot})}=5\times10^8$; $k_{4(CF_3^{\cdot})}=5\times10^9$; $k_{4(\text{isopropyl})}=4\times10^8$ l. mol^{-1}sec^{-1}) seem to be rather low.

An interesting study of the rate of recombination of $CF_3^{\cdot}$ radicals was performed by Ogawa, Carlson, and Pimentel[57]. It was based on the flash photolysis of trifluoromethyl iodide, coupled with rapid scan infrared spectroscopy. They determined the quantum yield for the dimerization of the radicals. Then, from measurements of the final concentration of hexafluoroethane and from the optical density of the $CF_3^{\cdot}$ radicals, they were able to calculate both the $CF_3^{\cdot}$ extinction coefficient at 1266 cm^{-1} and the recombination rate constant. They noticed a temperature effect which, due to experimental uncertainty, corresponds to an activation energy between 0.3 and 2.5 Kcal/mol. The extrapolated value of k_4 at 127°C (at which Ayscough[42] made his measurements) was of the order of 1×10^{10} l. mol^{-1} sec^{-1}.

Basco and Hathorn also measured the rate of recombination of $CF_3^{\cdot}$ radicals, in the flash photolysis of hexafluoroacetone[58]. An electronic absorption spectrum in the region 165 to 146 nm was assigned to the trifluoromethyl. The 1:1 correspondence of $[C_2F_6]_f$ and $[CO]_f$ found chromatographically was used in conjunction with plate photometry of three of the $CF_3^{\cdot}$ bands and the (0,0) band of the (A $\longleftarrow$ X) system of CO to obtain a quantitative estimate of the radical concentration. The plot of $1/[CF_3^{\cdot}]$ against time yielded a straight line and the slope of such a graph gave the value of the second order rate constant. It was found to be $\sim 3 \times 10^9$ l. $mol^{-1}sec^{-1}$, at 300^oK, in the presence of 100 torr of Argon.

Skorobogatov, Seleznev, and Slesar determined the rates of combination of some perfluorinated radicals at three different temperatures by the use of the method of overlapping relaxations[51]. The method consists of photolysing the perfluoroalkyl iodides into radicals (R·) and iodine atoms ($^2P_{3/2}$ and $^2P_{\frac{1}{2}}$) (by supplying a first disturbing pulse at a time t_1) and subsequently increasing the concentration of excited iodine atoms ($^2P_{\frac{1}{2}}$) (by supplying a second disturbing pulse, qualitatively different from the first one, at a time t_2). The dependence on ($\Delta t = t_2 - t_1$) of the final concentrations of the products is recorded. The values found for the rates of recombination of $CF_3^{\cdot}$, $C_2F_5^{\cdot}$, n-$C_3F_7^{\cdot}$ and n-$C_4F_9^{\cdot}$ are 1×10^{10}, 3.3×10^9, 2.2×10^9 and 2×10^9 l. $mol^{-1}sec^{-1}$ respectively.

The rotating sector technique is the most popular method of determining the k_4 values. It is applicable to all reactions for which the rate is proportional to a power of the light intensity less than unity. When a system is illuminated by an intermittent source of irradiation, a pseudo-stationary state is set up. The average concentration of radicals will be different for different intermittencies and will also be different from the concentration of radicals under steady illumination. The most frequent case to be considered is that for which the reaction rate is dependent on the square root of the light intensity.

$$\text{Rate} = kI^{\frac{1}{2}}$$

Suppose the system is illuminated by an intermittent source such that the duration of the light period is one third of the duration of the dark period. At very fast intermittencies, the effect will be as if the system were illuminated by a source of one quarter the intensity. The ratio of the rates under intermittent and steady illumination will be

$$\frac{\text{Rate (intermittent)}}{\text{Rate (steady)}} = \frac{k(I/4)^{\frac{1}{2}}}{kI^{\frac{1}{2}}} = 0.5$$

At very slow intermittencies, the effect will be as if the system were illuminated by the full intensity for a quarter of the time. The ratio of the rates can then be written:

$$\frac{\text{Rate (intermittent)}}{\text{Rate (steady)}} = \frac{\frac{1}{4}\,kI^{\frac{1}{2}}}{kI^{\frac{1}{2}}} = 0.25$$

As the intermittency changes from very fast to very slow, the rate ratio changes from 0.5 to 0.25. The mathematical treatment of the simple rotating sector theory has been described by Melville and Burnett[54].

O.K. Rice[37] and Dodd[36], applied this technique to the photolysis of acetaldehyde, but the results were not of much value, because of the complexity of the mechanism of the reaction.

Gomer and Kistiakowsky used the rotating sector method to study the photolysis of acetone and dimethylmercury[31]. They found the rate constant for recombination of methyl radicals to be 4.45×10^{10} l. $mol^{-1}sec^{-1}$ at 125-200°C. Later Kistiakowsky made a more refined study of the same reaction and obtained a value for $k_{4(CH_3^{\cdot})}$ of 3.7×10^{10} l. $mol^{-1}sec^{-1}$ at 165°C [39].

These results were later reinterpreted by Shepp who modified the mathematical treatment of the rotating sector method to allow for both first and second order termination reactions[52]. He found a value for $k_{4(CH_3^{\cdot})}$ of 2×10^{10} l. $mol^{-1}sec^{-1}$. Shepp also recalculated the results obtained by Kistiakowsky in the photolysis of hexadeuteroacetone and found $k_{4(CD_3^{\cdot})}$ to be 3.8×10^{10} l. $mol^{-1}sec^{-1}$. These results probably represent the most accurate determination of a recombination rate. Shepp and co-workers also determined the rate of recombination of ethyl radicals and found $k_{4(C_2H_5^{\cdot})}$ to be $1.6 \times 10^{11} \exp(-2000/2.303\ RT)$[53].

Ayscough, using the same mathematical treatment, determined the rate of recombination of trifluoromethyl radicals in the photolysis of hexafluoroacetone[42]. This value of $k_{4(CF_3^{\cdot})} = 2.34 \times 10^{10}$ at 127°C seems very satisfactory.

Fessenden used a variation of the rotating sector method in a study of the reaction kinetics of ethyl radicals produced in liquid ethane, at -177^{o}C, by radiolysis with a 2.8-MeV electron beam from a Van de Graaff accelerator[55]. The average concentrations were measured from the intensity of the ethyl radical e.s.r. signal. In a first series of experiments, pulsed beams of electrons were used and the usual sector theory was applied. In a second series of experiments, a sampling technique was employed, in which the rise and decay of the ethyl concentration during and after a pulse was measured. The value of $k_{4(C_2H_5^{\cdot})}$ was found to be $1.3 \times 10^{10} \exp(-830_{/RT})$ 1. $mol^{-1}sec^{-1}$.

Another variation of the intermittent illumination method was used by March and Polanyi[56]. In this method the duration of the light pulses was about a thousand times smaller than that of the light pulses in the sector method, which means that the length of a pulse was negligible compared to the lifetime of the radical and the time between pulses. It follows that, if the light absorption was measured and the quantum yield of the reactant known, the increase in radical concentration after each pulse could be determined. A theoretical equation was worked out, relating the rates of formation of product from competing reactions of different order in radicals, to the number of quanta absorbed per light pulse (q) and to the time interval between pulses (t). The only two unknowns in the equation were the two rate constants. It was sufficient to perform two photolyses, making some change in q or t or both, in order to have a system of two equations with two unknowns. The method was applied to the photolysis of acetone and the value of $k_{4(CH_3^{\cdot})}$ was found to be 2.3 x 10^{10} $l.mol^{-1}.sec^{-1}$ at 134°C. It is in excellent agreement with the best determinations.

The rotating sector method gives results at least as good as any other method and, since the apparatus can be easily set up, this technique was chosen to investigate the rate of recombination of $(CF_3)_2CF^{\cdot}$ radicals. However, the use of the technique requires a well established reaction sequence.

Mercury was put into the system to trap the iodine atoms formed in the photolysis of 2-iodoheptafluoropropane and, by doing so, to prevent their recombination with the radicals. The ϕI_a values measured in the reactions with mercury were noticeably higher than those measured in the reactions without mercury.(table 3-4)

The photolysis took place in the presence of trifluoroethylene. A series of experiments was carried out at various values of the incident light intensity. The gradient (-0.47) of the plot of log ($[(CF_3)_2CFCHFCF_2I]_f / [(CF_3)_2CFCF(CF_3)_2]_f$) against the logarithm of the relative light intensity showed the dependence of the rate of adduct formation on the square root of the light intensity.(table 3-2)

Two experiments conducted in the dark showed that a certain amount of thermal initiation occurred at the same time as the photochemical initiation.

The presence of $(CF_3)_2CFCHFCF_2CF(CF_3)_2$ amongst the products showed that the $(CF_3)_2CF^{\cdot}$ radicals were consumed in a first order termination process as well as in a dimerization reaction.

Hence, the reaction sequence can be written as :

$(CF_3)_2CFI \xrightarrow{h\nu} (CF_3)_2CF^{\cdot} + I^{\cdot}$ (1) ϕI_a

$(CF_3)_2CFI \xrightarrow{\Delta T} (CF_3)_2CF^{\cdot} + I^{\cdot}$ (1') k_{th}

$(CF_3)_2CF^{\cdot} + CHF{=}CF_2 \longrightarrow (CF_3)_2CFCHFCF_2^{\cdot}$ (2) k_2

$(CF_3)_2CFCHFCF_2^{\cdot} + (CF_3)_2CFI \longrightarrow (CF_3)_2CFCHFCF_2I + (CF_3)_2CF^{\cdot}$ (3) k_3

$2\ (CF_3)_2CF^{\cdot} \longrightarrow (CF_3)_2CFCF(CF_3)_2$ (4) k_4

$(CF_3)_2CF^{\cdot} + (CF_3)_2CFCHFCF_2^{\cdot} \longrightarrow (CF_3)_2CFCHFCF_2CF(CF_3)_2$ (5) k_5

Because of reactions (1') and (5), the simple sector theory given by Melville and Burnett[54] could not be applied. The thermal decomposition of the perfluoroisopropyl iodide also prevented Shepp's theory[52] from being applied without substantial modification. Therefore, Shepp's mathematical treatment was modified, allowing for both first and second order termination reactions and for a thermal reaction.

THEORY

Consider the following gas phase mechanism :

initiation	$K \xrightarrow{h\nu} R^{\cdot} + X$	ϕI_a
	$K \xrightarrow{\Delta T} R^{\cdot} + X$	k_{th}
chain	$R^{\cdot} + B_i \longrightarrow P_{ci}$	k_{ci}
	$P_{ci} \longrightarrow$ chain	
2nd order termination	$2\ R^{\cdot} \longrightarrow P_{b1}$	k_{b1}

	$2\ R^{\cdot} \longrightarrow P_{bi}$	k_{bi}
1st order termination	$R^{\cdot} + A_1 \longrightarrow P_{f1}$	k_{f1}

	$R^{\cdot} + A_i \longrightarrow P_{fi}$	k_{fi}

K is the photolysed molecule, $R^{\cdot}$ the radical of interest and X a non reactive product. Some of the various products P may be radicals. They may appear again as A_i or B_i. Any number of chain steps of the type shown may be included, as they do not affect the concentration of the $R^{\cdot}$ radicals. It is convenient to define the following :

$$\begin{aligned} K_b &= \sum_i k_{bi} \\ K_f &= \sum_i k_{fi}[A_i] \\ \Phi &= \tfrac{1}{2}\phi I_a \qquad (1) \\ M &= [R^{\cdot}] \end{aligned}$$

The rate of thermal decomposition of the iodide (Rate_{th}) can be expressed as a fraction n of the value of ϕI_a

$$\mathrm{Rate}_{th} = n\phi I_a$$

Letting the subscript c refer to the steady state conditions under constant illumination, we can write

$$2(n + 1)\Phi_c = K_f M_c + 2K_b M_c^2 \qquad (2)$$

A dimensionless parameter α_c is defined as the ratio

$$\alpha_c = K_f/2K_b M_c \qquad (3)$$

From equations (2) and (3), it can be shown that α_c is a function of Φ_c and the rate constants only. Let us consider the behaviour of the photolysis under intermittent illumination. The subscript l refers to behaviour during the light period only and subscript d refers to behaviour during the dark period only. $\overline{M}$ is the average concentration over the entire photolysis; $\overline{M}_l$ and $\overline{M}_d$ are the average concentrations during light and dark periods respectively. To correct properly for light intensity fluctuations, M_s is the hypothetical steady state value that M would have reached had the run not been sectored. $M_l(t)$ and $M_d(t)$ represent the time dependent behaviour of M during light and dark periods respectively. Replacing $\dot{M}_c$ by M_s, equations (2) and (3) become :

$$2(n + 1)\phi_s = K_f M_s + 2K_b M_s^2 \tag{4}$$

$$\alpha_s = K_f / 2K_b M_s \tag{5}$$

It is convenient to drop the subscript s on α_s. If p is the dark to light ratio, the average radical concentration over the entire photolysis is given by :

$$\overline{M} = (\overline{M}_1 + p\overline{M}_d)/p+1 \tag{6}$$

and, if λ is the duration of one light period, it is easy to see that

$$\overline{M}_1 = 1/\lambda \int M_1(t)dt \tag{7}$$

$$\overline{M}_d = 1/p\lambda \int M_d(t)dt \tag{8}$$

The behaviour of $M_1(t)$ can be written as :

$$- dM_1(t)/dt = 2K_b M_1^2(t) + K_f M_1(t) - 2(n+1)\phi_s \tag{9}$$

Using equations (4) and (5), it becomes

$$\frac{dM_1(t)}{2K_b M_1^2(t) + 2K_b M_s \alpha M_1(t) - 2K_b M_s^2(\alpha+1)} = - dt$$

After integration, the solution of this equation is

$$2K_b M_s (2+\alpha) t = \ln\left[(M_1(t)/M_s + 1 + \alpha)/(M_1(t)/M_s - 1)\right] + C_1 \tag{10}$$

where C_1 is the integration constant. Similarily, the behaviour of $M_d(t)$ can be written

$$- dM_d(t)/dt = 2K_b M_d^2(t) + K_f M_d(t) - 2n\phi_s \tag{11}$$

Using equations (4) and (5), it becomes

$$\frac{dM_d(t)}{2K_b M_d^2(t) + 2K_b M_s \alpha M_d(t) - 2\frac{n}{n+1} M_s^2 K_b (1+\alpha)} = - dt$$

After integration, the solution of this equation is

$$2K_b M_s ct = \ln\left(\frac{2M_d(t)/M_s + \alpha + c}{2M_d(t)/M_s + \alpha - c}\right) + C_d \tag{12}$$

where C_d is the integration constant and $c = (\alpha^2 + 4\frac{n}{n+1}(1+\alpha))^{\frac{1}{2}}$

Let us characterize the end of the i^{th} light period by

$$M(t) = M_1 \ ; \ t = (i+(i-1)p)\lambda$$

and the end of the i^{th} dark period by

$$M(t) = M_2 \ ; \ t = i(p+1)\lambda$$

A dimensionless parameter β is now defined. It is the ratio of λ to the half time of bimolecular disappearance of the radicals :

$$\beta = \lambda/(1/2K_b M_s) = 2K_b M_s \lambda \qquad (13)$$

The integration constant (C_1), in equation (10) can be eliminated by evaluating it from the end of the i^{th} dark period to the end of the $(i+1)^{th}$ light period. The resulting equation, using (13), is

$$(2+\alpha)\beta = \ln \frac{(M_1/M_s+1+\alpha)(M_2/M_s-1)}{(M_2/M_s+1+\alpha)(M_1/M_s-1)} \qquad (14)$$

Similarily, C_d, in equation (12), was eliminated by evaluating it from the end of the i^{th} light period to the end of the i^{th} dark period. Again using (13), the resulting equation is

$$pc\beta = \ln \frac{(2M_2/M_s+\alpha+c)(2M_1/M_s+\alpha-c)}{(2M_2/M_s+\alpha-c)(2M_1/M_s+\alpha+c)} \qquad (15)$$

Solving (14) and (15), one obtains

$$M_1/M_s = (M_2/M_s(a+\alpha+1)+a(\alpha+1)-\alpha-1)/(M_2/M_s(a-1)+a(\alpha+1)+1) \qquad (16)$$

$$M_2/M_s = (-B-(B^2-4AC)^{\frac{1}{2}})/(2A) \qquad (17)$$

where $a = \exp(\beta(2+\alpha))$

$$b = \exp(pc\beta)$$

$$c = (\alpha^2+4\frac{n}{n+1}(1+\alpha))^{\frac{1}{2}}$$

$$A = 2(a(2+\alpha-c)+\alpha+c+2)-2b(a(2+\alpha+c)+2+\alpha-c)$$

$$B = a\alpha(8+3\alpha-2c)+c(2\alpha-ac+c)+\alpha^2+4a-4$$
$$-b(a\alpha(8+3\alpha+2c)-c(2\alpha-c+ac)+\alpha^2+4a-4)$$

$$C = a\alpha(3\alpha+\alpha^2+2+2c-c^2)+c(2a-2\alpha-2-ac-c)-\alpha^2-2\alpha$$
$$-b(a\alpha(3\alpha+\alpha^2+2-2c-c^2)+c(2\alpha+2-2a-ac-c)-2\alpha-\alpha^2)$$

From (7) and (9), the equation for $\overline{M}_1$ is

$$\overline{M}_1 = 1/\lambda \int M_1(t)\,dt$$

$$= -1/\lambda \int_{M_2}^{M_1} \frac{M_1(t)\,dM_1(t)}{2K_b M_1^2(t) + K_f M_1(t) - 2(n+1)\phi_s}$$

Using (4), (5) and (13), and dividing by M_s, the solution of that equation is

$$\frac{\overline{M}_1}{M_s} = 1+(1/\beta)\ \ln \frac{(M_2/M_s+1+\alpha)}{(M_1/M_s+1+\alpha)} \qquad (18)$$

Similarily, from (8) and (11), the equation for $\overline{M}_d$ is

$$\overline{M}_d = 1/p\lambda \int M_d(t)\,dt$$

$$= -1/p\lambda \int_{M_1}^{M_2} \frac{M_d(t)\,dM_d(t)}{2K_b M_d^2(t) + K_f M_d(t) - 2n\phi_s}$$

Using equations (4), (5) and (13), and dividing by M_s, the solution is

$$\frac{\overline{M}_d}{M_s} = (1/2p\beta)\left[\ln \frac{(M_1/M_s)^2+\alpha(M_1/M_s)-\frac{n}{n+1}(1+\alpha)}{(M_2/M_s)^2+\alpha(M_2/M_s)-\frac{n}{n+1}(1+\alpha)} + \frac{\alpha}{c}\ \ln \frac{(2M_1/M_s+\alpha+c)(2M_2/M_s+\alpha-c)}{(2M_2/M_s+\alpha+c)(2M_1/M_s+\alpha-c)}\right] \qquad (19)$$

From (6),(18) and (19), the final equation is

$$\frac{\overline{M}}{M_s} = 1/(p+1)\left[1+(1/\beta)\ \ln \frac{(M_2/M_s+1+\alpha)}{(M_1/M_s+1+\alpha)} + (1/2\beta)\ \ln \frac{(M_1/M_s)^2+\alpha(M_1/M_s)-\frac{n}{n+1}(1+\alpha)}{(M_2/M_s)^2+\alpha(M_2/M_s)-\frac{n}{n+1}(1+\alpha)} + \frac{\alpha}{2c\beta}\ \ln \frac{(2M_1/M_s+\alpha+c)(2M_2/M_s+\alpha-c)}{(2M_2/M_s+\alpha+c)(2M_1/M_s+\alpha-c)}\right] \qquad (20)$$

Equations (16), (17) and (20) define the sector curve. Values of $\overline{M}/M_s$, M_1/M_s and M_2/M_s against β , for p=3, n=0.00963 and α=0.478, are shown in table 3-1.

Table 3-1 : Values of M_1/M_s, M_2/M_s and $\overline{M}/M_s$ against β .

p=3 n=0.00963 α=0.478

β	M_1/M_s	M_2/M_s	$\overline{M}/M_s$
0.01	0.428	0.417	0.4222
0.0159	0.431	0.414	0.4222
0.0251	0.436	0.409	0.4222
0.0398	0.443	0.401	0.4221
0.0631	0.457	0.388	0.4220
0.1	0.479	0.369	0.4215
0.1585	0.512	0.340	0.4203
0.2512	0.566	0.298	0.4176
0.3981	0.649	0.240	0.4114
0.5012	0.703	0.206	0.4060
0.631	0.764	0.171	0.3986
0.794	0.828	0.136	0.3888
1.0	0.888	0.104	0.3770
1.259	0.937	0.078	0.3635
1.585	0.970	0.056	0.3495
1.995	0.989	0.042	0.3359
2.511	0.997	0.034	0.3237
3.162	0.999	0.030	0.3133
3.981	1.0	0.029	0.3047
5.012	1.0	0.028	0.2978
6.310	1.0	0.0279	0.2923
7.943	1.0	0.0279	0.2879
10.0	1.0	0.0279	0.2844

CORRELATION WITH EXPERIMENT

a. ϕI_a

From the reaction mechanism, if R' is the perfluoroisopropyl radical and E is trifluoroethylene, it can be seen that

$$\text{Rate}_{(\text{dimer})} = \frac{d[R-R]}{dt} = k_4[R^\cdot]^2$$
$$\text{Rate}_{(R-E-R)} = \frac{d[R-E-R]}{dt} = k_5[R^\cdot][RE^\cdot]$$

The steady state conditions for the two radicals can be written

- under constant illumination :

$$\frac{d[R^\cdot]}{dt} = 0 = (n+1)\phi I_a - k_2[R^\cdot][E] + k_3[RE^\cdot][RI] - 2k_4[R^\cdot]^2 - k_5[R^\cdot][RE^\cdot] \qquad (21)$$

and

$$\frac{d[RE^\cdot]}{dt} = 0 = k_2[R^\cdot][E] - k_3[RE^\cdot][RI] - k_5[R^\cdot][RE^\cdot] \qquad (22)$$

By adding (21) and (22), one obtains

$$0 = (n+1)\phi I_a - 2k_4[R^\cdot]^2 - 2k_5[R^\cdot][RE^\cdot]$$

Hence, $$\phi I_a = \frac{2}{n+1}\left(\text{Rate}_{(\text{dimer})} + \text{Rate}_{(R-E-R)}\right) \qquad (23)$$

- under sectored illumination :

$$\frac{d[R^\cdot]}{dt} = 0 = \frac{4n+1}{4}\phi I_a - k_2[R^\cdot][E] + k_3[RE^\cdot][RI] - 2k_4[R^\cdot]^2 - k_5[R^\cdot][RE^\cdot] \qquad (24)$$

and

$$\frac{d[RE^\cdot]}{dt} = 0 = k_2[R^\cdot][E] - k_3[RE^\cdot][RI] - k_5[R^\cdot][RE^\cdot] \qquad (25)$$

By adding (24) and (25), one obtains

$$0 = \frac{4n+1}{4}\phi I_a - 2k_4[R^\cdot]^2 - 2k_5[R^\cdot][RE^\cdot]$$

Hence, $$\phi I_a = \frac{8}{4n+1}\,(\text{Rate}_{(\text{dimer})} + \text{Rate}_{(\text{R-B-R})}) \qquad (26)$$

b. $\underline{\alpha_s}$

From the definition of K_f and K_b, in (1), and from (21) and (22), it can be shown that, for this reaction.

$$K_f = 2k_5\,[\text{RB}^\cdot] \qquad (27)$$

$$K_b = k_4 \qquad (28)$$

From (3), (27) and (28),

$$\alpha_s = \frac{2k_5\,[\text{RB}^\cdot]_s}{2k_4\,[\text{R}^\cdot]_s} = \frac{\text{Rate}_{(\text{R-B-R})}}{\text{Rate}_{(\text{dimer})}}$$

c. $\underline{\overline{M}/M_s}$

The addition reaction of the radical to trifluoroethylene (k_2) is used to find $\overline{M}/M_s$. The rate of that reaction is determined by measuring the amounts of final products derived from the adduct radical ($\text{RB}^\cdot$), namely the adduct and the first order termination product. It is easy to see that

$$\frac{\overline{[\text{R}^\cdot]}}{[\text{R}^\cdot]_c} = \frac{\overline{M}}{M_c} = \frac{(\overline{\text{Rate}_{(\text{adduct})}} + \overline{\text{Rate}_{(\text{R-B-R})}})}{(\text{Rate}_{(\text{adduct})} + \text{Rate}_{(\text{R-B-R})})_c} = \frac{[\overline{\text{adduct}}] + [\overline{\text{R-B-R}}]}{[\text{adduct}]_c + [\text{R-B-R}]_c} \qquad (29)$$

We now have to relate M_c to M_s. $\alpha_c \cong \alpha_s$, since they only differ because of light intensity fluctuations. Using (2), (3), (4) and (5), the relation between M_c and M_s is

$$M_c/M_s = (\phi_c/\phi_s)^{\frac{1}{2}} \qquad (30)$$

From (29) and (30), the equation relating $\overline{M}/M_s$ to the experiment is

$$\overline{M}/M_s = \frac{([\overline{\text{adduct}}] + [\overline{\text{R-B-R}}])}{([\text{adduct}]_c + [\text{R-B-R}]_c)} \times (\phi_c/\phi_s)^{\frac{1}{2}}$$

d. Determination of k_4

Equation (13) offers β in terms of M_s and λ. Using (4), (5) and (28), we have

$$M_s = (\phi_s(n+1)/k_4)^{\frac{1}{2}}(1+\alpha)^{-\frac{1}{2}}$$

Hence $$\beta = 2(k_4(n+1)/(1+\alpha))^{\frac{1}{2}}\lambda\phi_s^{-\frac{1}{2}} \qquad (31)$$

Therefore, to measure k_4, one determines a series of $\overline{M}/M_s$ values for various values of λ. The data are plotted and compared to the theoretical curve given by (20), for which the correct value of α, n and p have been determined. Superposition of the theoretical and experimental curves gives a value of β corresponding to a value of λ and k_4 is solved by (31).

EXPERIMENTAL

1. Material

Commercial 2-iodoheptafluoropropane (Bristol Organics Ltd) was purified by preparative g.l.c., using a column packed with squalene fitted on a pye 105 instrument. It was thereafter degassed and trap to trap distilled to eliminate water.

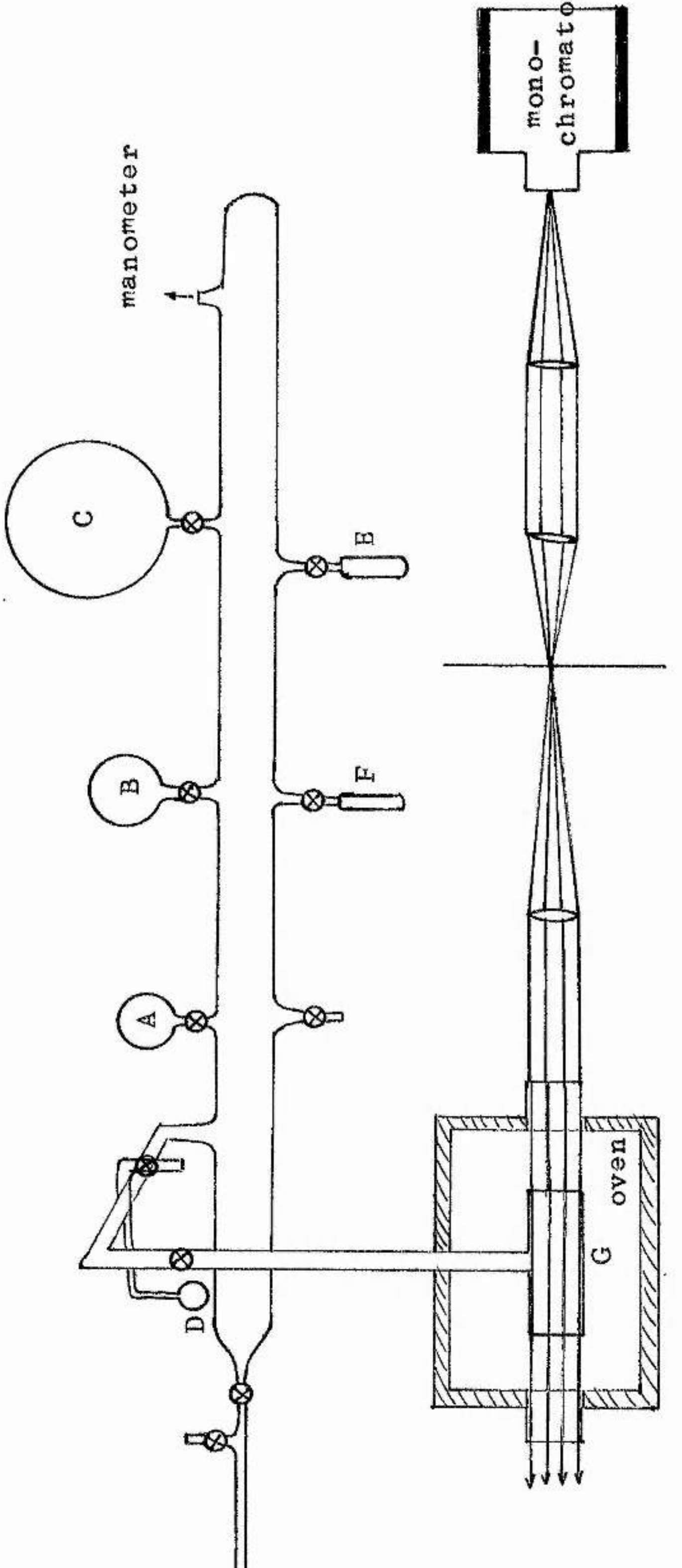
Commercial trifluoroethylene (Pennisular Chem. Research) was degassed and trap to trap distilled.

Commercial Diethyl-ether was dried on $CaCl_2$, filtered, distilled and dried on Sodium wires. It was then trap to trap distilled and degassed.

2. Apparatus

The experiment was performed in a cylindrical quartz reaction vessel (G) of capacity 205 ml, connected to a conventional vacuum line. The vacuum was maintained at a pressure of 10^{-3} to 10^{-5} torr by means of an Edwards silicone oil diffusion pump, backed by a NGN PSR I rotary piston pump. The reactant pressures were measured using a mercury manometer and volumes were measured into storage bulbs on the line, namely bulbs A, B, C and D of capacity 148.5 ml, 319 ml, 2,250 ml and 23 ml respectively.

The 2-iodoheptafluoropropane was stored in a pyrex tube (F) closed by a greaseless tap. The tube was kept in liquid nitrogen and remained connected to the line all the time. The ether was stored in a similar pyrex tube (E), which remained connected to the line as well. For the experiments conducted at 46°C and 75°C,


manometer
mono-
chromator
A
B
C
D
E
F
G
oven
trap
pump

a furnace at the required temperature was put around the reaction vessel. The furnace had two windows at diametrically opposite sides, which allowed light to pass through the system.

The temperature, measured by a mercury in glass thermometer could be maintained to ± 2^oC using a 0-250 Volt "Variac" transformer. For the experiments conducted at 7^oC, the furnace was replaced by a water bath. A continuous supply of cold water was pumped through a metal spiral. The spiral, placed in the water bath, kept it at the required temperature. Photolitic reactions were initiated by 365 nm wavelength light from a Bausch & Lomb monochromator fitted with a Sp 200 super pressure mercury lamp. The light was collimated by the optical system shown schematically on page 123. The super pressure mercury lamp was run on 240 Volts 50 c/s A.C. At this frequency the lamp gives $\sim$ 6000 pulses a minute, which is equivalent to steady illumination for the $(CF_3)_2CF^\cdot$ radicals. It has been shown by Gomer and Kistiakowsky that A.C. illumination was justified in the case of methyl radicals[31]. The light from the monochromator was brought to a focus on the sector by lenses L_1 and L_2. The light spot on the sector was a vertical line; its width was about 2 mm. Since the width of the slots cut in the sector was 100 mm at this point, the time of partial illumination was only about 4% of the total time of illumination. Effects due to non-square wave pulses can therefore be neglected. The sector was made from blackened aluminium sheet, circular, of 305 mm diameter, and had two slots cut in it, each occupying $\frac{1}{2}$ a segment ($\pi/4$). The dark to light ratio was therefore three.

The light was brought into a nearly parallel beam by the quartz lens L_3 and illuminated, nearly evenly, the whole vessel.

A "Garrard induction motor" and a system of pulleys drove the sector. The sector speed was found by counting revolutions and timing with a stopclock. In all runs, the sector was timed periodically and the speeds were found to be constant to within $\pm$ 1% during any run. At 46°C, in the runs at $<$10 rev./min., the sector was moved by hand after a measured time interval.

At 7°C, in the runs at$<$35 rev./min. a magnetically operated shutter was used instead of the sector. An electronic timer switched the magnet on or off for measured lengths of time. When the magnet was switched on, it lifted a small aluminium sheet and the light could reach the reaction vessel. When the magnet was switched off, the reaction was shielded from light.

3. Method

About 1 g of mercury was weighed into the reaction vessel. The 2-iodoheptafluoropropane and trifluoroethylene were measured into storage bulbs and then distilled into the reaction vessel (G) which was then isolated from the rest of the line by a greaseless tap. A furnace at the required temperature was put around the reaction vessel. The mixture was irradiated for measured lengths of time. Meanwhile ether was measured into bulb D. After reaction, the mixture and the ether were distilled together into a tube and the analysis was performed immediately.

4. Analysis and identification

Methods of analysis and identification were as in part 1. Only one product had not been identified in previous experiments. To be able to identify it by mass spectrometry, a preliminary experiment was carried out in which 2-iodoheptafluoropropane (1.374×10^{-3} moles) and trifluoroethylene (1.61×10^{-4} moles) were irradiated for 20 hours in the presence of mercury (1.1 g). The g.l.c. trace showed three products: $(CF_3)_2CFCF(CF_3)_2$; $(CF_3)_2CFCHFCF_2CF(CF_3)_2$ and $(CF_3)_2CFCHFCF_2I$ eluted in that order on a 15 ft squalene column.

The mass spectrum of the second product is shown below.

$(CF_3)_2CFCHFCF_2CF(CF_3)_2$

m/e	rel. Abundance	Assignment
420	very weak	$C_8HF_{17}^+$
313	1.5	$C_7HF_{12}^+$
251	14.3	$C_5HF_{10}^+$
219	11.4	$C_4F_9^+$
181	5.7	$C_4F_7^+$
163	28.6	$C_4HF_6^+$
131	27.1	$C_3F_5^+$
119	8.5	$C_2F_5^+$
113	38.6	$C_3HF_4^+$
101	14.3	$C_2HF_4^+$
100	10.0	$C_2F_4^+$
93	5.7	$C_3F_3^+$
82	8.5	$C_2HF_3^+$
75	7.1	$C_3HF_2^+$
69	100	CF_3^+
51	31.4	CHF_2^+
50	7.1	CF_2^+

5. Details of experiments

A. Experiments at 46°C

1. Variation of light intensity

In a series of reactions, 2-iodoheptafluoropropane (1.37×10^{-3} moles) and trifluoroethylene (1.61×10^{-4} moles) were irradiated for 5 hours in the reaction vessel, in the presence of mercury (1.1 g). Different light intensities were obtained by varying the width of the exit slit of the monochromator between 0.3 mm and 1 mm. Peak areas were measured relative to that of the dimer which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCF(CF_3)_2$

a_2 = the relative area of $(CF_3)_2CFCHFCF_2I$

Slit width: 1 mm
temperature 45°C

	a_1	a_2
	100	634.5
	100	635.6
	100	635.0
mean	100	635.0

Slit width: 0.9 mm
temperature 46°C

	a_1	a_2
	100	672.0
	100	666.0
	100	706.0
mean	100	681.3

Slit width: 0.6 mm
temperature 46°C

	a_1	a_2
	100	769.0
	100	785.0
	100	786.0
mean	100	780.0

Slit width: 0.5 mm
temperature 48°C

	a_1	a_2
	100	1033.0
	100	1033.0
	100	1031.0
mean	100	1032.3

Slit width: 0.4 mm
temperature 46°C

	a_1	a_2
	100	941.0
	100	940.0
	100	910.0
mean	100	930.3

Slit width: 0.3 mm
temperature 46°C

	a_1	a_2
	100	1110.0
	100	1140.0
	100	1143.0
mean	100	1131.0

The relative concentrations of the two products are shown in table 3-2.

Table 3-2 Effect of the variation of the incident light intensity on the relative concentration of products.

Temp. °C	$I_{relative}$	$\frac{[(CF_3)_2CFCHFCF_2I)]_f}{[(CF_3)_2CFCF(CF_3)_2]_f}$
45	1	5.625
46	0.9	6.03
46	0.6	6.91
48	0.5	9.15
46	0.4	8.24
46	0.3	10.02

A least squares plot of log $([(CF_3)_2CFCHFCF_2I]_f / [(CF_3)_2CFCF(CF_3)_2]_f$ against log I_{rel} gave an intercept of 0.757 and a gradient of -0.471 The correlation coefficient was 0.948.

2. Sector runs

In this series of experiments, 2-iodoheptafluoropropane (1.37×10^{-3} moles) and trifluoroethylene (1.61×10^{-4} moles) were irradiated in the reaction vessel in the presence of mercury (1.1 g). The reactions took place for measured lengths of time. Ether (2.54×10^{-5} moles) was added after reaction. Peak areas were measured relative to that of the ether, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCF(CF_3)_2$
a_2 = the relative area of $(CF_3)_2CFCHFCF_2I$
a_3 = the relative area of $(CF_3)_2CFCHFCF_2CF(CF_3)_2$
a_4 = the relative area of $C_2H_5OC_2H_5$

Temp. 46°C time 300 min
steady illumination

	a_1	a_2	a_3	a_4
	23.2	171.0	12.0	100
	24.0	178.0	14.0	100
	22.9	181.0	13.4	100
mean	23.4	176.7	13.1	100

Temp. 47°C time 300 min
$\lambda = 0.663$ sec.

	a_1	a_2	a_3	a_4
	6.0	87.0	3.8	100
	5.8	84.0	3.5	100
	5.6	84.0	3.7	100
mean	5.8	85.0	3.67	100

Temp. 45°C time 300 min
$\lambda = 60$ sec

	a_1	a_2	a_3	a_4
	5.7	68.5	3.7	100
	5.9	67.2	3.4	100
	5.8	66.7	3.3	100
mean	5.8	67.46	3.47	100

Temp. 48°C time 300 min
steady illumination

	a_1	a_2	a_3	a_4
	23.0	174.0	13.0	100
	22.7	181.0	15.0	100
mean	22.85	177.5	14.0	100

Temp. 46 °C time 300 min
λ = 1800 sec

	a_1	a_2	a_3	a_4
	5.33	53.4	2.83	100
	5.67	52.0	2.83	100
	5.52	52.9	-	100
mean	5.51	52.77	2.83	100

Temp. 46 °C time 300 min
λ = 300 sec

	a_1	a_2	a_3	a_4
	5.1	54.3	3.6	100
	5.4	55.0	3.1	100
mean	5.25	54.65	3.35	100

Temp. 45 °C time 300 min
steady illumination

	a_1	a_2	a_3	a_4
	28.0	202.0	18.0	100
	27.5	212.0	16.9	100
	27.7	205.0	17.5	100
mean	27.73	206.3	17.47	100

Temp. 47 °C time 300 min
steady illumination

	a_1	a_2	a_3	a_4
	23.2	232.0	14.3	100
	21.8	232.5	14.3	100
	22.4	233.0	14.6	100
mean	22.47	232.5	14.4	100

Temp. 46 °C time 300 min
λ = 0.222 sec

	a_1	a_2	a_3	a_4
	6.0	106.7	4.0	100
	5.7	109.3	3.7	100
mean	5.85	108.0	3.85	100

Temp. 44 °C time 300 min
λ = 900 sec

	a_1	a_2	a_3	a_4
	5.0	64.0	3.0	100
	4.8	67.0	2.9	100
mean	4.9	65.5	2.95	100

Temp. 46 °C time 300 min
λ = 0.052 sec

	a_1	a_2	a_3	a_4
	6.4	99.0	4.05	100
	6.5	104.0	4.0	100
mean	6.45	101.5	4.03	100

Temp. 46 °C time 360 min
λ = 2250 sec

	a_1	a_2	a_3	a_4
	6.24	68.4	3.96	100
	6.72	70.6	4.2	100
mean	6.48	69.5	4.08	100

Temp. 46°C time 120 min
steady illumination

	a_1	a_2	a_3	a_4
	11.5	98.0	6.0	100
	11.47	93.0	5.88	100
mean	11.49	95.5	5.94	100

Temp. 46°C time 180 min
$\lambda = 15$ sec

	a_1	a_2	a_3	a_4
	5.2	65.0	2.8	100
	5.0	63.0	2.78	100
mean	5.1	64.0	2.79	100

Temp. 46°C time 180 min
$\lambda = 45$ sec

	a_1	a_2	a_3	a_4
	5.0	55.0	3.0	100
	5.6	56.0	2.8	100
mean	5.3	55.5	2.9	100

Temp. 45°C time 150 min
steady illumination

	a_1	a_2	a_3	a_4
	10.3	93.4	5.88	100
	10.5	95.5	6.45	100
mean	10.4	94.45	6.17	100

Temp. 44°C time 550 min
steady illumination

	a_1	a_2	a_3	a_4
	62.1	439.0	38.0	100
	62.5	447.0	38.3	100
mean	62.3	443.0	38.15	100

Temp. 46°C time 150 min
$\lambda = 30$ sec

	a_1	a_2	a_3	a_4
	4.6	54.8	2.55	100
	4.5	52.7	2.59	100
mean	4.55	53.8	2.57	100

Temp. 44°C time 60 min
steady illumination

	a_1	a_2	a_3	a_4
	6.7	51.2	4.4	100
	6.8	51.9	4.1	100
mean	6.75	51.55	4.25	100

Temp. 47°C time 120 min
$\lambda = 5$ sec

	a_1	a_2	a_3	a_4
	2.14	33.0	1.14	100
	2.47	32.4	1.35	100
mean	2.31	32.7	1.25	100

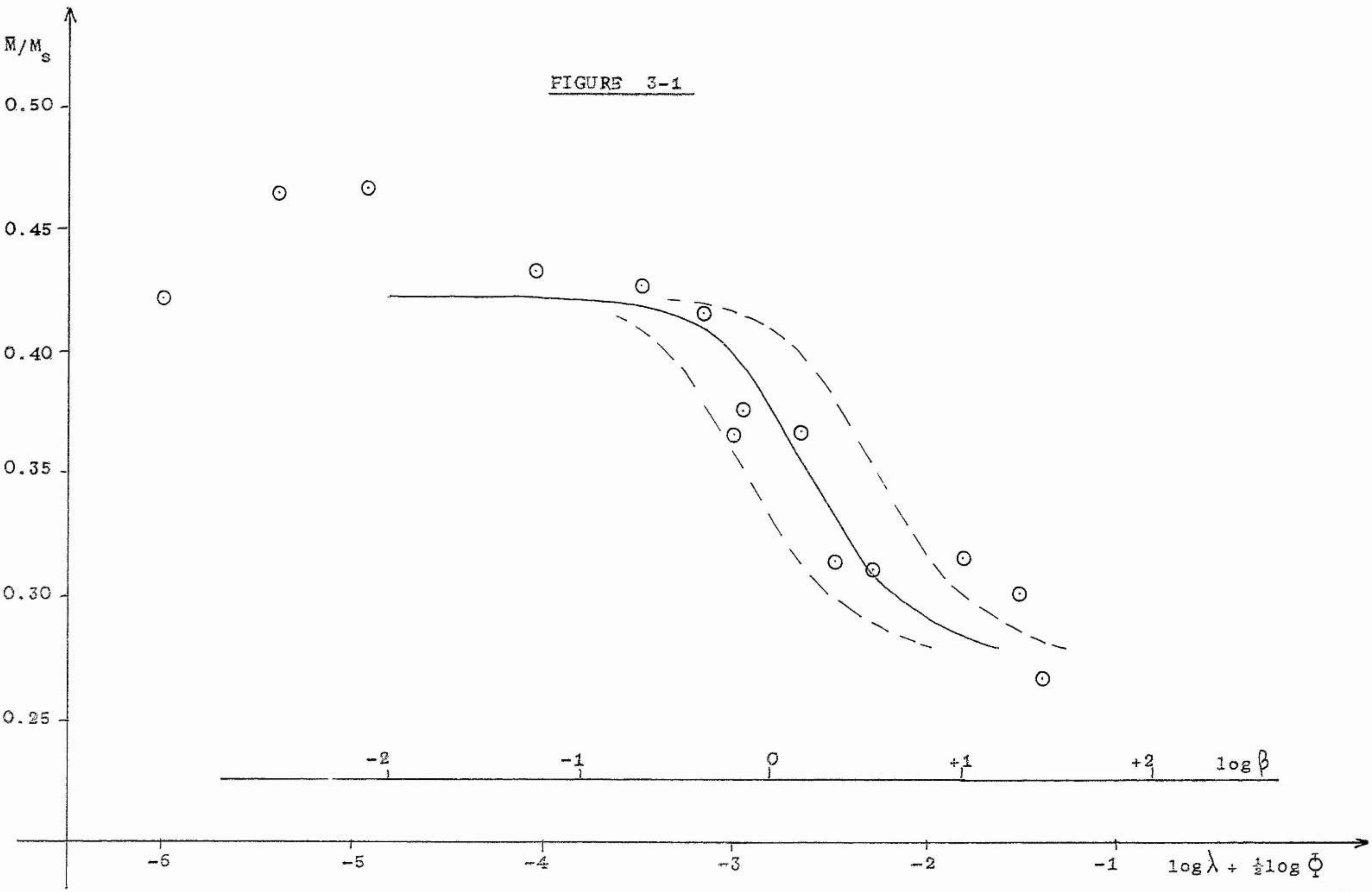
Table 3-3 Experiments at 46°C

λ (sec)	$[(CF_3)_2CFCF(CF_3)_2]_f$ [a] x 10^6	$[(CF_3)_2CFCHFCF_2I]_f$ [a] x 10^5	$[(CF_3)_2CFCHFCF_2CF(CF_3)_2]_f$ [a] x 10^6	α_s	ϕIa [a]	$\log\lambda + \frac{1}{2}\log\phi$	$\bar{M}/_{Ms}$
steady	4.309	2.882	1.908	0.442	6.842	-	-
0.663	1.068	1.386	0.535	-	6.857	-4.910	0.467
60	1.068	1.100	0.505	-	6.730	-2.958	0.377
steady	4.208	2.895	2.039	0.484	6.875	-	-
1800	1.015	0.861	0.412	-	6.106	-1.502	0.300
300	0.967	0.891	0.488	-	6.225	-2.276	0.310
steady	5.106	3.365	2.544	0.498	8.419	-	-
steady	4.138	3.792	2.097	0.506	6.862	-	-
0.222	1.077	1.762	0.561	-	7.007	-5.381	0.464
900	0.902	1.068	0.430	-	5.698	-1.818	0.315
0.052	1.188	1.655	0.587	-	7.593	-5.994	0.421
2250	0.994	0.944	0.495	-	6.370	-1.396	0.266
steady	5.290	3.895	2.163	0.408	8.202	-	-
steady	6.258	3.941	3.030	0.484	10.222	-	-
15	1.565	1.740	0.677	-	9.590	-3.484	0.426
30	1.676	1.755	0.749	-	10.375	-3.165	0.415
45	1.627	1.509	0.704	-	9.971	-2.998	0.365
steady	6.215	4.204	3.095	0.498	10.245	-	-
steady	3.830	3.081	1.797	0.470	6.192	-	-
5	1.064	1.333	0.455	-	6.498	-4.045	0.432
120	1.045	1.130	0.488	-	6.557	-2.663	0.367
180	1.137	1.000	0.535	-	7.152	-2.468	0.314
steady	4.088	2.993	2.083	0.510	6.792	-	-
dark	0.112	0.382	-	-	-	-	-
dark	0.141	0.337	-	-	-	-	-

a : concentrations are in $mol.1^{-1}$ and ϕIa is in $mol.1^{-1}.sec^{-1}$

A plot of $\bar{M}/_{Ms}$ against $(\log\lambda + \frac{1}{2}\log\phi)$ is shown in fig. 3-1

FIGURE 3-1


$\bar{M}/M_s$
0.50
0.45
0.40
0.35
0.30
0.25
-2
-1
0
+1
+2
$\log \beta$
-6
-5
-4
-3
-2
-1
$\log \lambda + \frac{1}{2} \log \Phi$

Temp. 46 °C time 120 min
λ = 120 sec

	a_1	a_2	a_3	a_4
	2.29	27.4	1.43	100
	2.25	28.0	1.25	100
mean	2.27	27.7	1.34	100

Temp. 46 °C time 120 min
λ = 180 sec

	a_1	a_2	a_3	a_4
	2.5	24.47	1.47	100
	2.44	24.57	1.46	100
mean	2.47	24.52	1.47	100

Temp. 46 °C time 300 min
steady illumination

	a_1	a_2	a_3	a_4
	22.3	179.0	14.3	100
	22.1	188.0	14.3	100
mean	22.2	183.5	14.3	100

The product concentrations, corrected for a reaction time of 300 minutes, are shown in table 3-3.

3. Thermal reaction

Two experiments were carried out in which 2-iodoheptafluoropropane (1.37×10^{-3} moles) and trifluoroethylene (1.61×10^{-4} moles) were reacted in the dark for 5 hours, in the presence of mercury (1.1 g). After reaction, diethyl-ether (1.001×10^{-4} moles) was added and the mixture was analysed. The peak areas were measured relative to that of ether, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCF(CF_3)_2$
a_2 = the relative area of $(CF_3)_2CFCHFCF_2I$
a_3 = the relative area of $(CF_3)_2CFCHFCF_2CF(CF_3)_2$
a_4 = the relative area of $C_2H_5OC_2H_5$

run 1 temp. 46°C

	a_1	a_2	a_3	a_4
	0.15	5.9	-	100
	0.16	6	-	100
mean	0.155	5.95	-	100

run 2 temp. 45°C

	a_1	a_2	a_3	a_4
	0.20	5.6	-	100
	0.19	4.8	-	100
mean	0.195	5.2	-	100

From this it can be calculated that

$$\left(\frac{n}{n+1}\right)^{\frac{1}{2}} \equiv \frac{\text{Thermal reaction}}{\text{Photochemical reaction}} = 0.0977$$

4. Effect of mercury

In this series of experiments, 2-iodoheptafluoropropane (1.37×10^{-3} moles) and trifluoroethylene (1.001×10^{-4} moles) were irradiated in the reaction vessel for two hours. In the first two runs, the reaction vessel contained no mercury. In the other two, mercury (1.1 g) was present. The ether (1.001×10^{-4} moles) was added after reaction. Peak areas were measured relative to that of $C_2H_5OC_2H_5$, which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCF(CF_3)_2$

a_2 = the relative area of $(CF_3)_2CFCHFCF_2I$

a_3 = the relative area of $(CF_3)_2CFCHFCF_2CF(CF_3)_2$

a_4 = the relative area of $C_2H_5OC_2H_5$

run 1 no mercury

	a_1	a_2	a_3	a_4
	0.94	7.8	0.39	100
	0.91	7.5	0.43	100
mean	0.925	7.65	0.41	100

run 2 no mercury

	a_1	a_2	a_3	a_4
	1.06	7.3	0.53	100
	1.08	8.4	0.41	100
mean	1.07	7.9	0.47	100

Table 3-4 The effect of mercury on the experimental ϕIa

run	$[(CF_3)_2CFCF(CF_3)_2]_f^{a}$ x 10^6	$[(CF_3)_2CFCHFCF_2I]_f^{a}$ x 10^6	$[(CF_3)_2CFCHFCF_2CF(CF_3)_2]_f^{a}$ x 10^7	$\phi 1a^{a}$ x 10^{10}
1	0.670	4.909	2.349	2.51
2	0.775	5.069	2.693	2.90
3	1.289	8.598	3.552	4.57
4	1.261	9.047	3.380	4.44

a : concentrations are in $mol.1^{-1}$ and ϕIa is in $mol.1^{-1}.sec^{-1}$

run 3 1.1 g of mercury

	a_1	a_2	a_3	a_4
	1.76	13.5	0.60	100
	1.80	13.3	0.64	100
mean	1.78	13.4	0.62	100

run 4 1.1 g of mercury

	a_1	a_2	a_3	a_4
	1.73	14.0	0.56	100
	1.75	14.2	0.62	100
mean	1.74	14.1	0.59	100

The concentrations after two hours reaction are shown in table 3-4.

B. Experiments at 75°C

2-Iodoheptafluoropropane (1.37×10^{-3} moles) and trifluoroethylene (1.001×10^{-4} moles) were reacted in the reaction vessel for 2 hours, in the presence of mercury (1.1 g). In the first two experiments, the reaction mixture was irradiated. In the last two experiments, it was kept in the dark. Ether (1.001×10^{-4} moles) was added after reaction. The peak areas were measured relative to that of the ether which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCF(CF_3)_2$
a_2 = the relative area of $(CF_3)_2CFCHFCF_2I$
a_3 = the relative area of $(CF_3)_2CFCHFCF_2CF(CF_3)_2$
a_4 = the relative area of $C_2H_5OC_2H_5$

run 1 light initiated
reaction temp. 75°C

	a_1	a_2	a_3	a_4
	14.5	144.0	5.2	100
	15.1	142.0	5.3	100
mean	14.8	143.0	5.25	100

run 2 light initiated
reaction temp. 74°C

	a_1	a_2	a_3	a_4
	15.0	146.0	6.0	100
	15.2	142.0	5.8	100
mean	15.1	144.0	5.9	100

Table 3-5 Comparison between thermal and photochemical reaction at 75°C

run	$[(CF_3)_2CFCF(CF_3)_2]_f$ [a] x 10^5	$[(CF_3)_2CFCHFCF_2I]_f$ [a] x 10^5	$[(CF_3)_2CFCHFCF_2CF(CF_3)_2]_f$ [a] x 10^6
1	1.072	9.175	3.036
2	1.094	9.240	3.380
3	0.254	3.946	1.203
4	0.297	3.882	1.490

a : Concentrations are in mol l^{-1}

run 3 reaction in the dark
temp. 75°C

	a_1	a_2	a_3	a_4
	3.4	62.0	2.2	100
	3.6	61.0	2.0	100
mean	3.5	61.5	2.1	100

run 4 reaction in the dark
temp. 75°C

	a_1	a_2	a_3	a_4
	4.4	60.0	3.0	100
	3.8	61.0	2.2	100
mean	4.1	60.5	2.6	100

The product concentrations are shown in table 3-5.

It can be calculated that

$$\left(\frac{n}{n+1}\right)^{\frac{1}{2}} \equiv \frac{\text{Thermal reaction}}{\text{Photochemical reaction}} = 0.425$$

C. Experiments at 7°C

1. Thermal reaction

In the first two experiments, 2-iodoheptafluoropropane (1.37×10^{-3} moles) and trifluoroethylene (1.001×10^{-4} moles) were reacted in the dark for 22 hours in the presence of mercury (1.1 g). The peaks corresponding to $(CF_3)_2CFCF(CF_3)_2$, $(CF_3)_2CFCHFCF_2I$ and $(CF_3)_2CFCHFCF_2CF(CF_3)_2$ were absent on the g.l.c. trace.

2. Sector runs

In this series of experiments, 2-iodoheptafluoropropane (1.37×10^{-3} moles) and trifluoroethylene (1.001×10^{-4} moles) were irradiated in the reaction vessel in the presence of mercury (1.1 g). The reactions took place for measured lengths of time. Diethyl ether (1.001×10^{-4} moles) was added after reaction. Peak areas were measured relative to that of the ether which was set equal to 100.

let a_1 = the relative area of $(CF_3)_2CFCF(CF_3)_2$

a_2 = the relative area of $(CF_3)_2CFCHFCF_2I$

a_3 = the relative area of $(CF_3)_2CFCHFCF_2CF(CF_3)_2$

a_4 = the relative area of $C_2H_5OC_2H_5$

Temp. 7°C time 720 min.
steady illumination

	a_1	a_2	a_3	a_4
	8.7	18.0	3.1	100
	8.4	18.0	3.2	100
mean	8.55	18.0	3.15	100

Temp. 6°C time 780 min.
λ = 0.221 sec

	a_1	a_2	a_3	a_4
	4.58	10.1	1.25	100
	4.53	10.2	1.28	100
mean	4.555	10.15	1.265	100

Temp. 7°C time 340 min.
steady illumination

	a_1	a_2	a_3	a_4
	5.76	7.1	1.52	100
	5.75	7.5	1.54	100
mean	5.755	7.3	1.53	100

Temp. 7°C time 390 min.
λ = 0.025 sec

	a_1	a_2	a_3	a_4
	2.6	7.2	0.89	100
	2.7	7.14	0.95	100
mean	2.65	7.17	0.92	100

Temp. 6°C time 340 min.
steady illumination

	a_1	a_2	a_3	a_4
	5.5	7.5	1.59	100
	5.5	7.5	1.38	100
mean	5.5	7.5	1.485	100

Temp. 7°C time 390 min.
λ = 0.052 sec.

	a_1	a_2	a_3	a_4
	2.5	5.1	0.6	100
	2.45	4.9	0.59	100
mean	2.475	5.0	0.595	100

Temp. 6°C time 360 min.
λ = 3 sec.

	a_1	a_2	a_3	a_4
	2.03	4.47	0.58	100
	2.00	4.00	0.50	100
mean	2.015	4.235	0.54	100

Temp. 7°C time 360 min
λ = 0.025 sec

	a_1	a_2	a_3	a_4
	1.51	5.6	0.56	100
	1.54	5.7	0.57	100
mean	1.525	5.65	0.565	100

Temp. 7°C time 375 min.
λ = 0.105 sec

	a_1	a_2	a_3	a_4
	1.15	5.21	0.423	100
	1.09	5.13	0.449	100
mean	1.12	5.17	0.436	100

Temp. 7°C time 240 min
steady illumination

	a_1	a_2	a_3	a_4
	5.24	6.77	1.65	100
	5.36	6.57	1.60	100
mean	5.30	6.67	1.625	100

Temp. 7°C time 720 min.
steady illumination

	a_1	a_2	a_3	a_4
	15.2	16.4	3.51	100
	14.5	16.4	3.63	100
mean	14.85	16.4	3.57	100

Temp. 8°C time 345 min.
steady illumination

	a_1	a_2	a_3	a_4
	12.4	11.6	3.2	100
	12.1	12.0	3.0	100
mean	12.25	11.8	3.1	100

Temp. 7°C time 300 min.
λ = 22 sec.

	a_1	a_2	a_3	a_4
	1.67	3.85	0.64	100
	1.63	3.75	0.625	100
mean	1.65	3.80	0.633	100

The product concentrations, corrected for a reaction time of 360 minutes, are shown in table 3-6.

Table 3-6 Experiments at 7°C

λ	$[(CF_3)_2CFCF(CF_3)_2]_f^a$ x 10^6	$[(CF_3)_2CFCHFCF_2I]_f^a$ x10^6	$[(CF_3)_2CFCHFCF_2CF(CF_3)_2]_f^a$ x10^6		ϕI_a^a x10^{10}	$\log\lambda + \frac{1}{2}\log\phi$	$\frac{\bar{M}}{\bar{M}s}$
steady	3.097	5.775	0.902	0.291	3.703	-	-
0.221	1.523	3.006	0.334	-	6.878	-5.387	0.421
steady	4.414	4.959	0.928	0.210	4.946	-	-
0.025	1.772	4.247	0.487	-	8.367	-6.291	0.607
steady	4.219	5.095	0.901	0.214	4.741	-	-
0.052	1.655	2.961	0.315	-	7.296	-6.003	0.455
3	1.460	2.717	0.309	-	6.552	-4.265	0.444
steady	5.379	5.261	1.023	0.190	5.928	-	-
0.025	1.105	3.625	0.324	-	5.293	-6.391	0.604
steady	9.260	7.901	1.853	0.200	10.290	-	-
0.105	0.779	3.185	0.240	-	3.774	-5.841	0.580
22	1.434	2.926	0.435	-	6.922	-3.388	0.420
steady	5.759	6.420	1.396	0.242	6.625	-	-

a: Concentrations are in mol.1^{-1} and $\phi 1_a$ is in mol.1^{-1}.sec^{-1}

Reactions in the presence of CF_3I

Trifluoromethyl iodide (7.75×10^{-5} moles) and perfluoroisopropyl iodide (2.32×10^{-4} moles), were measured into storage bulbs of 144 ml and 215 ml respectively. The system was then pumped down until a good vacuum was obtained. The taps of the two bulbs were opened and the reactants were allowed to expand into the line and into the pre-heated reaction vessel. The latter was then isolated from the rest of the line and kept in the dark, for various lengths of time. The temperature was varied from 240°C to 293°C. After reaction, the mixture was distilled into a tube. The hexafluoroethane, formed in the reaction, being a very volatile product, the tube was sealed and placed into a cruncher attached to the g.l.c. apparatus. The injection was made by crunching the glass tube. For this reason, only one analysis could be performed for each experiment.

Three products could be seen on the g.l.c. trace. The first two could not be separated properly on a variety of columns. They were identified by coupled g.l.c. - mass spectrometry as hexafluoroethane and perfluoroisobutane. The third product was the perfluoro-diisopropyl.

Since C_2F_6 and $CF_3CF(CF_3)_2$ could not be measured separately, the total area of the two peaks together was compared to the area of the peak corresponding to $(CF_3)_2CFCF(CF_3)_2$, which was set equal to 100.

let a_1 = the combined relative area of CF_3CF_3 and $CF_3CF(CF_3)_2$

a_2 = the relative area of $(CF_3)_2CFCF(CF_3)_2$

Temp. 240°C time 180 min.

run	a_1	a_2
1	149	100
2	137	100
mean	143	100

Temp. 293°C time 30 min.

run	a_1	a_2
1	7.8	100
2	9.2	100
mean	8.5	100

Temp. 283°C time 60 min.

run	a_1	a_2
1	33.7	100
2	31.4	100
mean	32.55	100

Temp. 265°C time 60 min.

run	a_1	a_2
1	98.3	100
2	96.1	100
mean	97.2	100

Discussion.

The reaction sequence for the rotating sector experiments is shown in the introduction to this chapter. The concentration of a product P was calculated using the following equation

$$[P]_f = \frac{A_p}{A_{ether}} \times \frac{M_{ether}-28}{M_p-28} \times [ether]$$

where A_p and A_{ether} are the relative areas of P and $C_2H_5OC_2H_5$ respectively, M_p and M_{ether} are their respective molecular weight and [ether] is the hypothetical concentration, in $mol.1^{-1}$, of ether in the reaction vessel.

The results of the experiments at 46°C (table 3-3) were plotted in the form $\overline{M}/M_s$ against $(\log \lambda + \frac{1}{2}\log\Phi)$, as shown in figure 3-1. Also shown in the figure is the theoretical curve of $\overline{M}/M_s$ against $\log\beta$ for α=0.478, n=0.0096 and p=3 (data in table 3-1). The $(\log \lambda + \frac{1}{2}\log\Phi)$ and $\log\beta$ axes were adjusted relative to each other to give the best fit between the experimental points and the theoretical curve. The value of $(\log \lambda + \frac{1}{2}\log\Phi)$ corresponding to any value of $\log\beta$ can be directly read off the plot. The rate constant for the recombination of perfluoroisopropyl radicals, at 46°C, was found to be $k_{4(46^\circ)} = 1.46 \times 10^5 \ 1.mol^{-1}.sec^{-1}$.

Melville and Burnett[54] have shown that, for values of the ratio of thermal to photochemical reaction, $(n/(n+1))^{\frac{1}{2}}$, greater than 0.3, the rotating sector method cannot be applied .

At 75^{o}C, the value of $(n/(n+1))^{\frac{1}{2}}$ was found to be 0.42, as shown in table 3-5. It was therefore not possible to determine k_4 at that temperature. The determination of the rate constant at temperatures between 50^{o}C and 60^{o}C was not justified, since the difference with $k_{4(46^{o})}$, if any, would be well in the range of the experimental error.

No dark reaction was observed at 7^{o}C, but the measured ϕI_a values are scattered and the experimental values of $\overline{M}/M_s$ are certainly peculiar, as shown in table 3-6. A possible explanation to the observed phenomenon is that, at that temperature, some of the reactants or products may be partly in the liquid phase. k_4 could not be determined at that temperature either.

Probably the most direct method of evaluating the rate of a simple reaction is to calculate the number of collisions between the reactants, per unit volume and per second. It is also necessary to determine the fraction of these collisions which will result in chemical change. The collision number (Z) for two identical radicals is given by

$$Z = 2(\pi RT/M)^{\frac{1}{2}}\sigma^2 N$$

where M is the molecular weight of the radical, σ is its collision diameter and N is Avogadro's number. Z represents the rate, in $cm^3.mol^{-1}.sec^{-1}$, of a reaction for which every collision is effective. In actual fact, this is never the case : a probability factor (p) has to be considered. p takes into account factors like the relative orientation of the molecules at the moment of impact. The activation energy being very close to zero for most radicals, the equation for k_4 is

$$k_4 = A_4 = pZ$$

To calculate Z, one needs to know the collision diameter of the radical. It is not known for $(CF_3)_2CF^{\cdot}$ radicals, but the diameters of all ordinary gases lie in the range 2 to 6 A^o. The value of some collision diameters is shown in table 3-7. It seems reasonable to addopt a value of 6 A^o (the upper limit of the range) for perfluoroisopropyl radicals. The assumption is supported by the values of d_c shown in table 2-10.

Table 3-7 : Collision diameters for some simple radicals.

Radicals	$CH_3^{\cdot}$[52]	$CF_3^{\cdot}$[42]	$C_2H_5^{\cdot}$[53]	$i-C_3H_7^{\cdot}$[107]	$t-C_4F_9^{\cdot}$[108]	$CCl_3^{\cdot}$*
σ (A^o)	3.5	4.0	5.0	4.8	5.2	5.1

* average between several values found in the literature.

The calculated value of Z, at 46^{o}C, for $(CF_3)_2CF^{\cdot}$ radicals, using $\sigma = 6A^o$, is $10^{11.0}$ $l.mol^{-1}.sec^{-1}$. This value is very close to the value of k_4 10^{11} $l.mol^{-1}.sec^{-1}$, predicted by the transition state theory, for all the radicals listed in table 3-7. The value of the probability factor (p) can be as low as 10^{-4}. For the combination reactions of simple radicals, however, the lower limit for p appears to be 10^{-2}, as shown in table 3-8.

Table 3-8 : Calculated and observed rate constants.

Radical	$k_{4(obs)}$ $l.mol^{-1}.sec^{-1}$		Z $l.mol^{-1}.sec^{-1}$
$CH_3^{\cdot}$	$10^{10.3}$	a	$10^{11.1}$
	$10^{10.4}$	b	
$CF_3^{\cdot}$	$10^{10.4}$	c	$10^{10.9}$
	$10^{10.0}$	d	
$C_2H_5^{\cdot}$	$10^{11.5}$	e	$10^{11.2}$
$i-C_3H_7^{\cdot}$	$10^{10.8}$	f	$10^{11.1}$
$t-C_4H_9^{\cdot}$	$10^{9.5}$	g	$10^{11.1}$
$C_2F_5^{\cdot}$	$10^{9.5}$	d	---
$n-C_3F_7^{\cdot}$	$10^{9.3}$	d	---
$n-C_4F_9^{\cdot}$	$10^{9.3}$	d	---

a = ref.52 b = ref.56 c = ref.42 d = ref.51

e = ref.53 f = ref.107 g = ref.108

Even if, in the case of perfluoroisopropyl radicals, p has a value as low as 10^{-3}, it would only bring the calculated value of A_4 down to 10^8 $l.mol^{-1}.sec^{-1}$, which is still nearly three orders of magnitude higher than the value obtained at 46 °C, in this work. If the mechanism is as shown in the introduction, if no undetected reaction occurs and if the reaction products do not undergo further transformation (decomposition...), the most likely explanation for the slow rate of combination is that, unlike most of the other radicals, the activation energy for the combination of perfluoroisopropyl radicals is different from zero.

A further evidence supporting that hypothesis is found in the thermal reaction between CF_3I and $(CF_3)_2CFI$. The reaction sequence for this system can be written

$$
\begin{array}{llll}
CF_3^{\cdot} + (CF_3)_2CFI & \rightleftharpoons & CF_3I + (CF_3)_2CF^{\cdot} & K \\
(CF_3)_2CF^{\cdot} + (CF_3)_2CF^{\cdot} & \longrightarrow & (CF_3)_2CFCF(CF_3)_2 & k_4 \\
(CF_3)_2CF^{\cdot} + CF_3^{\cdot} & \longrightarrow & (CF_3)_2CFCF_3 & k_5 \\
CF_3^{\cdot} + CF_3^{\cdot} & \longrightarrow & C_2F_6 & k_6
\end{array}
$$

It can be shown that, if the thermolysis takes place at a temperature T_1,

$$\left[\frac{[C_2F_6]_f}{[(CF_3)_2CFCF(CF_3)_2]_f}\right]_1 = (k_6/k_4) \times \left[\frac{[CF_3^{\cdot}]^2}{[(CF_3)_2CF^{\cdot}]^2}\right]_1$$

Using the definition of the equilibrium constant, it can be seen that

$$\left[\frac{[CF_3^{\cdot}]}{[(CF_3)_2CF^{\cdot}]}\right]_1 = 1/K_1 \times \frac{[CF_3I]}{[(CF_3)_2CFI]}$$

Substituting the ratio of the radical concentrations in the first equation, it becomes

$$\left[\frac{[C_2F_6]_f}{[(CF_3)_2CFCF(CF_3)_2]_f}\right]_1 = (k_6/k_4) \times K_1^{-2} \times \frac{[CF_3I]^2}{[(CF_3)_2CFI]^2} \qquad (i)$$

Similarily, it can be shown that

$$\left[\frac{[CF_3CF(CF_3)_2]_f}{[(CF_3)_2CFCF(CF_3)_2]_f}\right]_1 = (k_5/k_4) \times \left[\frac{[CF_3^{\cdot}]}{[(CF_3)_2CF^{\cdot}]}\right]_1$$

Introducing the value of the equilibrium constant, the equation becomes

$$\left[\frac{[CF_3CF(CF_3)_2]_f}{[(CF_3)_2CFCF(CF_3)_2]_f}\right]_1 = (k_5/k_4) \times K_1^{-1} \times \frac{[CF_3I]}{[(CF_3)_2CFI]} \qquad \text{(ii)}$$

Adding (i) and (ii), one obtains

$$\left[\frac{[C_2F_6]_f + [CF_3CF(CF_3)_2]_f}{[(CF_3)_2CFCF(CF_3)_2]_f}\right]_1 = \frac{[CF_3I]}{k_4K_1[(CF_3)_2CFI]} \times \left[\frac{k_6[CF_3I]}{K_1[(CF_3)_2CFI]} + k_5\right] \qquad \text{(iii)}$$

A similar equation can be obtained for the thermolysis at a temperature $T_2 > T_1$

$$\left[\frac{[C_2F_6]_f + [CF_3CF(CF_3)_2]_f}{[(CF_3)_2CFCF(CF_3)_2]_f}\right]_2 = \frac{[CF_3I]}{k_4K_2[(CF_3)_2CFI]} \times \left[\frac{k_6[CF_3I]}{K_2[(CF_3)_2CFI]} + k_5\right] \qquad \text{(iv)}$$

If we assume that none of the combination reactions has an activation energy, the only temperature dependent term is K.

Dividing (iii) by (iv), one obtains

$$\frac{\left[\dfrac{[C_2F_6]_f + [CF_3CF(CF_3)_2]_f}{[(CF_3)_2CFCF(CF_3)_2]_f}\right]_1}{\left[\dfrac{[C_2F_6]_f + [CF_3CF(CF_3)_2]_f}{[(CF_3)_2CFCF(CF_3)_2]_f}\right]_2} = \left[\frac{k_6\,[CF_3I]/[(CF_3)_2CFI] + k_5K_1}{k_6\,[CF_3I]/[(CF_3)_2CFI] + k_5K_2}\right] x \,\frac{K_2^2}{K_1^2} \qquad (v)$$

Okafo and Whittle[109] have shown that the C-I bond dissociation energy for $(CF_3)_2CFI$ is about 3.4 Kcal/mol smaller than for the trifluoromethyl iodide. Therefore, it can be assumed that ΔH^o (and ΔG^o) for the equilibrium is negative. Thus, an increase in temperature will result in a decrease of the equilibrium constant and

$$K_2 < K_1$$

Hence, it can be seen that the right-hand side of equation (v) is less than unity. In other words, the concentration of $(CF_3)_2CFCF(CF_3)_2$ relative to the sum of the concentrations of the other combination products should decrease when the temperature increases. The results show the exact opposite (table 3-9).

Table 3-9 : Relative areas of products for the thermolysis of CF_3I and $(CF_3)_2CFI$ at various temperatures.

Temperature (^oC)	$(CF_3CF(CF_3)_2+C_2F_6$	$(CF_3)_2CFCF(CF_3)_2$
240	143	100
265	97.2	100
283	32.55	100
293	8.5	100

The only way to explain both this phenomenon and the low value found for $k_{4(46^{o})}$, is to attribute an activation energy to the combination reaction of $(CF_3)_2CF^{\cdot}$ radicals.

It is possible to estimate the value of this activation energy, if one assumes that the probability factor is close to 10^{-2}. In which case,

$$A_4 = pZ = 10^{-2} \times 10^{11} = 10^{9} \text{ l.mol}^{-1}.\text{sec}^{-1}$$

Using the Arrhenius equation ($k_4 = A_4 \times e^{-E_4/RT}$), one can estimate the activation energy to be in the order of 5.6 Kcal/mol. This is certainly not impossible, since Shepp and Kutschke[53] found an activation energy of 2Kcal/mol for the recombination of ethyl radicals.

CHAPTER 4:

THE ORIENTATION OF THE ADDITION OF MONOIODOMETHYL RADICALS.

Introduction.

As a class, the polyhalomethanes have received the greatest amount of study in radical addition reactions. In 1945, Kharasch, Jensen and Urry[75] showed that polyhalogenomethanes can add to olefins by a free radical mechanism. They reported the addition of carbon tetrabromide to ethylenic compounds[76]. The reaction was induced either by methyl radicals (from acetyl peroxide) or by irradiation using visible light. The product of addition to oct-1-ene was found to be the 1,1,1,3-tetrabromo-n-nonane. They also reported the addition of carbon tetrachloride, chloroform and bromoform[77] to a series of unsaturated compounds. They showed that CCl_4 tends to add to the olefins to yield polymers, whereas addition of CBr_4 favours the formation of the one to one adduct. It also appeared that bromoform and chloroform react more slowly and that, whereas chloroform transfers a hydrogen atom, bromoform transfers a bromine atom. Iodoform was later shown to behave like bromoform[78].

Kharasch and his group[79] compared the addition of bromotrichloromethane and carbon tetrachloride to simple olefins and they found that, in each case, the trichloromethyl radicals add to the least substituted carbon atom of the double bond. The original work of Kharasch formed the basis of many of the later studies and Walling and Huyser[91] compiled the results obtained in this field up to 1961.

Other sources of trichloromethyl radicals were investigated. David and Gosselain[80] obtained $CCl_3^{\cdot}$ radicals by γ-radiolysis of carbon tetrachloride and Mellows and Burton[81] used the γ-radiolysis of chloroform. Both groups of workers observed the telomerization of ethylene, initiated by the radicals.

Hautcloque[82] and Tomkinson, Galvin and Pritchard[83] produced the trichloromethyl radicals by photolysing hexachloroacetone. Unfortunately, two primary processes occur in that system : both $CCl_3^{\cdot}$ radicals and chlorine atoms are produced and, since chlorine atoms are much more reactive than the radicals, the reaction mechanism is very much complicated.

$$CCl_3COCCl_3 \xrightarrow{h\nu} CCl_3^{\cdot} + CCl_3CO^{\cdot}$$

$$CCl_3COCCl_3 \xrightarrow{h\nu} Cl^{\cdot} + CCl_3COCCl_2^{\cdot}$$

Most of this early work with $CCl_3^{\cdot}$ radicals was carried out in solution. Wijnen and co-workers[84] studied the gas phase reaction of carbon tetrachloride with ethylene. The photolysis of CCl_4 produces chlorine atoms and trichloromethyl radicals. The same group studied the gas phase photolysis of CCl_4 in the presence of various mixtures of ethylene and ethane[85]. They showed that the chlorine atoms react with ethylene to form $C_2H_4Cl^{\cdot}$ radicals and that they abstract hydrogen from ethane. The formation of the final products was explained by combination and disproportionation of the three radicals : $C_2H_5^{\cdot}$, $C_2H_4Cl^{\cdot}$ and $CCl_3^{\cdot}$

Tedder and Walton[86] investigated the light-induced addition of bromotrichloromethane to ethylene, in the gas phase. They found that, when CCl_3Br is in excess, the combination of trichloromethyl radicals is the main termination step, whereas, with ethylene in large excess, the combination of the adduct radicals ($CCl_3CH_2CH_2^{\cdot}$) is the predominant chain termination process. Using literature data for the rate of $CCl_3^{\cdot}$ recombination, they calculated the rate of addition of the radicals to ethylene to be $4.2\times10^5 \exp(-3240/RT)$ $1.mol^{-1}.sec^{-1}$. Later, they determined Arrhenius parameters for the addition of $CCl_3^{\cdot}$ radicals to fluoroethylenes[24]. For the unsymmetric olefins, the parameters were determined for the addition to each end of the double bond. A reasonable correlation was obtained between the observed activation energies and the atom localization energies calculated from simple Hückel m.o. theory.

Addition reactions of several other polyhalomethyl radicals have been carried out. Kharasch, Kuderna and Urry[87] reported the addition, in solution, of dichloromethyl and bromodichloromethyl radicals to olefins. The addition, again, occurs at the least substituted end of the double bond.

Tarrant and Lovelace[88] observed the addition of dibromodifluoromethane to various methyl substituted ethylenes and the same group of workers studied the addition of dibromodifluoromethane to fluorinated olefins[89]. They observed that the addition to the fluoro-olefins was slower than to ethylene itself and that progressive substitution of hydrogen by fluorine in the olefin, gave increasing quantities of telomers. The addition was reported to occur at the least fluorinated end of the double bond only.

In 1961, however, Coscia[90] carried out the same reaction as Tarrant et al. and showed that the addition of $CF_2Br^{\cdot}$ radicals to trifluoroethylene produced two one to one adducts ($CF_2BrCHFCF_2Br$ and CF_2BrCF_2CHFBr) in a ratio very close to 1, at 120°C.

Tedder and his group have been very active in the field of the gas phase addition of halogenomethyl radicals to olefins. They studied the addition of dibromodifluoromethane to ethylene and trifluoroethylene[92] and noticed that $CF_2Br^{\cdot}$ radicals show the same trend as $CCl_3^{\cdot}$ radicals, but that they are more reactive and less selective than the latter. Ashton, Tedder and Walton[93] also studied the telomerization of tetrafluoroethylene, induced by trifluoromethyl or bromodifluoromethyl radicals. The transfer constant was determined for radicals containing various numbers of tetrafluoroethylene units and Arrhenius parameters were measured from temperature variation data. Tedder and Walton[94] investigated the kinetics of the addition of bromodifluoromethyl radicals to vinyl fluoride, 1,1-difluoroethylene and tetrafluoroethylene. The chains were shown to be terminated not only by dimerization of the halomethyl radicals, but also by cross-terminations involving $CF_2Br^{\cdot}$ and adduct radicals. An estimate of the absolute Arrhenius parameters for the addition of $CF_2Br^{\cdot}$ radicals to ethylene was also given.

Sloan, Tedder and Walton[95] photolysed tribromofluoromethane in the presence of a series of fluoro-olefins. Relative Arrhenius parameters were determined. The products included those from addition of $CFBr_2^{\cdot}$ radicals as well as cyclopropanes from addition of bromofluorocarbene. Again, this radical shows the same trend as trichloromethyl and bromodifluoromethyl radicals. The order of selectivity is

$$CCl_3^{\bullet} > CFBr_2^{\bullet} > CF_2Br^{\bullet}$$

Tedder and co-workers[96] investigated the photolysis of bromodichloromethane in the presence of ethylene and vinyl fluoride. The almost equal abstraction of bromine and hydrogen from the halogenomethane leads to a mixture of products coming from both of the chain carrying species. The radical that predominates in the addition reactions is shown to be the $CCl_2Br^{\bullet}$ radical.

Difluoroiodomethane has been photolysed in the presence of ethylene and fluoroethylenes[97]. Two radicals were found to add to the olefins : $CF_2H^{\bullet}$ and $CF_2I^{\bullet}$, arising from iodine or hydrogen abstraction respectively. The photolysis produces excited $CF_2H^{\bullet}$ radicals, which are very unselective. It was found that only at high temperatures are the chains sufficiently long for addition by thermal radicals to predominate.

The same authors[98] photolysed fluoroiodomethane in the presence of olefins and it was shown that the main product is the adduct from addition of $CHFI^{\bullet}$ to the alkenes. Arrhenius parameters were determined for the addition of fluoromethyl radicals and the results were compared with similar data for $CH_3^{\bullet}$, $CHF_2^{\bullet}$ and $CF_3^{\bullet}$.The activation energy difference shows a continuous decrease from $CF_3^{\bullet}$ to $CH_3^{\bullet}$.

Very few investigations of the free radical reactions of dihalogenomethanes have been reported. We, therefore, embarked on a study of the peroxide-initiated addition of chloroiodo- and diiodo-methane to a series of fluoroalkenes[99] (chapter 4 of this thesis) to determine if they also act as dual radical sources. A second objective was to obtain orientation ratios for the addition of $CH_2Cl^{\cdot}$ and $CH_2I^{\cdot}$ radicals to unsymmetrical olefins.

EXPERIMENTAL

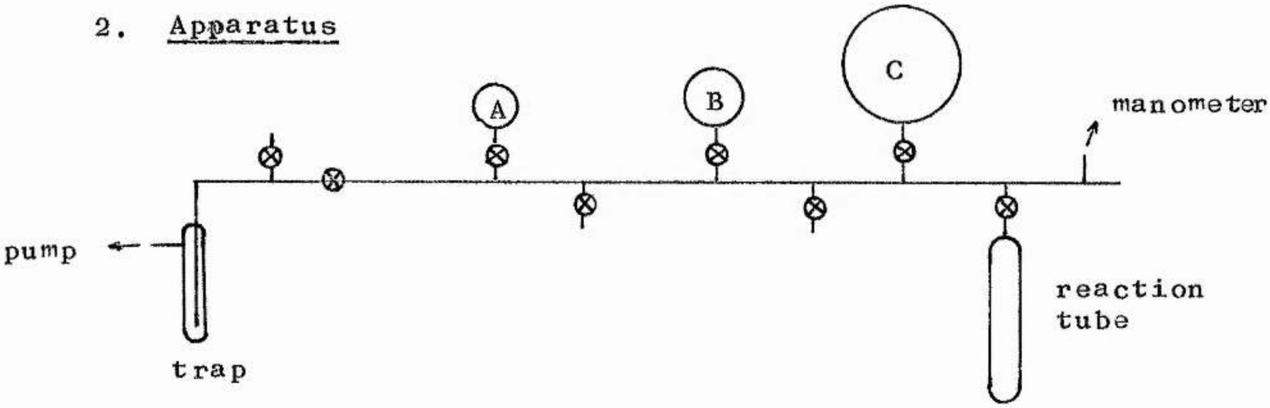
1. Material

Commercial diiodomethane (Hopkin & Williams) was redistilled before use (b.p. 63 °C/14 mm). The distillate was still slightly pink, but g.l.c. analysis showed no impurities.

Di-t-butyl peroxide was washed with ferrous sulphate, several times with water and distilled under reduced pressure (b.p. 38°C/14mm).

Commercial ethylene (B.O.C. medical anaesthetic grade), vinyl fluoride (Matheson), 1,1-difluoroethylene (Matheson), trifluoroethylene (Peninsular Chem. Research), tetrafluoroethylene (ICI) and hexafluoropropene (Bristol Organics) were dried and trap to trap distilled and degassed before use; g.l.c. showed no impurities.

2. Apparatus



All experiments were carried out in a thick walled sealed pyrex tube (c.a. 100 ml). The tube was attached to a conventional pyrex glass vacuum line. The vacuum was maintained at a pressure of 10^{-3} to 10^{-5} torr by means of an

Edwards silicone oil diffusion pump, backed by an NGN PSR1 rotary piston pump. The reactant pressures were measured using a mercury manometer and volumes were measured into storage bulbs on the line, namely bulbs A, B, and C of capacity 148.5 ml, 319.0 ml and 2,250 ml respectively.

3. Method

About 1 g of diiodomethane was weighed into the pyrex tube which was then connected to the vacuum line. The iodide was thoroughly degassed. Measured amounts of di-t-butylperoxide and of the appropriate alkene were distilled into the tube. It was sealed under vacuum and transferred to a furnace at $150 \pm 5^{\circ}C$, where the reaction took place for approximately 18 hours.

After reaction, the mixture was cooled in liquid nitrogen, the tube opened and the contents analysed directly.

4. Analysis

Methods of analysis were as in part 1, the only difference being that no squalene column was used.

5. Identification

The methods of product identification were as in part 1.

In one case, the products were separated by preparative g.l.c. on a Pye 105 instrument and ^{1}H nmr spectra were recorded on the products at room temperature using CCl_4 solutions in microcells containing traces of Me_4Si and CCl_3F as internal standards. A Varian HA-100 instrument was employed. In all experiments, acetone and methyl iodide were detected but they were not quantitatively analysed.

6. Experimental Details

A. Vinyl fluoride

In a first experiment, diiodomethane (3.56×10^{-3} moles) was reacted with vinyl fluoride (3.61×10^{-3} moles) in the presence of di-t-butyl peroxide (6.42×10^{-5} moles) for 18 hours. The g.l.c. trace of the reaction mixture showed two products; they were identified by mass spectrometry as the normal and reverse adducts of iodomethyl radicals to vinyl fluoride, namely the 1- and 2-fluoro-1,3-diiodopropane, respectively. Unfortunately, they could not be separated well enough, on a variety of columns (15% silicone oil on embacel, 15% tritolylphosphate on chromosorb G, 15% dinonylphtalate on embacel , squalene) and no orientation ratio was obtained.

In a second experiment, diiodomethane (4.18×10^{-3} moles) was reacted with vinyl fluoride (3.61×10^{-3} moles) and ethylene (5.12×10^{-4} moles), in the presence of di-t-butyl peroxide (6.42×10^{-5} moles). The g.l.c. trace of the mixture, after 19 hours reaction, showed the same two products as in the first experiment, together with a third one and a telomer. The third product was identified by mass spectrometry as the ethylene adduct, the 1,3-diiodopropane. The concentration of the telomer was too small for it to be identified, but it was assumed that it was a cross-telomer since none was detected when vinyl fluoride was reacted without ethylene. Peak areas were measured relative to the ethylene adduct, which was set equal to 100.

let a_1 = relative area of $CH_2I\text{-}CH_2\text{-}CH_2I$

a_2 = relative area of both isomers of the vinyl fluoride adduct ($C_3H_5FI_2$)

a_3 = relative area of the telomer $C_5H_9I_2F$

	a_1	a_2	a_3
	100	588.2	82.3
	100	606.1	78.8
	100	588.2	79.4
	100	606.1	75.8
mean	100	579.15	79.1

From there, we can calculate the relative reactivities:

$$\frac{k_2 + k'_2}{k_{2e}} = 0.793 \pm 0.012$$

where k_2 and k'_2 are the rate constants for the formation of the normal and reverse radical adducts of vinyl fluoride, respectively.

The mass spectra of the products are shown below:

A-1: $CH_2I\text{-}CH_2\text{-}CH_2I$

m/e	rel. Abundance	Assignment
296	17	$C_3H_6I_2^+$
254	6	I_2^+
169	56	$C_3H_6I^+$
155	5	$C_2H_4I^+$
141	17	CH_2I^+
128	14	HI^+
127	24	I^+

A-1 (cont)

m/e	rel. Abundance	Assignment
41	100	$C_3H_5^+$
40	24	$C_3H_4^+$
39	36	$C_3H_3^+$

A-2: $C_3H_5FI_2$ isomers

m/e	rel. Abundance	Assignment
314	14	$C_3H_5FI_2^+$
254	13	I_2^+
187	100	$C_3H_5FI^+$
159	9	$CHFI^+$
141	42	CH_2I^+
128	21	HI^+
127	39	I^+
60	21	$C_3H_5F^+$
59	90	$C_3H_4F^+$
58	3	$C_3H_3F^+$
57	10	$C_3H_2F^+$
46	3	$C_2H_3F^+$
45	3	$C_2H_2F^+$
41	8	$C_3H_5^+$
40	5	$C_3H_4^+$
39	22	$C_3H_3^+$
38	6	$C_3H_2^+$
33	29	CH_2F^+

B. 1,1-Difluoroethylene

Two experiments have been carried out in which diiodomethane (3.7×10^{-3} moles and 3.88×10^{-3} moles), 1,1-difluoroethylene (3.61×10^{-3} moles) and di-t-butyl peroxide (6.42×10^{-5} moles) were reacted together. After 18 hours reaction, two adducts were identified by mass spectrometry: $CH_2ICH_2CF_2I$ and $CH_2ICF_2CH_2I$. Peak areas were measured relative to the normal adduct, which was set equal to 100.

let a_1 = the relative area of the normal adduct

a_2 = the relative area of the reverse adduct.

The term "normal", refers to the product of addition to the least substituted end of an unsymmetric olefin and the term "reverse" refers to the product of addition to the most substituted end.

run 1

	a_1	a_2
	100	11
	100	10.5
	100	11
	100	10
mean	100	10.6

run 2

	a_1	a_2
	100	10
	100	10
	100	10.2
	100	10
mean	100	10.1

From these we were able to calculate the orientation ratio $\frac{k'_2}{k_2}$, where k'_2 and k_2 are the rate constants for addition to the most and least substituted ends of Difluoroethylene respectively.

Run	k_2'/k_2
1	0.106
2	0.101
mean	0.104

Another two experiments were carried out in which diiodomethane (3.99×10^{-3} moles and 3.58×10^{-3} moles), 1,1-difluoroethylene (3.61×10^{-3} moles) and ethylene (5.12×10^{-4} moles) were reacted in the presence of di-t-butyl peroxide (6.42×10^{-5} moles). After 18 hours reaction, the two difluoroethylene adducts, $CH_2ICH_2CF_2I$ and $CH_2ICF_2CH_2I$, were detected and identified by mass spectrometry, together with the ethylene adduct and two cross-telomers. As for the vinyl fluoride, the cross-telomers couldn't be identified. Peak areas were measured relative to the ethylene adduct, which was set equal to 100.

let a_1 = relative area of $CH_2I\text{-}CH_2\text{-}CF_2I$

a_2 = relative area of $CH_2I\text{-}CF_2\text{-}CH_2I$

a_3 = relative area of $CH_2I\text{-}CH_2\text{-}CH_2I$

a_4 = relative area of telomer A

a_5 = relative area of telomer B

Run 1

	a_1	a_2	a_3	a_4	a_5
	175.4	21.9	100	70.2	43.9
	192.3	24.0	100	67.3	57.7
	188.7	23.5	100	56.6	47.2
	192.3	23.1	100	76.9	57.7
mean	187.1	23.1	100	67.8	51.6

Run 2

	a_1	a_2	a_3	a_4	a_5
	166.7	21.7	100	50	33.3
	172.4	22.4	100	58.6	34.5
	169.5	20.3	100	59.3	50.8
	166.7	21.7	100	66.7	41.7
mean	168.8	21.5	100	58.7	40.1

We calculated the orientation ratio and the reactivities relative to ethylene

Run	k'_2/k_2	k_2/k_{2e}	k'_2/k_{2e}
1	0.123	0.468	0.058
2	0.127	0.422	0.054
mean	0.125	0.445	0.056

The mass spectra of the products are as shown below:

B-1:- $CH_2I-CH_2-CF_2I$

m/e	rel. Abundance	Assignment
332	4	$C_3H_4F_2I_2^+$
254	3	I_2^+
205	100	$C_3H_4F_2I^+$
177	5	CF_2I^+
158	4	CFI^+
155	5	$C_2H_4I^+$
141	77	CH_2I^+

B-1:(cont)

m/e	rel. Abundance	Assignment
128	31	HI^+
127	63	I^+
78	16	$C_3H_4F_2{}^+$
77	86	$C_3H_3F_2{}^+$
59	15	$C_3H_4F^+$
51	48	$CHF_2{}^+$

B-2:- $CH_2I\text{-}CF_2\text{-}CH_2I$

m/e	rel. Abundance	Assignment
332	30	$C_3H_4F_2I_2{}^+$
254	20	$I_2{}^+$
205	100	$C_3H_4F_2I^+$
155	20	$C_2H_4I^+$
141	90	CH_2I^+
128	30	HI^+
127	80	I^+
78	25	$C_3H_4F_2{}^+$
77	60	$C_3H_3F_2{}^+$
59	50	$C_3H_4F^+$
51	60	$CHF_2{}^+$

C. Trifluoroethylene

In the first two experiments, diiodomethane (3.98×10^{-3} moles) was reacted with trifluoroethylene (3.61×10^{-3} moles) in the presence of di-t-butyl peroxide (6.42×10^{-5} moles). The reaction took place for 18 hours. The g.l.c. trace of the mixture showed two addition products: $CH_2I-CHF-CF_2I$ and CH_2I-CF_2-CHFI. They were identified by mass spectrometry and ^1H nmr. The nmr spectrum of $CH_2ICH_aFCF_2I$ was very similar to that of $CH_2ClCHFCF_2I$; δ 2.5-3.1 (2H,m); δ3.7 (1H,m). $CH_2ICF_bF_cCHF_aI$ had a nmr spectrum very similar to that of CH_2ClCF_2CHFI; δ 3.95 (2H,t,J=13Hz), δ 7.15 (H,dt, $J_{HF_a}=46$, $J_{HF_b}=J_{HF_c}=8.5Hz$). Peak areas were measured relative to the normal adduct, which was set equal to 100.

let a_1 = the relative area of $CH_2I-CHF-CF_2I$

a_2 = the relative area of CH_2I-CF_2-CHFI

run 1

	a_1	a_2
	100	87
	100	91.5
	100	93.5
	100	94
mean	100	91.5

run 2

	a_1	a_2
	100	91.5
	100	92
	100	93
	100	93
mean	100	92.4

The orientation ratio was found to be:

run	k'_2/k_2
1	0.915
2	0.924
mean	0.920

In a third experiment, diiodomethane (3.99×10^{-3} moles) was reacted with trifluoroethylene (3.61×10^{-3} moles) and ethylene (5.12×10^{-4} moles) in the presence of di-t-butyl peroxide (6.42×10^{-5} moles). The two trifluoroethylene adducts and the ethylene adduct were detected by g.l.c. as well as two telomers (A and B). Again, the telomers could not be identified. Peak areas were measured relative to the ethylene adduct which was set equal to 100.

let a_1 = the relative area of $CH_2I\text{-}CHF\text{-}CF_2I$

a_2 = the relative area of $CH_2I\text{-}CF_2\text{-}CHFI$

a_3 = the relative area of $CH_2I\text{-}CH_2\text{-}CH_2I$

a_4 = the relative area of telomer A

a_5 = the relative area of telomer B

	a_1	a_2	a_3	a_4	a_5
	333.3	330	100	333.3	166.7
	294.1	288.2	100	-	-
	294.1	294.1	100	294.1	141.2
	294.1	300	100	300	141.2
mean	303.9	303.1	100	309.1	149.7

The orientation ratio and relative reactivities were calculated:

$\frac{k'_2}{k_2}$	k_2/k_{2e}	$\frac{k'_2}{k_{2e}}$
0.997	0.359	0.358

The mass spectra of the reaction products are as follows:

C-1:- $CH_2I-CHF-CF_2I$

m/e	rel. Abundance	Assignment
350	8.6	$C_3H_3F_3I_2{}^+$
254	7	$I_2{}^+$
223	100	$C_3H_3F_3I^+$
203	14	$C_3H_2F_2I^+$
177	14	CF_2I^+
159	20	$CHFI^+$
153	9	$C_2H_2I^+$
141	27	CH_2I^+
127	31	I^+
96	5	$C_3H_3F_3{}^+$
95	14	$C_3H_2F_3{}^+$
77	33	$C_3H_3F_2{}^+$
75	7	$C_3HF_2{}^+$
69	14	$CF_3{}^+$
51	23	$C_4F_2{}^+$
46	11	$C_2H_3F^+$
45	8	$C_2H_2F^+$

C-2:- CH_2I-CF_2-CHFI

m/e	rel. Abundance	Assignment
350	18	$C_3H_3F_3I_2{}^+$
254	10	$I_2{}^+$

C-2(cont)

m/e	rel. Abundance	Assignment
223	100	$C_3H_3F_3I^+$
203	6	$C_3H_2F_2I^+$
177	6	CF_2I^+
159	33	$CHFI^+$
153	12	$C_2H_2I^+$
141	16	CH_2I^+
127	35	I^+
95	14	$C_3H_2F_3^+$
77	37	$C_3H_3F_2^+$
75	10	$C_3HF_2^+$
69	37	CF_3^+
51	59	CHF_2^+

D. Tetrafluoroethylene

Two experiments were carried out in which diiodomethane (4.1×10^{-3} moles and 4.48×10^{-3} moles) and tetrafluoroethylene (3.61×10^{-3} moles) were reacted in the presence of di-t-butyl peroxide (6.42×10^{-5} moles).

In another experiment, diiodomethane (3.9×10^{-3} moles) was reacted with tetrafluoroethylene (3.61×10^{-3} moles) and ethylene (5.12×10^{-4} moles) in the presence of di-t-butyl peroxide (6.42×10^{-5} moles).

The 18 hour reactions, in the presence and absence of ethylene, resulted in a solid mass of polymer which was not further analysed.

B. Hexafluoropropene

In a first experiment, diiodomethane (4.66×10^{-3} moles), hexafluoropropene (3.61×10^{-3} moles) and di-t-butyl peroxide (6.42×10^{-5} moles) were reacted together for 18 hours. The g.l.c. analysis of the reaction mixture showed the two expected adducts together with two telomers. The adducts were identified by mass spectrometry; the telomers were not identified. Peak areas were measured relative to the normal adduct, which was set equal to 100.

let a_1 = the relative area of $CH_2I-CF_2-CF(CF_3)I$
a_2 = the relative area of $CH_2I-CF(CF_3)-CF_2I$
a_3 = the relative area of telomer A
a_4 = the relative area of telomer B

	a_1	a_2	a_3	a_4
	100	16	6	27
	100	16.5	5.5	26
	100	17	6.5	26
	100	16.5	7	26.5
mean	100	16.5	6.25	26.4

The orientation ratio was found to be

$$k'_2/k_2 = 0.165$$

In a second experiment, diiodomethane (3.92×10^{-3} moles), hexafluoropropene (3.61×10^{-3} moles), ethylene (5.12×10^{-4} moles) and di-t-butyl peroxide (6.42×10^{-5} moles) were reacted for 18 hours. A solid mass of polymers similar to that obtained in the case of tetrafluoroethylene was obtained and not further analysed.

The mass spectra of the two adducts are shown below:

B-1:- $CH_2I-CF_2-CF(CF_3)I$

m/e	rel. Abundance	Assignment
418	3	$C_4H_2F_6I_2^+$
291	9	$C_4H_2F_6I^+$
254	4	I_2^+
177	4	CF_2I^+
145.5=291/2	8	$C_4H_2F_6I^{++}$
141	15	CH_2I^+
128	49	HI^+
127	35	I^+
95	7	$C_3H_2F_3^+$
69	10	CF_3^+
64	36	$C_2H_2F_2^+$
57	14	$C_3H_2F^+$
55	16	C_3F^+

B-2:- $CH_2I-CF(CF_3)-CF_2I$

m/e	rel. Abundance	Assignment
418	20	$C_4H_2F_6I_2^+$
291	68.5	$C_4H_2F_6I^+$
254	18.5	I_2^+
227	4.3	$C_2F_4I^+$
191	17.1	$C_2H_2F_2I^+$

B-2(cont)

m/e	rel. Abundance	Assignment
177	7.1	CF_2I^+
145.5=291/2	30	$C_4H_2F_6I^{++}$
141	37	CH_2I^+
128	58	HI^+
127	63	I^+
100	10	$C_2F_4{}^+$
95	67	$C_3H_2F_3{}^+$
69	46	$CF_3{}^+$
64	41	$C_2H_2F_2{}^+$
57	14	$C_3H_2F^+$
55	17	C_3F^+

Discussion.

The thermolysis of t-butyl peroxide at 150°C produces methyl radicals and acetone :

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{\Delta T} 2\ (CH_3)_3CO^{\cdot}$$
$$(CH_3)_3CO^{\cdot} \longrightarrow CH_3COCH_3 + CH_3^{\cdot}$$

The methyl radicals initiate the addition of iodomethyl radicals to a fluoro-olefin (B) by abstracting iodine from diiodomethane

$$CH_3^{\cdot} + CH_2I_2 \longrightarrow ICH_2^{\cdot} + CH_3I \qquad (1)$$
$$ICH_2^{\cdot} + B \longrightarrow ICH_2B^{\cdot} \qquad (2)$$
$$ICH_2^{\cdot} + B \longrightarrow ICH_2B'^{\cdot} \qquad (2')$$
$$ICH_2B^{\cdot} + CH_2I_2 \longrightarrow ICH_2BI + ICH_2^{\cdot} \qquad (3)$$
$$ICH_2B'^{\cdot} + CH_2I_2 \longrightarrow ICH_2B'I + ICH_2^{\cdot} \qquad (3')$$

where ICH_2BI and $ICH_2B'I$ are the normal and reverse adducts respectively and $ICH_2B^{\cdot}$ and $ICH_2B'^{\cdot}$ the corresponding adduct radicals.

Unlike difluoroiodomethane[97] and fluoroiodomethane[98], both of which act as dual radical sources, the only chain-carrying species, in the case of CH_2I_2, is the iodomethyl radical. Hydrogen abstraction is not competitive with iodine abstraction under the conditions of the present experiments. Acetone and methyl iodide were detected, but not quantitatively analysed. The principal termination process involves combination of the iodomethyl radicals :

$$ICH_2^{\cdot} + ICH_2^{\cdot} \longrightarrow ICH_2CH_2I \qquad (4)$$

The main products of the reaction were the one to one adducts, except in the reactions with tetrafluoroethylene, which showed extensive polymerization. In the runs with ethylene (used as a standard), the amount of telomer formation increases. It was not possible to identify all the telomers and especially to decide whether they were derived from the normal or from the reverse adduct radical. Therefore, the orientation ratios determined in the presence of ethylene cannot be accurate and only the values obtained in runs without the reference olefin will be considered in the discussion.

Table 4-1 : Relative concentrations of products from reactions of CH_2I_2 with fluoroalkenes at 150°C.

Olefin	no ethylene present		
	ICH_2BI	$ICH_2B'I$	Telomers
CH_2CHF	---	---	---
CH_2CF_2	100	10.4	---
$CHFCF_2$	100	92.0	---
CF_2CF_2			a
CF_3CFCF_2	100	16.5	32.7

Table 4-1 (continue)

Olefin	competition with ethylene			
	$I(CH_2)_3I$	ICH_2EI	$ICH_2E'I$	Telomers
CH_2CHF	100	559.6		67.5
CH_2CF_2	100	156.9	19.7	109.1 [b]
$CHFCF_2$	100	252.9	252.3	458.8 [b]
CF_2CF_2				[a]
CF_3CFCF_2				[a]

[a] main product polymer

[b] relative areas

The orientation ratios were calculated as shown in chapter 2. They are compared with other orientation ratios obtained for some related radicals. Table 4-2 shows the uniform decrease of the orientation ratios along the series $CH_2F^{\cdot}$, $CH_2Cl^{\cdot}$, $CH_2I^{\cdot}$. Chloromethyl and fluoromethyl radicals add preferentially to the more substituted end of trifluoroethylene, but iodomethyl radicals show the more usual orientation. It is also clear, from table 4-2, that trichloromethyl is much more selective than the other three.

The orientation ratios for the iodomethyl radicals conform to the correlation, described in chapter 2, between log Or and the diameter (d_c) of the attacking radical, as shown in figure 2-5. This shows the influence of steric factors on the addition reaction.

Table 4-2 : Orientation of the addition of halogenomethyl radicals to fluoroalkenes at 150°C.

Radical	Or (150°C)				Reference
	CH_2CHF	CH_2CF_2	$CHFCF_2$	CF_3CFCF_2	
$CH_2F^{\cdot}$	0.29	0.45	2.04	---	98
$CH_2Cl^{\cdot}$	0.18	0.14	1.03	0.19	99
$CH_2I^{\cdot}$	---	0.10	0.92	0.17	This work
$CCl_3^{\cdot}$	0.07	0.012	0.29	0.02*	24

* Upper limit

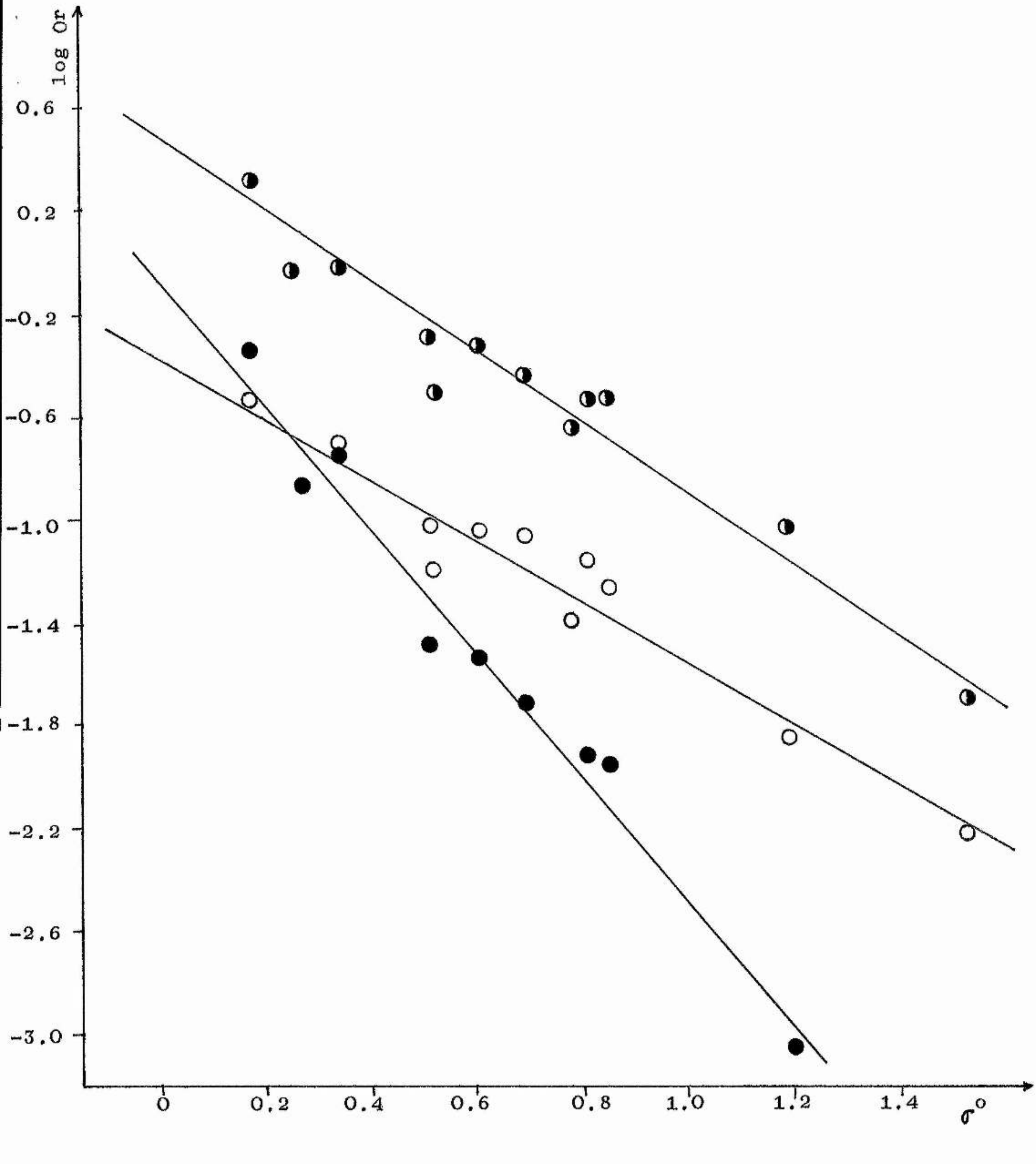
Good correlations (figure 4-1) were observed between the logarithm of the orientation ratios and Taft σ^{o} values for the radicals listed in table 4-4. The σ^{o} constant of a radical is defined as the algebraic sum of the substituent constants of the groups attached to the radical centre. The orientation ratios used in figure 4-1 are listed in table 2-10.

The good correlations encouraged us to apply to the results the "patterns of reactivity" approach, developed by Bamford and Jenkins[106] for interpreting polymer radical reactivities. According to this approach, the velocity constant (k_s) for a radical reaction is given by

$$\log k_s = \log k_{3,T} + \alpha\sigma + \beta$$

where $k_{3,T}$ is the rate constant for the abstraction reaction of the radical with toluene, σ is the substituent constant of the radical and α and β are constants for a given olefin.

Figure 4-1 : Correlation between Taft σ^{o} constants and log Or (150^{o}C) for the addition of a series of halogenoalkyl radicals to $CH_2=CHF$ ○, $CH_2=CF_2$ ● and $CHF=CF_2$ ◑.



A simple extention of this equation gives an expression for the orientation ratio of the addition of a radical to an unsymmetrical alkene . The rate constant for the addition to one end will be

$$\log k_2 = \log k_{3,T} + \alpha\sigma + \beta$$

and that for the addition to the other end will be

$$\log k_2' = \log k_{3,T} + \alpha'\sigma + \beta'$$

where α, β, α' and β' now characterize the respective ends of an alkene. Hence

$$\log \mathrm{Or} = \log (k_2'/k_2) = \sigma(\alpha'-\alpha) + (\beta'-\beta)$$

The values of $(\alpha'-\alpha)$ and $(\beta'-\beta)$ can be determined for vinyl fluoride, 1,1-difluoroethylene and trifluoroethylene from the gradients and intercepts of the graphs shown in figure 4-1. Bamford and Jenkins have shown that the α value of an olefin is related to its polarity by the approximate empirical equation

$$\alpha = -5.3\,\sigma$$

where σ here refers to the substituent constant of the adduct radical formed from the olefin. The α values calculated this way are in reasonable agreement with the experimental values (table 4-3), although the experimental ones are consistently higher.

Figure 4-2 : Correlation between $\sigma^{o}(\alpha'-\alpha)+(\beta'-\beta)$ and log Or for the addition of a series of halogenoalkyl radicals to CH_2CHF ○, CH_2CF_2 ● and $CHFCF_2$ ◑.

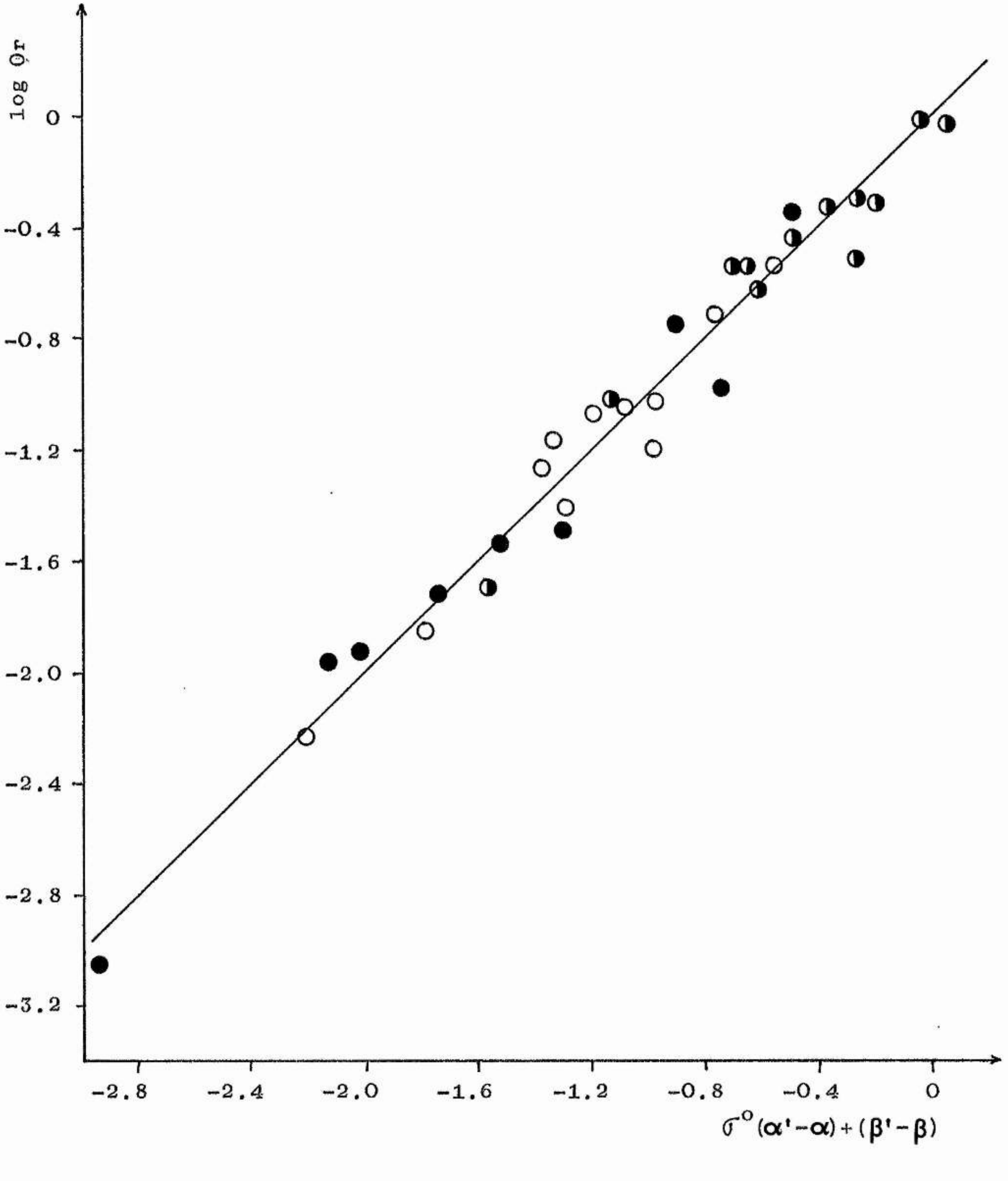


Table 4-3 : Comparison of experimental and calculated olefin reactivity constants.

Olefin	$(\beta'-\beta)_{expt}$	$(\alpha'-\alpha)_{expt}$	$(\alpha'-\alpha)_{calc}$
$CH_2=CHF$	-0.35	-1.21	-0.90
$CH_2=CF_2$	-0.08	-2.40	-1.80
$CHF=CF_2$	+0.41	-1.29	-0.90

Figure 4-2 shows a plot of log Or against $\sigma^{o}(\alpha'-\alpha) + (\beta'-\beta)$. In fact, it is a correlation between log Or and σ^{o} ; the $(\alpha'-\alpha)$ and $(\beta'-\beta)$ values only serve to bring the results from the three fluoro-olefins into one single straight line of slope 1.0 and correlation coefficient of 0.985. Table 4-4 gives the values of σ^{o} and $\sigma^{o}(\alpha'-\alpha)+(\beta'-\beta)$ for a series of halogenomethyl radicals, which were used in figure 4-2.

The succes of this modified "patterns of reactivity" treatment shows that the orientation of free-radical addition is governed by familiar polar forces . The correlation also indicates that both the polarity of the olefin and the polar character of the radical are important.

An attempt was made to determine relative rates of addition of iodomethyl radicals to fluoro-olefins by adding ethylene as a standard, but telomerization was increased to such an extent, that those results are worthless for kinetic purposes.

Table 4-4 : Data used in figure 4-2.

Radical	σ^{o}	$\sigma^{o}(\alpha'-\alpha)+(\beta'-\beta)$		
		$CH_2{=}CHF$	$CH_2{=}CF_2$	$CHF{=}CF_2$
$CH_2I^{\cdot}$	0.27	---	-0.73	0.06
$CH_2F^{\cdot}$	0.17	-0.56	-0.49	0.19
$CHF_2^{\cdot}$	0.34	-0.76	-0.90	-0.03
$CF_3^{\cdot}$	0.51	-0.97	-1.30	-0.25
$CF_2Br^{\cdot}$	0.60	-1.08	-1.52	-0.36
$CF_3CF_2^{\cdot}$	0.85	-1.38	-2.12	-0.69
$CCl_3^{\cdot}$	0.81	-1.33	-2.02	-0.64
$CFBr_2^{\cdot}$	0.69	-1.19	-1.74	-0.48
$CHBr_2^{\cdot}$	0.52	-0.98	---	-0.26
$CBr_3^{\cdot}$	0.78	-1.29	---	-0.60
$(CF_3)_2CF^{\cdot}$	1.19	-1.79	-2.94	-1.13
$(CF_3)_3C^{\cdot}$	1.53	-2.20	---	-1.56

Conclusion

Although the orientation ratios given in chapters 1, 2 and 4 of this thesis might be interpreted by the Walling and Mayo hypothesis, the kinetics of the addition reactions are in direct contradiction with their theory in its simplest form: the substituents on the carbon where the new bond is formed have a much greater influence on the rate of addition than the substituents on the carbon carrying the unpaired electron in the adduct radical.

A comparison between the orientation ratios, for the addition to vinyl fluoride, 1,1-difluoroethylene and trifluoroethylene, of some straight chain radicals ($CF_3^{\cdot}$, $C_2F_5^{\cdot}$, n-$C_3F_7^{\cdot}$, n-$C_4F_9^{\cdot}$, n-$C_7F_{15}^{\cdot}$, n-$C_8F_{17}^{\cdot}$) and of some branched chain radicals ($CF_3^{\cdot}$, $CF_3CF_2^{\cdot}$, $(CF_3)_2CF^{\cdot}$ $(CF_3)_3C^{\cdot}$), shows the importance of the size and shape of the attacking radicals.

The kinetic data, compiled in table 2-6, follow the same pattern for the four radicals of the branched chain series. However, the selectivity of the addition reaction increases noticeably from $CF_3^{\cdot}$ to $(CF_3)_3C^{\cdot}$. This increase in selectivity appears to be mainly due to the activation energy term. The maximum variation in the ratios of the A factors is only just over one order of magnitude, compared with three orders of magnitude for the relative rate constants.

A good correlation was found between the logarithm of the orientation ratio and Taft σ^* constants. The orientation ratios also correlate with the diameter (d_c) of the radicals. This suggests that both steric and polar factors work hand in hand in these addition reactions.

The success of the modified "patterns of reactivity" approach, for a series of radicals including $(CF_3)_2CF^\cdot$, $(CF_3)_3C^\cdot$ and $CH_2I^\cdot$, shows the importance of the polar characters of both the radical and the olefin.

The absolute rate constant was determined for the recombination of perfluoroisopropyl radicals at 46°C. The low value of $k_{4(46^o)}$ (1.46×10^5 l. mol^{-1} sec^{-1}) suggests that, unlike simple hydrocarbon radicals, the activation energy is different from zero. This hypothesis is supported by the results obtained in the thermal reaction between CF_3I and $(CF_3)_3CFI$. It can be estimated that the activation energy for the combination reaction is of the order of 5.6 Kcal/mol.

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