AN EXPERIMENTAL AND THEORETICAL STUDY OF FREE RADICAL ADDITION TO FLUORO ETHYLENES

Keith D. R. Winton

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews

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A

Thesis

Presented for

the Degree of

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University of St. Andrews

St. Andrews

March 1973

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.

Keith D.R. Winton

CERTIFICATE

I certify that Keith David Roy Winton, B.Sc., has spent ten 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 Ph.D.

Professor Lord Tedder

ACKNOWLEDGEMENTS

I wish to express my deep gratitude to Professor Lord Tedder for his continual encouragement and advice. I also thank him and Professor P.A.H. Wyatt for facilities provided during the period of this research. I must thank my colleagues in the laboratory, especially Dr. D.S. Ashton, for many helpful discussions and pieces of advice at various times during my research, a note of thanks should also go to Dr. J.C. Walton.

My appreciation of and my thanks to the staff and services of the Computing Laboratory must not go unrecorded. Especially, I must thank the operators who, but for me, might frequently have been able to go home to bed much earlier.

I thank the British Petroleum Company Limited for financial support in the form of a Research Studentship.

Lastly, but by no means least, Eleanor, my wife, must be thanked not only for her typing of this thesis, but also for her forbearance during the past two years.

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INTRODUCTION

INTRODUCTION

Bond fission in organic chemistry may proceed in two different ways, a) heterolytically and b) homolytically. In the first of these, the electrons in the bond are redistributed so that one of the fragments has an overall positive charge, and the other an overall negative charge. In the second case, the electrons are redistributed so that neither fragment is charged but both take on one electron. Normally, this process yields two fragments each with a singly occupied orbital (although in some molecules, different fragments are observed, cf diazomethane). That is, free radicals are formed. These fragments are extremely reactive, seldom existing for very long, and have unique chemical and physical properties not associated with other organic moieties.

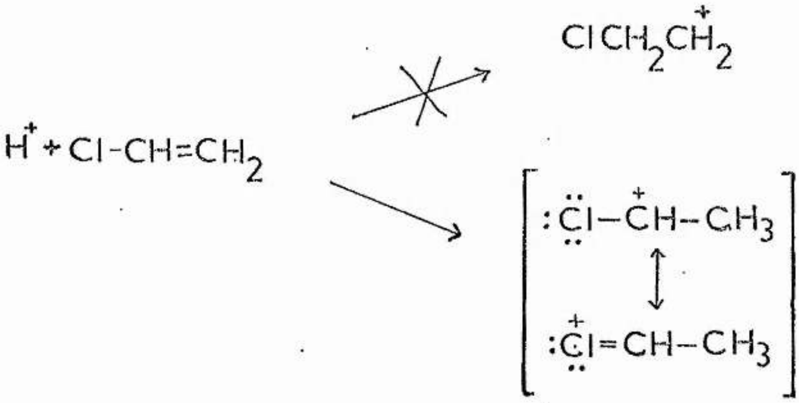
The first discovery of a free radical was made by Gomberg in 1900.[1] His report of triphenylmethyl was met with much disbelief but his conclusions were well supported experimentally. He had in fact come across one of the class of radicals with a long lifetime. In some cases, the lifetime is long enough that the radicals are capable of stable existence. The existence of the "short-life" radicals was not shown for some time.

In 1929, Paneth and Hofeditz[2] demonstrated the existence of free methyl radicals. By heating a film of tetramethyl lead and flushing the radicals on to a mirror of lead deposited on the glass tubing surface, they showed the lifetime to be of the order of 10^{-3} seconds.

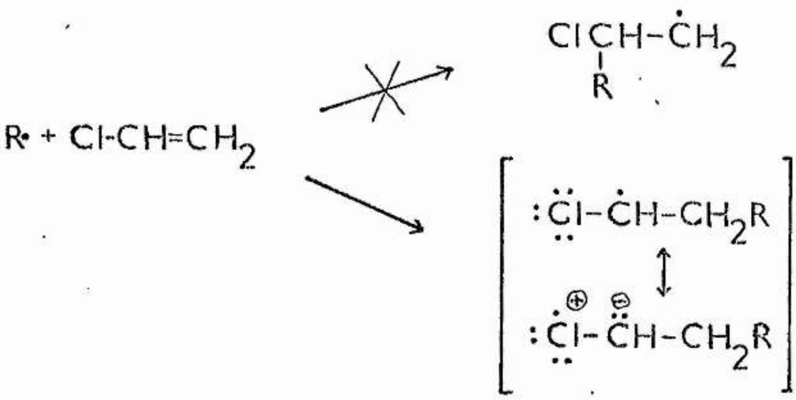
The reactions of free radicals can be broadly put into two categories, a) those which are radical propogating and b) those which are radical destroying. In the latter category, we find such reactions as combination and disproportionation. The former includes abstraction, addition and rearrangement. Not all of these reactions have received equal attention. The most well studied reactions are abstraction and addition.

Addition by a free radical mechanism to unsaturated centres was first qualititatively studied in the addition of hydrogen bromide to allyl bromide[3]. But it was not until 1937 that a theoretical explanation was put forward independently by Hey and Waters[4] and by Kharasch, Engelman and Mayo.[5] Both sets of workers postulated that the so-called "anti-Markownikow" addition was due to a self-propogating reaction involving atomic bromine.

The number of additions studied grew very quickly and theories for the orientation of addition were advanced. These have been summarised by Cadogan and Hey.[6] The most popular theory was that of Mayo and Walling[7] who proposed that the orientation of radical addition to an unsymmetric olefin was determined by the relative stabilities of the two possible addend radicals. The relative stabilities could be deduced by analogy with the addends formed in heterolytic addition. A proton adds to vinyl chloride at the unsubstituted carbon because this leads to a resonance stabilised carbonium ion:-



In the same way, it was assumed that a radical would add to the unsubstituted carbon because of the possible stabilisation of the addend radical:-



The stabilisation of the radical could be due either to a mesomeric or an inductive effect. Thus, hydrogen chloride was found to add ionically to give the "Markownikow" product while, in the presence of U.V. light or peroxides, hydrogen bromide added to give the "anti-Markownikow" product:-

$$ClCH{=}CH_2 \xrightarrow{H^+} Cl\overset{+}{C}H{-}CH_3 \xrightarrow{Cl^-} CHCl_2{-}CH_3$$

$$ClCH{=}CH_2 \xrightarrow{Br\cdot} Cl\dot{C}H{-}CH_2Br \xrightarrow{HBr} CH_2Cl{-}CH_2Br + Br\cdot$$

This was the Mayo-Walling theory in its simplest form.

The theory has also been considered as applying to the thermodynamic stabilities of the addend radicals. That is, the possible electron delocalisation at the site of the odd electron is not the criterion of position of addition but the stability of the radical as a whole in each case is. The reaction which is more exothermic is faster, thus determining the direction of addition.

The theory in its simplest form remained in vogue until work on the addition of trichloromethyl radicals to fluoro-ethylenes[8] brought it into question. The mechanism of the light-induced addition of bromotrichloromethane to ethylene had earlier been established[9] and the same mechanism was assumed to be true for the fluoro-ethylenes. This was the first attempt at measuring the Arrhenius parameters for addition at the two different ends of an unsymmetrical olefin, in an attempt to introduce a quantitative aspect into the theories of addition. Up until this time, the formulation of a truly predictive theory was hampered by two main factors: a) that although much early work had been done, it was of a qualitative or at best a semi-quantitative nature, emphasis being placed on the identity of the adducts and b) that in subsequent quantitative kinetic work, only overall addition rate parameters were determined.

The kinetics of the addition process have been studied both in solution and in the gas phase. In solution, valid information can be obtained about the orientation ratios and in many cases the rates measured competitively with abstraction from the solvent itself. This has been the approach of Szwarc and his co-workers in their extensive studies on methyl radical addition. In the gas phase, however, intermolecular forces are relatively small and, in particular, solvation effects do not exist. Thus the experimentally derived properties are closer to those of isolated molecules or groups of isolated molecules. Many of the modern theories of kinetics are based on the behaviour of these small isolated groups and so experiments carried out in the gas phase constitute a good test-bed for those theories.

Necessarily, for experimental reasons, gas phase experiments are carried out on smaller molecules and groups.

However, in the case of the smaller molecules and radicals, the partition functions are more easily calculated, there being fewer degrees of freedom with which to contend. The possible calculation of associated properties such as the Arrhenius pre-exponential factor is greatly facilitated.

Although many theories of the addition reaction have been proposed, no truly predictive qualitative theory is available. Obviously, then, we must treat with reserve the quantitative theories which have been proposed. The purpose of this thesis is to provide more kinetic data for the addition of free radicals to the opposite ends of unsymmetrical olefins in order that theories may have a broader experimental basis. In particular, the nature of the attacking radical has been altered, keeping the olefins fixed, from the electrophilic radical $C_3F_7^{\cdot}$, through alkyl radicals to the nucleophilic radical $Me_3Ge^{\cdot}$. This may provide a possible insight to any polar effects associated with free radicals. Some theoretical calculations using the INDO method have also been attempted.

PART I

The Addition of n-Heptafluoropropyl Radicals to Fluoro-ethylenes

PART I

INTRODUCTION

Fluoroalkyl, and in particular perfluoroalkyl, compounds have been found to have very important properties from the standpoint of surface chemistry.[10] Perfluoroalkane sulphonic acids and perfluoroalkane carboxylic acids and their respective derivatives show excellent surface activities, while polymers with perfluoroalkyl groups in their side chains have good water and oil repellencies. These compounds are synthesized from the corresponding fluoroalkyl iodides. These in turn can be efficiently prepared by addition of lower fluoroalkyl iodides to fluoro-ethylenes and subsequent telomerisation of the addend radicals to the extent required for optimisation of the telomer of interest. Thus the kinetics of addition of the perfluoroalkyl iodides to fluoro-ethylenes is of considerable commercial importance.

In the fluoroalkyl radical series, most attention has been devoted to the reactions of trifluoromethyl. Several sources of $CF_3^{\cdot}$ radicals have been used. The photochemical dissociation of trifluoromethyl iodide is the most common source, but the photolysis of trifluoroacetaldehyde[11], trifluoroacetone[12], hexafluoroacetone[13] and hexafluoro-azomethane[14] have also been used. The last two named have the added attraction that the amount of carbon monoxide or nitrogen produced can help determine the quantum yield.

A great deal of work has been done by Haszeldine and co-workers on the addition reactions of trifluoromethyl radicals[15], however, this is largely of a qualitative nature. The only quantitative data we can obtain are on isomer ratios for the products. Quantitative studies of the addition of trifluoromethyl radical have been reported[16] but there are few data available for addition at one end of an olefinic bond[17].

The reaction of pentafluoroethyl and n-heptafluoropropyl radicals are less well documented. The reactions of n-heptafluoropropyl with other molecules have only been studied quantitatively in reactions involving hydrogen abstraction from cyclohexane[18], methane and ethane[19] and hydrogen and deuterium[20], although its combination with other radicals has received attention[21]. The addition reactions have attracted little attention, and that only qualitative. Brace has studied the addition to bicyclic olefins[22] and to 1,6-heptadiene[23] and Burton and Kehoe[24] have studied the cuprous chloride-ethanolamine catalysed addition reaction, though in neither case kinetically. The nearest approach to quantitative studies have been researches into the use of n-heptafluoropropyl iodide and i-heptafluoropropyl iodide as telogens by Chambers et al[25] and by Ono and Ukihashi[26]. But the kinetics of the processes are not given consideration.

Perfluoropropyl radicals have been produced from several sources. These are, in general, analogous to the methods for producing alkyl radicals. The sources include

C_3F_7COEt,[12d] $(C_3F_7)_2CO$[12a,10,11a,9] and C_3F_7CHO[12b,11b]. In this kinetic study of the addition to fluoro-olefins, the source of perfluoropropyl radicals is photolysis of n-heptafluoropropyl iodide.

PART I

EXPERIMENTAL

1. Materials

The heptafluoropropyl iodide (Koch-Light), trifluoroethylene (Peninsular Chemresearch), 1,1-difluoroethylene (Matheson), vinyl fluoride (Matheson), ethylene (B.O.C. medical anaesthetic grade) and tetrafluoroethylene (I.C.I.) were all purified by trap to trap distillation, a middle fraction being taken in each case. The gases were stored on the line in bulbs constructed with a side-arm which could be surrounded by liquid nitrogen to freeze out the gas from the bulb. The n-heptafluoropropyl iodide was stored in a tube on the line at liquid nitrogen temperature. Each of the reactants showed only one peak on g.l.c. analysis. The reactants were thoroughly degassed before use.

2. Apparatus

The experiments were carried out using a conventional vacuum line (figure I-1) made of "Pyrex" glass. The vacuum was maintained using an Edwards "Speedivac" silicone oil diffusion pump backed by an Edwards "Spedivac" two stage rotary pump, model 2SC20A. Reactant pressures were measured, initially, using a mercury manometer, but this was later substituted by an Edwards capsule gauge type CG3. The reactant volumes were measured into bulbs I and II with volumes

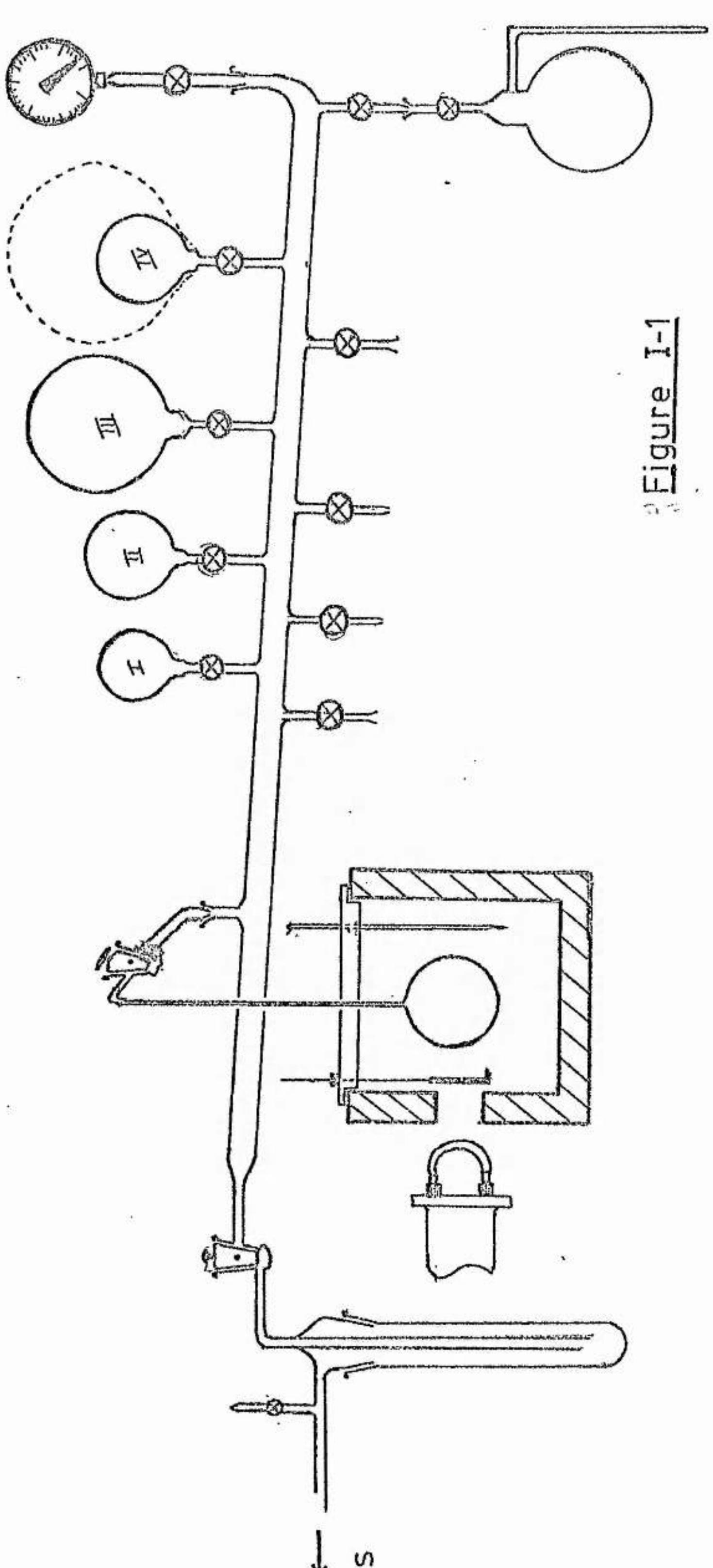


Figure I-1

229.5 ml and 529.5 ml respectively. In some of the preparative experiments, bulb III (volume = 2.621 l) was used. Bulb IV (volume about 5 l) was not used at all and was substituted by a bulb of volume 526 ml and then used in later competitive experiments. All volumes were measured by weight of water.

The reaction vessel was spherical (286 ml) and made of "Pyrex" glass, this serving as a filter for light with wavelength less than 2800 Å. The vessel was connected to the main manifold via 2 mm capillary tubing, in order that reaction occurring outside the furnace be minimised.

The furnace consisted of an electrically heated hot-plate inside a well insulated aluminium cylinder. The temperature, measured with a mercury-in-glass thermometer, was uniform throughout the furnace and could be maintained to ±2°C using a 0-250 volt "variac" transformer. A circular hole in one side of the furnace allowed the passage of light into the reaction vessel. This hole had a removable shutter. The light source was a "Hanovia" UVS 220 medium pressure mercury arc. Care was taken to ensure that, through any series of reactions, the lamp was always at the same distance from the reaction vessel.

3. Procedure

The line was allowed to pump for at least one hour, and generally longer, with liquid nitrogen round the trap. The n-heptafluoropropyl iodide was degassed and allowed to expand into the line and into bulb II. When a suitable pressure was registered on the pressure-measuring device, the bulb was isolated and the n-heptafluoropropyl iodide condensed back into the storage tube by cooling with liquid nitrogen. The line was again pumped for a short time. The process was repeated with the olefin, expanding it into bulb I. After the line had again been evacuated, the reaction vessel was surrounded by liquid nitrogen and the reactants allowed to distil into the vessel. Not less than half an hour was allowed for this distillation, and in any case until there was no discharge when the line was tested with a high frequency tester.

After distillation, the reaction vessel was closed off, the liquid nitrogen removed, the vessel allowed to come to room temperature and dried of any condensed water vapour. It was then surrounded by the furnace and the temperature allowed to equilibrate. The lamp was switched on to warm up for ten minutes. During this time, final adjustments were made to the voltage supply to the furnace and then the shutter opened.

After the photolysis, the lamp was switched off and the reaction mixture distilled into an evacuated tube attached to the main manifold. Distillation was again for not less than half an hour, and until there was no discharge with the tester. The tube was then removed from the line, stoppered and stored under liquid nitrogen. Samples were taken from this tube for gas chromatographic analysis of the products.

4. Analysis

Analyses were carried out on a "Griffin and George" D6 gas chromatograph. In this instrument, an oven, the columns, the detector and carrier gas control network are housed in one unit and an amplifier and recorder are housed in another. The column used was 6ft x ¼in stainless steel tubing, made in two straight parallel 3ft tubes connected by a capillary U-tube, packed with 10% silicone oil on 60-100 mesh 'Embacel'. Injections were made on to the column using a 4 µl stainless steel capillary needle. Just at the top of the filling level of the needle, is a small hole. When the needle is introduced through the serum cap at the top of the column, the nitrogen flow blowing into this hole forces the sample on to the column.

The detector in this instrument is a gas density balance and the chromatograms were recorded on a "Honeywell-

Brown" 1 mv recorder. When a weight of sample, q, passes through this detector in a stream of carrier gas of molecular weight, m, then if M is the molecular weight of the sample and A is the area under the peak then the relationship

$$q \doteq kAM/(M-m)$$

(where k is a constant characteristic of the detector) holds. Thus the concentration of the sample is given by

$$q/M \doteq kA/(M-m)$$

and relative concentrations of components in a mixture are readily found from the respective areas under the peaks on the chromatogram.

The areas were measured using a "Honeywell" Precision Integrator or a "Dupont" 310 Curve Resolver. In mixtures in which a component concentration was very small, better accuracy in the areas of its chromatographic peak could be obtained using a fixed arm planimeter.

Usually about four or five analyses were made of a reaction mixture and an average concentration for each component obtained.

5. Identification of Products

Since trichloromethyl and heptafluoropropyl radicals could both reasonably be assumed to be electrophilic in nature, it was presumed that the orders of the relative concentrations of the two adducts might be similar. On this basis the peaks on the chromatograms could be fairly sensibly assigned. There appeared, in the case of an unsymmetrical fluoro-ethylene, only two peaks other than the two starting materials. (The fluoro-ethylenes were known not to decompose under the conditions of reactions.) The identifications were confirmed by mass spectrometry.

Mass spectra were obtained on an A.E.I. MS 12 mass spectrometer. The inlet was from a Perkin-Elmer F11 gas chromatograph using a silicon oil capillary column with helium as carrier gas, and via a Biemann separator. The spectra were recorded when the monitor reached its maximum. The spectra of the predominantly formed adducts from the unsymmetrical fluoro-ethylenes are shown in table I-1.

6. Details of Reactions

The results of the kinetic reactions are shown in tables I-2 to I-8.

Table I-1 Mass Spectra of the Predominantly Formed Adducts of the Unsymmetrical Fluoro-Ethylenes.

$C_3F_7CHFCF_2I$			$C_3F_7CH_2CF_2I$		
m/e	%	assignment	m/e	%	assignment
51	35.1	CHF_2^+	51	2.2	CHF_2^+
69	52.0	CF_3^+	64	4.0	$CH_2CF_2^+$
82	3.5	$C_2HF_3^+$	69	70.7	CF_3^+
101	2.1	$C_2HF_4^+$	94	8.4	$C_3H_2F_3^+$
113	9.5	$C_3HF_4^+$	113	4.0	$C_3HF_4^+$
119	13.4	$C_2F_5^+$	119	8.4	$C_2F_5^+$
127	4.8	I^+	127	3.5	I^+
131	2.2	$C_3F_5^+$	131	0.5	$C_3F_5^+$
151	1.3	$C_3F_6H^+$	169	10.2	$C_3F_7^+$
164	12.6	$C_4F_6H^+$	177	5.8	CF_2I^+
169	6.1	$C_3F_7^+$	181	0.4	$C_4F_7^+$
177	5.6	CF_2I^+	183	0.4	$C_3F_7CH_2^+$
182	0.9	$C_3F_7CH^+$	233	100.0	$M^+ - I$
251	100.0	$M^+ - I$	359	0.6	$M^+ - H$
378	25.5	M^+	360	0.4	M^+

Table I-1 (continued)

$C_3F_7CH_2CHFI$	m/e	%	assignment
	51	1.1	CHF_2^+
	64	2.0	$C_2F_2H^+$
	69	100.0	CF_3^+
	70	.5	CF_3H^+
	95	4.1	$C_3H_2F_3^+$
	113	2.0	$C_3HF_4^+$
	114	.4	$C_3H_2F_4^+$
	115	.4	$C_3H_3F_4^+$
	127	1.7	I^+
	145	5.3	$C_4F_5H_2^+$
	146	1.0	$C_4F_5H_3^+$
	159	.2	$CHFI^+$
	169	5.6	$C_3F_7^+$
	181	.5	$C_4F_7^+$
	183	.4	$C_4F_7H_2^+$
	195	.8	$C_5F_7H_2^+$
	215	80.9	$M^+ - I$
	342	.2	M^+

Table I-2 Variation of remperature on Addition to $CF_2:CFH$

Temp (^oC)	No of Runs	$[C_3F_7CFH\text{-}CF_2I] / [C_3F_7CF_2\text{-}CFHI]$	
154±2	6	3.95;4.33;3.86;4.07;4.01;4.01	ave = 4.04
120±2	3	4.50;4.26;5.20	ave = 4.65
102±2	6	4.31;4.85;4.98;5.07;4.80;4.98	ave = 4.83
	4	5.11;5.28;5.27;4.89	ave = 5.14
85±2	4	5.14;4.72;5.21;5.04	ave = 5.03

$[C_3F_7I] = 4.93 \times 10^{-3}$ mole l^{-1}; $[CF_2:CFH] = 1.88 \times 10^{-3}$ mole l^{-1}
Photolysis time = 7200 s.
Least squares plot of $\log\{[C_3F_7CFH\text{-}CF_2I] / [C_3F_7CF_2\text{-}CFHI]$ against $10^3/T$ gave gradient 0.23 ± 0.08 and intercept 0.08 ± 0.03.

Table I-3 Variation of remperature on Addition to $CF_2:CH_2$

Temp (^oC)	No. of Runs	$[C_3F_7CH_2\text{-}CF_2I] / [C_3F_7CF_2\text{-}CH_2I]$	
210±2	7	33.04;34.67;34.99;45.29;42.56; 44.26;41.11	ave = 39.42
192±2	4	39.72;58.83;47.10;48.75	ave = 47.35
186±2	3	60.53;88.10;61.94	ave = 70.19
163±2	4	87.10;88.51;84.53;85.51	ave = 86.41
140±2	6	95.50;91.62;97.50;89.95;123.9; 115.1	ave = 102.6

$[C_3F_7I] = 5.21 \times 10^{-3}$ mole l^{-1}; $[CF_2:CH_2] = 1.71 \times 10^{-3}$ mole l^{-1}
Photolysis time = 7200 s.
Least squares plot of $\log\{[C_3F_7CH_2\text{-}CF_2I] / [C_3F_7CF_2\text{-}CH_2I]\}$ against $10^3/T$ gave gradient 1.21 ± 0.23 and intercept -0.89 ± 0.11.

Table I-4 Variation of Temperature on Addition to $CFH:CH_2$

Temp (^oC)	No. of Runs	$[C_3F_7CH_2CFHI]/[C_3F_7CFHCH_2I]$	
224±2	3	13.40;18.20;16.60	ave = 16.07
184±2	7	11.61;21.18;21.48;14.00;18.71; 17.50;19.19	ave = 17.67
160±2	6	20.42;24.38;23.28;17.99;17.70; 17.18	ave = 20.16
130±2	6	24.72;25.76;29.99;29.99;28.77; 20.99	ave = 26.70
101±2	6	30.48;34.83;30.20;32.28;32.28; 27.73	ave = 31.23

$[C_3F_7I] = 5.49 \times 10^{-3}$ mole l^{-1}; $[CFH:CH_2] = 1.85 \times 10^{-3}$ mole l^{-1}
Photolysis time = 7200 s.
Least squares plot of $\log\{[C_3F_7CH_2\ CFHI]/[C_3F_7CFH\ CH_2I]\}$ against $10^3/T$ gave gradient 0.49 ± 0.14 and intercept 0.18 ± 0.06.

Table I-5 Variation of Temperature on Competitive Addition to $CHF:CH_2$ and $CH_2:CH_2$

Temp (^oC)	No. of Runs	$[C_3F_7CH_2CH_2I]/[C_3F_7CH_2CFHI]$	
160±2	4	2.99;2.99;2.75;3.08	ave = 2.95
140±2	6	3.33;3.24;3.66;3.21;3.21;3.52	ave = 3.36
130±2	5	3.11;3.11;3.11;2.92;2.83	ave = 3.02
104±2	4	4.06;4.10;3.96;3.96	ave = 4.02
90±2	5	3.66;3.66;3.70;3.49;3.49	ave = 3.60
84±2	5	3.52;3.54;3.51;3.60;3.44	ave = 3.52

$[C_3F_7I] = 2.47 \times 10^{-3}$ mole l^{-1}; $[CFH:CH_2] = 8.25 \times 10^{-4}$ mole l^{-1}
$[CH_2:CH_2] = 8.25 \times 10^{-3}$ mole l^{-1}; photolysis time = 10 800 s
Least squares plot of $\log\{[C_3F_7CH_2CH_2I]/[C_3F_7CH_2CFHI]\}$ against $10^3/T$ gave gradient 0.17 ± 0.09 and intercept 0.09 ± 0.04.

Table I-6 Variation of Temperature on Competitive Addition to $CF_2:CH_2$ and $CH_2:CH_2$

Temp (°C)	No. of Runs	$[C_3F_7CH_2CH_2I / C_3F_7CH_2CF_2I]$	
204±2	5	3.54;3.55;3.71;3.61;3.61	ave = 3.60
162±2	7	5.45;5.42;5.31;4.60;4.89;4.81;4.85	ave = 5.05
114±2	6	6.56;6.34;6.25;7.15;7.40;6.98	ave = 6.78
98±2	7	8.59;8.28;9.23;9.16;9.23;8.40;8.51	ave = 8.77
68±2	4	10.79;11.07;10.64;11.12	ave = 10.91

$[C_3F_7I] = 2.47 \times 10^{-3}$ mole l^{-1}; $[CF_2:CH_2] = 1.64 \times 10^{-3}$ mole l^{-1}; $[CH_2:CH_2] = 8.24 \times 10^{-3}$ mole l^{-1}; photolysis time = 7200 s.

Least squares plot of $\log\{[C_3F_7CH_2CH_2I]/[C_3F_7CH_2CF_2I]\}$ against $10^3/T$ gave gradient 0.59 ± 0.05 and intercept -0.66 ± 0.02.

Table I-7 Variation of Temperature on Competitive Addition to $CF_2:CFH$ and $CF_2:CH_2$

Temp (°C)	No. of Runs	$[C_3F_7CFHCF_2I]/[C_3F_7CH_2CF_2I]$	
202±2	6	4.67;4.04;4.34;4.37;4.37;3.97	ave = 4.24
168±2	6	3.86;3.97;3.74;4.09;3.97;3.83	ave = 3.91
130±2	5	4.67;4.37;3.97;3.63;4.51	ave = 4.23
106±2	5	5.18;5.18;4.82;4.46;5.00	ave = 4.93
84±2	5	5.59;5.00;4.67;4.37;4.51	ave = 4.83
42±2	5	4.37;5.00;5.00;5.38;4.67	ave = 4.88

$[C_3F_7I] = 2.47 \times 10^{-3}$mole l^{-1}; $[CF_2:CFH] = 8.24 \times 10^{-4}$ mole l^{-1}; $[CF_2:CH_2] = 8.24 \times 10^{-4}$ mole l^{-1}; photolysis time = 7200 s

Least squares plot of $\log\{[C_3F_7CFHCF_2I]/[C_3F_7CH_2CF_2I]\}$ against $10^3/T$ gave gradient 0.08 ± 0.05 and intercept 0.44 ± 0.02.

Table I-8 Variation of Temperature on Competitive Addition to $CH_2{:}CH_2$ and $CF_2{:}CF_2$

Temp (^{o}C)	No. of Runs	$[C_3F_7CH_2CH_2I]/[C_3F_7CF_2CF_2I]$	
149±2	4	5.64;5.77;5.20;5.42	ave =
119±2	5	14.62;13.93;15.38;15.38;14.62	ave =
110±2	5	13.24;14.55;14.66;14.66;13.90	ave =
104±2	5	19.50;19.19;19.86;21.13;22.34	ave =
75±2	4	15.81;15.07;15.42;16.26	ave =
58±2	3	24.72;31.19;27.93	ave =
47±2	4	51.76;52.60;53.83;53.70	ave =

$[C_3F_7I] = 2.47 \times 10^{-3}$ mole l^{-1}; $[CH_2{:}CH_2] = 3.84 \times 10^{-4}$ mole l^{-1}; $[CF_2{:}CF_2] = 3.84 \times 10^{-4}$ mole l^{-1}; photolysis time = 3600 s. Least squares plot of $\log\{[C_3F_7CH_2CH_2I]/[C_3F_7CF_2CF_2I]\}$ against $10^3/T$ gave gradient 1.02 ± 0.33 and intercept -0.16 ± 0.12.

PART I

DISCUSSION

The photolysis of n-heptafluoroiodopropane in presence of each of the unsymmetrical fluoro-ethylenes gave only two product peaks on g.l.c. analysis. The reaction with ethylene yielded only one peak, but the reaction with tetrafluoroethylene gave much smaller peaks due to the 2:1 and 3:1 telomers in addition to the main product peak due to the 1:1 adduct. The amount of telomerisation could be reduced by increase of the concentration of n-heptafluoroiodopropane. The product of the recombination of the n-heptafluoropropyl radicals, n-tetradecafluorohexane, was not observed under the chromatographic conditions employed.

The products and reaction conditions are consistent with a free radical chain mechanism analogous to that proposed for the addition of trifluoromethyl radicals generated from photolysis of iodotrifluoromethane.

$$C_3F_7I \longrightarrow C_3F_7^{\cdot} + I^{\cdot} \qquad (1)$$

$$C_3F_7^{\cdot} + Ol \longrightarrow C_3F_7Ol^{\cdot} \qquad (2)$$

$$C_3F_7Ol^{\cdot} + C_3F_7I \longrightarrow C_3F_7OlI + C_3F_7^{\cdot} \qquad (3)$$

(Where Ol represents fluoroethylene)

The primary step has not been studied in any detail, although the photolysis of trifluoroiodomethane has been studied by flash photolytic methods. These studies have been aimed, however, more at the nature of the iodine atoms produced than the trifluoromethyl radicals. The work of Donovan and his coworkers seems to indicate that the iodine atom is excited to the $^2P_{\frac{1}{2}}$ state. The principle line used for irradiation was that at 3130 Å, i.e. an energy of 90 kcal mole^{-1}. The bond dissociation energy of the CF_3-I bond, which will be similar to that of C_3F_7-I, is 56 kcal mole^{-1}. Thus, the perfluoropropyl radical formed will probably be thermally excited. However, the pressures at which the experiments were conducted make it probable that this excess energy is rapidly dissipated. Provided that the chains are reasonably long, the uncertainty in the primary step is unimportant.

The possible terminations include:

$$C_3F_7^\bullet + C_3F_7^\bullet \longrightarrow C_6F_{14} \qquad (4)$$

$$I^\bullet + I^\bullet + M \longrightarrow I_2 + M \qquad (5)$$

$$C_3F_7^\bullet + I^\bullet \longrightarrow C_3F_7I \qquad (-1)$$

If it is assumed that the adduct is formed only by reaction (3) and that it is not subsequently decomposed, and that steady state conditions apply, then the rate of formation of adduct is given by:

$$\mathcal{R}_{C_3F_7OlI} = k_2[C_3F_7^\bullet][Ol]. \qquad (a)$$

If two olefins are reacted competitively, then

$$\mathcal{R}_{C_3F_7Ol'I} \Big/ \mathcal{R}_{C_3F_7OlI} = k_2'[Ol']\Big/k_2[Ol] \qquad (b)$$

applies. If the two olefins are present in equal concentrations, or if the adducts, C_3F_7OlI and $C_3F_7Ol'I$, represent addition to the two ends of an unsymmetrical olefin, then for small conversions:

$$k_2'/k_2 = [C_3F_7Ol'I]_f / [C_3F_7OlI]_f \qquad (c)$$

where the subscripts indicate final concentrations. Thus, the method of measuring the relative concentrations of the two possible adducts at the end of each kinetic run at a different temperature provides a direct measure of the two relative rates of the addition processes. The results of these runs using the olefins singly and in competition with each other are shown in tables I-2 to I-8. These results were then used to determine the rate of addition to each specific site relative to addition to CH_2= in ethylene (table I-9).

Table I-9 shows two points about the addition reaction, a) that addition is predominantly at one end of the olefin (in the unsymmetrical olefins, this is the least-fluorinated end) although with trifluoroethylene at higher temperatures, there is significant addition at the other end, and b) that the rate of addition is affected by the number of fluorine atoms present. This latter effect has been seen by Whittle in the addition to fluorinated aromatic compounds.[28] In order to compare the affect of increasing number of fluorines with existing data, the overall rates obtained by adding the rate constants for addition at each end of the double bond are shown in table 1-10. They are compared with the data for addition of trichloromethyl radicals to the fluoro-ethylenes and with Whittle's data for addition of trifluoromethyl radicals.

The selectivities of the trichloromethyl and n-heptafluoropropyl radicals in addition to the fluoro-ethylenes are compared in table I-11. A striking feature of this table is the similarity in selectivity of the two radicals. An unexpected feature, however, is that, although n-heptafluoropropyl radicals are more reactive than trichloromethyl radicals, they are also slightly more selective. Values for the addition ratios for trifluoromethyl radicals are also shown in table I-11. It would appear that while $CF_3^{\cdot}$ has a reactivity close to that of $C_3F_7^{\cdot}$, its selectivity is closer to that of $CCl_3^{\cdot}$. The observed greater selectivity of $C_3F_7^{\cdot}$ may be a result of the stereochemistry of the reaction.

Because the n-tetradecafluorohexane formed by recombination of n-heptafluoropropyl radicals could not be observed under the chromatographic conditions employed, the kinetics of the addition could not be absolutely determined. However, by considering the Arrhenius parameters for addition of trifluoromethyl to ethylene[16] and by comparing the available abstraction data for both trifluoromethyl and n-heptafluoro-

Table I-9 The Addition of $C_3F_7^{\cdot}$ Radicals to Fluoroethylenes Relative to Addition to Ethylene.

Addend Radical	$\log A_2 - \log A_2'$	$E_2 - E_2'$	$\log k_2 - \log k_2'$ at 150°C.
$C_3F_7CH_2CHF$	-0.09	0.79	1.50
$C_3F_7CHFCH_2$	0.09	3.03	2.52
$C_3F_7CH_2CF_2$	0.66	2.67	1.28
$C_3F_7CF_2CH_2$	1.57	8.19	3.33
$C_3F_7CHFCF_2$	0.22	3.05	2.64
$C_3F_7CF_2CHF$	0.14	4.09	2.02
$C_3F_7CF_2CF_2$	0.16	4.67	3.74

A_2, E_2 and k_2 refer to addition to the fluoroethylene
A_2', E_2' and k_2' refer to addition to ethylene.

propyl radicals[31], a reasonable approximation to the Arrhenius parameters for the addition to ethylene by $C_3F_7^{\cdot}$ could be made. The approximated parameters are log $A_2 = 8.5$ and $E_2 = 3.10$ (A_2 in l $mole^{-1}$ s^{-1} and E_2 in kcal $mole^{-1}$). Kerr and Parsonage[32], however, have estimated the values to be 8.3 and 2.0 respectively. Using the former values and the data in table I-9, the Arrhenius parameters were calculated and are shown in table I-12. For comparison, the corresponding values for trichloromethyl addition are shown in table I-13.[27a]

Table I-10 Overall Rates of Addition to Fluorinated Olefins (relative to Ethylene)

No. of F atoms	Olefin	$\log (k_2/k_2')^a$			$\log (k_2/k_8^{\frac{1}{2}})^b$
		$C_3F_7\cdot$	$CCl_3\cdot$[27]	$CF_3\cdot$[32]	$CF_3\cdot$[28]
1	$CH_2{:}CHF$	1.24	1.49	0.42	—
	C_6H_5F	—	—	—	2.51
2	$CH_2{:}CF_2$	2.98	1.09	1.41	—
	$C_6H_4F_2$	—	—	—	o 2.35; m 2.22; p 2.38
3	$CHF{:}CF_2$	2.42	1.29	—	—
	11,2,4-$C_6H_3F_3$	—	—	—	2.04
	1,3,5-$C_6H_3F_3$	—	—	—	3.78
4	$CF_2{:}CF_2$	3.74	1.90	0.46	—
	1,2,3,4-$C_6H_2F_4$	—	—	—	3.90
	1,2,4,5-$C_6H_2F_4$	—	—	—	3.88
5	C_6HF_5	—	—	—	3.72
6	C_6F_6	—	—	—	3.57

[a] rate constants at 150°

[b] rate constants at 65°; k_8 = recombination rate constant for $CF_3\cdot$

Table I-11 Orientation of Radical Addition to Fluoroethylenes in the Gas Phase

Adding Radical	Fluoroethylene		
	CH_2=CHF	CH_2=CF_2	CHF=CF_2
$CCl_3\cdot$ [a]	1 : 0.077	1 : 0.012	1 : 0.29
$C_3F_7\cdot$ [b]	1 : 0.050	1 : 0.009	1 : 0.25
$CF_3\cdot$	1 : 0.094[c]	1 : 0.011[d]	1 : 0.29[e]

[a] ratios at 150°, ref 8,18,29

[b] ratios at 150°, this work

[c] ratio at 150°, ref 30

[d] ratio at 160°, ref 30

[e] ratio at 152°, ref 30.

Table I-12 Addition of $C_3F_7^{\bullet}$ Radicals to Fluoroethylenes in the Gas Phase

Addn. to $CH_2=$	log A_2	E_2	Addn. to CFH=	log A_2	E_2	Addn to $CF_2=$	log A_2	E_2
$CH_2=CH_2$	8.5	3.1	$CFH=CH_2$	8.6 ± .07	6.1 ± .8	$CF_2=CH_2$	10.1 ± .11	11.3 ± 1.1
$CH_2=CFH$	8.4 ± .04	3.9 ± .4				$CF_2=CFH$	8.6 ± .04	7.2 ± .5
$CH_2=CF_2$	9.2 ± .02	5.8 ± .3	$CFH=CF_2$	8.7 ± .03	6.2 ± .4	$CF_2=CF_2$	8.7 ± .12	7.8 ± 1.5

Table I-13 Addition of $CCl_3^{\bullet}$ Radicals to Fluoroethylenes in the Gas Phase

Addn. to $CH_2=$	log A_2	E_2	Addn to CFH=	log A_2	E_2	Addn to $CF_2=$	log A_2	E_2
$CH_2=CH_2$	8.3 ± .4	6.3 ± .8	$CFH=CH_2$	8.1 ± .3	8.4 ± .7	$CF_2=CH_2$	8.4 ± .4	11.4 ± 1.0
$CH_2=CFH$	8.1 ± .3	6.4 ± .7				$CF_2=CFH$	9.1 ± .5	10.2 ± 1.2
$CH_2=CF_2$	8.4 ± .4	7.7 ± .8	$CFH=CF_2$	9.1 ± .5	9.2 ± .9	$CF_2=CF_2$	9.7 ± .6	9.2 ± .9

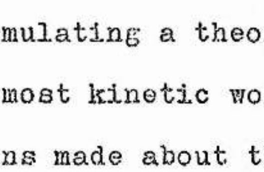
A_2 in l $mole^{-1}$ s^{-1}

E_2 in kcal $mole^{-1}$

The factors determining the orientation of addition to olefins have provoked much discussion. Some of the more important ideas have been summarised in reviews written some years ago.[6,33] It was concluded then that there existed no theory which could satisfactorily explain the observations. To some extent, this is still the case.

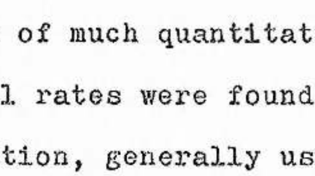
As has already been noted, the main difficulty to formulating a theory was the lack of much quantitative data. In most kinetic work, only overall rates were found and assumptions made about the site of addition, generally using the Mayo-Walling approach.

The orientation of addition depicted in table I-11 is entirely consistent with the predictions of the Mayo-Walling theory in its simplest form. For example, in the addition to 1,1-difluoroethylene, the two possible addend radicals are:



$C_3F_7-\underset{H}{\overset{H}{C}}-\underset{F}{\overset{F}{C}}\cdot$

(I)



$C_3F_7-\underset{F}{\overset{F}{C}}-\underset{H}{\overset{H}{C}}\cdot$

(II)

In (I), the lone electron can readily be delocalised into the p-orbitals of the fluorine atoms, but in (II), delocalisation into the orbitals of the hydrogen atoms is not as facile. Thus, (I) is said to be more stable than (II) and is preferentially formed in the addition step leading to $C_3F_7.CH_2.CF_2I$ as the predominant adduct formed. The analogous argument can be applied to each of the other olefins. However, when the relative rates between different olefins are examined, the results are not at all consistent with the theory.

In table I-12, the pre-exponential factors are found to be almost constant, with just one exception, so that differences in rates are determined by differences in activation energies. Considering the first column of table I-12, the activation energies are 3.1, 3.9 and 5.8 kcal mole^{-1} although the site of the lone electron changes from CH_2- to CFH- to CF_2-. In the simple Mayo-Walling theory, the delocalisation of the odd electron should differ markedly from one addend radical to the next and the resultant rates of addition be very different. Now considering the top row of table I-12,in each case the site of the odd electron is a CH_2- and yet the activation energy increases from 3.1 to 11.3 kcal mole^{-1}. The Mayo-Walling picture is inadequate to explain these observations. The stability of the addend radical has not, however, been ruled out as the controlling factor.

Tedder and Walton proposed that the site of attack should be the primary consideration, not the site of the odd electron.[34] Thus, again looking at the first column of table

I-12, in each case, the radical is attacking a CH_2= group and the new bond should be approximately the same regardless of the group at the opposite end of the double bond. The differences do occur because of the secondary effect of this group. For the results in the top row of table I-12, the radical is in each case attacking a different site and the strength of the new bond should, in each case, be different.

The n-heptafluoropropyl radical can be considered as being electron-attracting so that for addition to 1,1-difluoroethylene, the bond formed to the CF_2= should be, relatively, fairly weak, the carbon atom attacked then having three electron-attracting substituents attached to it. In the addition to ethylene, on the other hand, the bond formed with the CH_2= should be much stronger, only one such substituent then being attached to the attacked carbon atom. Addition to CFH= in vinyl fluoride is intermediate between these two. This trend is reflected in the increasing activation energy found when going along the top row of the table. The trend in the activation energies in the first column of the table cannot be so easily explained. The explanation may lie in repulsive forces in the transition state between the radical and the fluorine atoms on the olefin.

There have been many attempts at correlating the rates of addition and activation energies with theoretically calculated properties. Generally, these properties have been calculated using Hückel molecular orbital theory. As a result, correlations have almost invariably been drawn for reactions involving aromatic systems.

Two 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 and a σ-transition state in which the radical is associated with one of the terminal carbon atoms. A small kinetic isotope effect has been observed for several small alkyl radicals which shows that the transition state resembles reactants rather than products,[35,36] a conclusion which is supported by the small activation energies and exothermicities of the reactions. Probably, the reaction passes first through a π-complex state followed by a σ-transition state, but, in both, the electron distribution is closer to that of reactants than products. Stefani and co-workers have suggested that activation energies calculated from the rates of product formation will give data relating to the σ-transition state. The fact that the relative proportions of the two possible adducts from an unsymmetrical olefin varies with temperature means that, for $C_3F_7^{\bullet}$ and $CCl_3^{\bullet}$ radicals, the σ-complex represents the top of the potential energy pass. Correlation of rate data with atom rather than bond properties is therefore appropriate for these two radicals.

The course of a reaction may be represented by a potential energy curve. There have been four regions identified in this curve,[37] 1) an initial state (i.e. reactants), 2) a polarised state in which each of the reactants feels the presence of the other, 3) an activated state corresponding to the configuration with highest energy and 4) a final state (i.e. the products). These regions are shown in figure I-1 in which

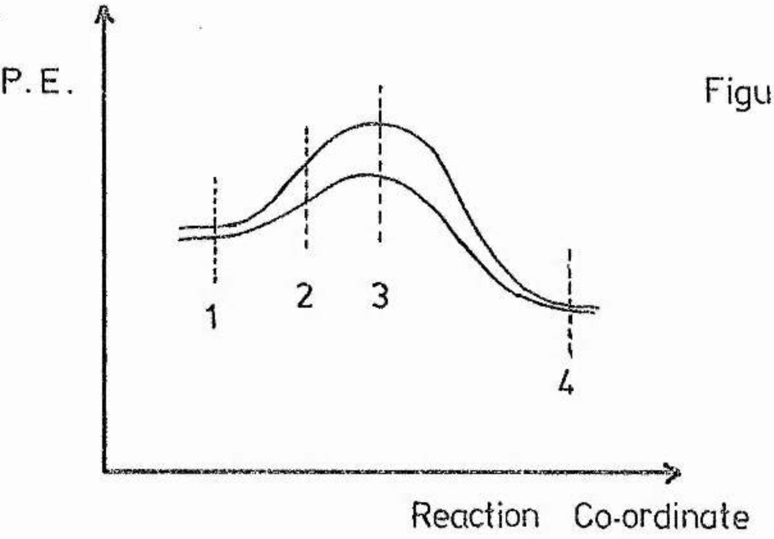


Figure I-1

potential energy curves are drawn for two similar reactions. The assumption that for similar reactions the potential energy curves are similar is then made. A theoretical viewpoint of the reactions can then be at (2) or (3), i.e. the polarised and activated states. No information about the course of the reactions can be obtained at (1) or (4). The theoretical studies thus divide themselves into the polarised state approximation and the activated state approximation.

Within the framework of the polarised state approximation, the Free Valence Index (f.v.i.) of Coulson[38] has been the most often used parameter. It is defined by equation (A) in which N_μ is the bond number of atom μ, equal to the sum of the π-electron bond orders, P_μ, emitting from atom μ, and N_{max} is the maximum possible value of N_μ. N_{max} has the value $\sqrt{3}$ as calculated for the central carbon atom in trimethylenemethane.

$$F_\mu = N_{max} - N_\mu \qquad -(A)$$

$$N_\mu = \sum_\mu P_\mu$$

Kooyman and Farenhorst[39] showed that the logarithm of the reaction rate constant for the addition of trichloromethyl radicals to aromatics was proportional to the f.v.i. of the most reactive positions. Coulson found a similar correlation for methyl radical addition[40], a correlation which was later extended by Binks and Szwarc.

The f.v.i. have been calculated for the fluoroethylenes using H.M.O.[8,41] and the values are shown in table I-14. The correlation between $\log_{10}k_2$ for addition of n-heptafluoropropyl radicals to the fluoro-ethylenes against the values of f.v.i. of Landau and co-workers is shown in figure I-2. Although the correlation is not very good, the f.v.i. always correctly predicts the orientation of addition to one olefin. This was also found in the addition of trichloro-

Table I-14. Free Valence Indices for the Carbon Atoms in Fluoro-ethylenes

Ethylene	Free Valence Index			
	C-atom 1		C-atom 2	
1 2	(ref 8)	(ref 41)	(ref 8)	(ref 41)
CH_2 : CH_2	0.732	0.732		
CH_2 : CHF	0.768	0.750	0.513	0.571
CH_2 : CF_2	0.811	0.770	0.291	0.401
CFH : CF_2	0.622	0.622	0.350	0.434
CF_2 : CF_2	0.419	0.470		

methyl radicals to the fluoro-ethylenes.

The orientation of addition of trichloromethyl radicals was also found to be correctly predicted by the charge densities, q_μ, on the carbon atoms of the olefins. It was supposed that the expected electrophilic nature of the trichloromethyl radical would give rise to a correlation. The calculated values of charge densities are shown in table I-15. As was the case with trichloromethyl radicals, the orientation of addition of n-heptafluoropropyl radicals can be correctly predicted but within the series, there is no correlation between the charge density and the rate or activation energy.

Figure I-2. Correlation of rate constants with f.v.i.

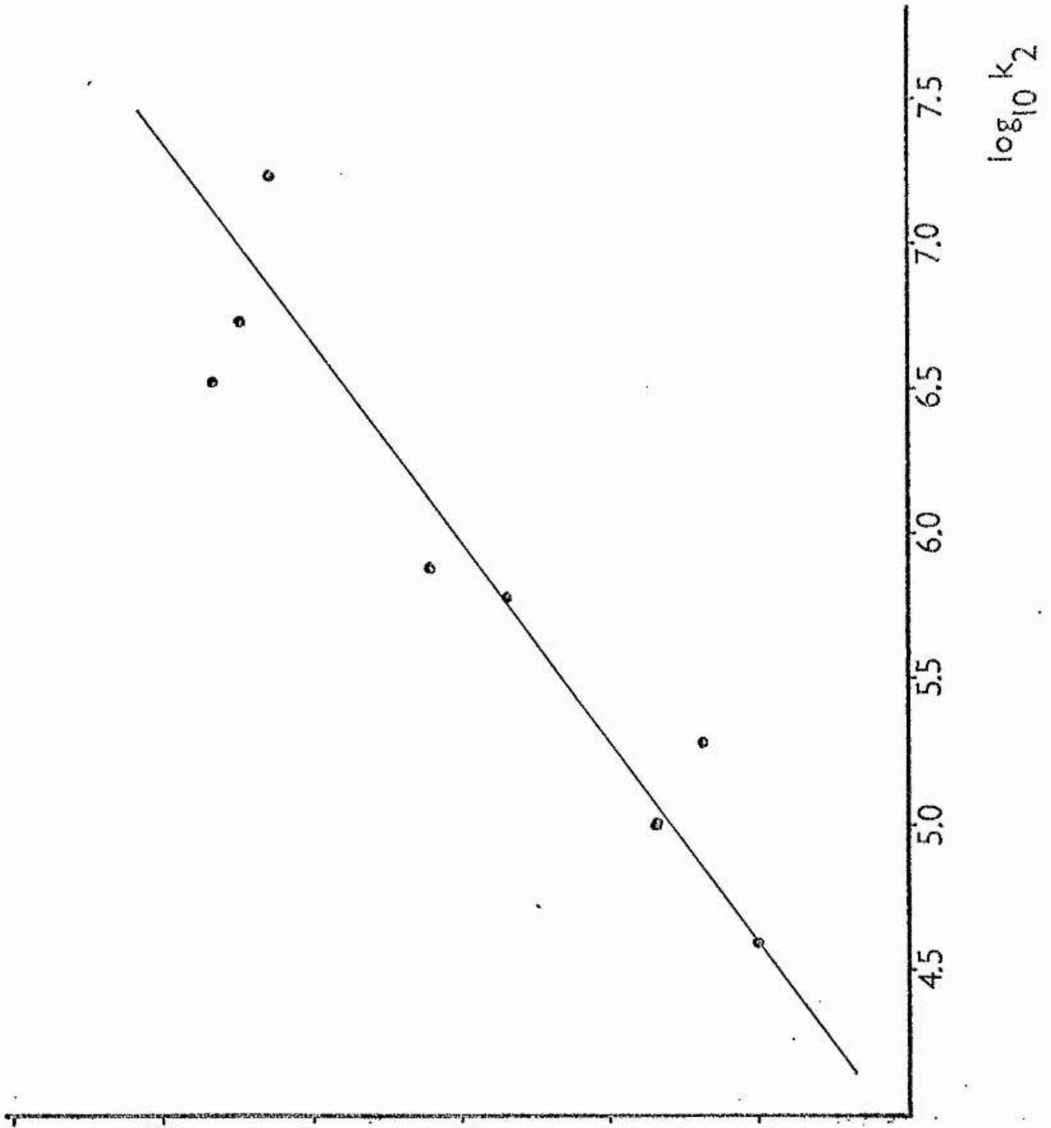


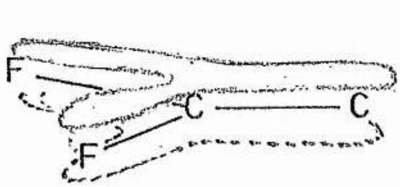
Table 1-15. Charge Densities on the Carbon Atoms of Fluoro-ethylenes

Ethylene	Charge Density			
	C-atom 1		C-atom 2	
1 2	(ref 8)	(ref 41)	(ref 8)	(ref 41)
CH_2 : CH_2	1.00	1.00		
CH_2 : CHF	1.13	1.075	0.93	0.956
CH_2 : CF_2	1.25	1.145	0.87	0.917
CHF : CF_2	1.17	1.097	0.98	0.985
CF_2 : CF_2	1.05	1.052		

The activated state approximation differs from the polarised state approach in that the configuration of radical and olefin is one that is further along the reaction co-ordinate. The configuration is one that attempts to imitate the transition state for the reaction. In the addition of the radical to the olefin, the π-bond in the olefin is broken and a new σ-bond is formed between the radical and one of the carbon atoms of the olefinic residue. The process can follow this pathway: 1) the π-bond is broken and one of the π-electrons is localised in a 2p orbital on the attacked carbon atom, 2) the orbitals on this carbon atom are subsequently rehybridised to sp^3, 3) the σ-bond is then formed between the singly occupied orbital on the radical and a carbon sp^3 orbital, 4) the orbitals on this σ-complex are rehybridised to give the "stable" addend radical. This is a crude picture of what may happen in the reaction.

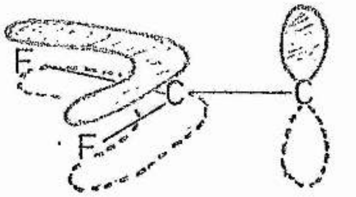
Whereas, in the polarised state approximation, the reactivity indices are associated with the olefin, in the activated state approximation, a reactivity index associated with the σ-complex must be found. This new parameter is the localisation energy, L_{μ}. The localisation energy is the energy required to localise one of the π-electrons at a particular atom, and it can be calculated using H.M.O. theory.

In H.M.O. theory, σ-π separability is assumed, so that only the π-orbitals need be considered, the σ-electrons are assumed to be part of a non-polarisable core. In the fluoro-ethylenes, the π-orbitals are constructed from the carbon 2p orbitals and one of the fluorine 2p orbitals. The electrons from each of the contributing atoms are then fed into the molecular orbitals and the sum of the resulting electronic energies gives the total π-energy of the olefin, E_{π}. When a π-electron is localised at one of the atoms, as is demanded by the reaction pathway above, the π-system is split into fragments which no longer interact. Thus, using 1,1-difluoroethylene as an example, the π-electron system encompasses the two carbon atoms and the two fluorine atoms:



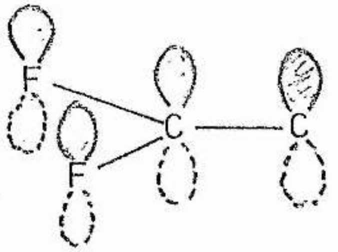
(III)

If one electron is localised at C(2), the π-electron system changes:



(IV)

and localising the electron at C(1):



(V)

Each of these localised models, (IV) and (V), has associated with it a different π-electronic energy, say E_{π}^{IV} and E_{π}^{V}, which is the sum of the π-electron energies of the separate fragments. The localisation energy is then the difference between the π-energy of the fully delocalised molecule, (III), and the π-energy of the localised molecule.

That is:

$$L_{\mu} = E_{\pi} - E_{\pi}^{\prime} \qquad -(B)$$

(the subscript, μ, indicates the atom at which the electron is localised)

The localisation energy has been found to correlate very well with rates of radical addition. Streitweiser has found good correlation for addition to aromatics[42] and one of the successes is the correlation of localisation energy and rate for hydrogen atom addition when there was no correlation found with the f.v.i.[43]

In order to calculate the π-electron energies for the fluoroethylenes from H.M.O. theory, values for the fluorine coulomb and resonance integrals, α_F and β_{FC}, are necessary. The values of these integrals for hetero-atoms are usually expressed in terms of the values for carbon and so

$$\alpha_F = \alpha_C + h\beta_{CC} \quad \text{and} \quad \beta_{FC} = k\beta_{CC} \qquad \text{-(C)}$$

Streitweiser has suggested values for these integrals, obtained from the properties of aromatic compounds.[42] The values of h and k have been varied[44] in the ranges suggested by Streitweiser and the following values for the integrals were taken: $\alpha_C = 10\beta_0$, $\alpha_F = 12.73\beta_0$, and $\beta_{FC} = 0.908\beta_0$. The localisation energies are shown in table I-16.

The correlations of localisation energy against activation energy for addition of trichloromethyl radicals and of n-heptafluoropropyl radicals to the fluoroethylenes are shown in figure I-3. For both radicals, reasonable correlations are obtained and the localisation energies correctly predict the orientation of addition.

Figure I-3. Correlation of activation energy with localisation energy for addition of $C_3F_7^\cdot$ and $CCl_3^\cdot$ radicals to fluoro-ethylenes

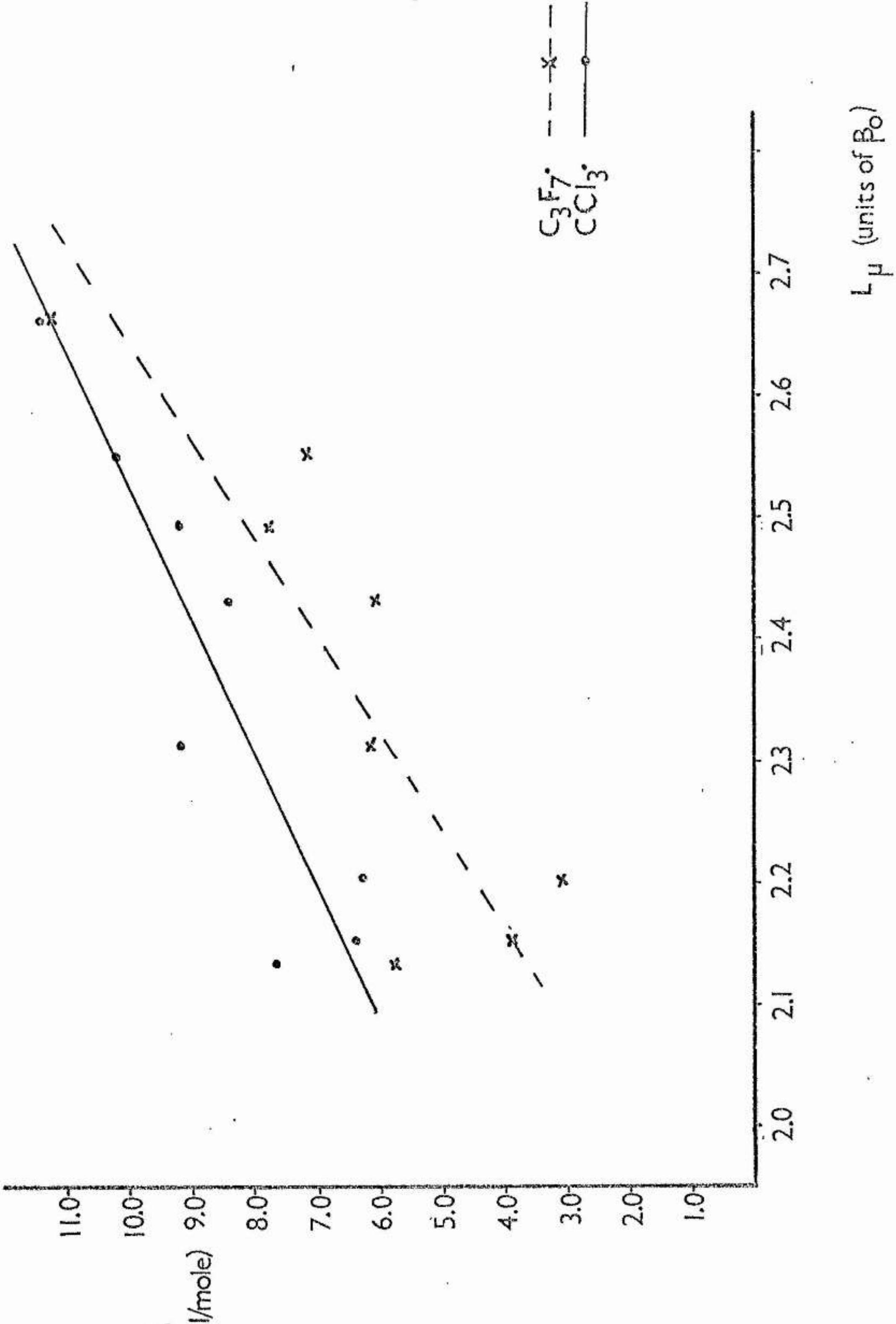


Table I-16. Localisation Energies and Net Atom Charges for Fluoroethylenes

Ethylene	Localisation energy		Net atom charge	
	Attack at	Attack at	Attack at	Attack at
1 2	C-atom 1	C-atom 2	C-atom 1	C-atom 2
CH_2 : CH_2	2.20		0.00	
CH_2 : CHF	2.15	2.43	+0.13	-0.07
CH_2 : CF_2	2.13	2.66	+0.25	-0.13
CHF : CF_2	2.31	2.55	+0.17	-0.02
CF_2 : CF_2	2.49		+0.05	

(Localisation energies are in units of β_0)

In order to improve the correlation in the addition of trichloromethyl radicals, a polar term was introduced.[45] This new term was to take account of the electrostatic repulsion between the radical and the attacked site in the olefin. It is thus proportional to the charges on each, but since the radical is remaining constant within a series, the contribution from the electrostatic charge on the radical is constant and the new term is proportional to the net charge on the carbon atom attacked. The net atom charges, ΔQ_μ, are shown in table I-16. The correlation between activation energy and calculated parameters now can be represented by:

$$E_2 = AL_{\mu} - B\Delta Q_{\mu} \qquad -(D)$$

(A & B are constants).

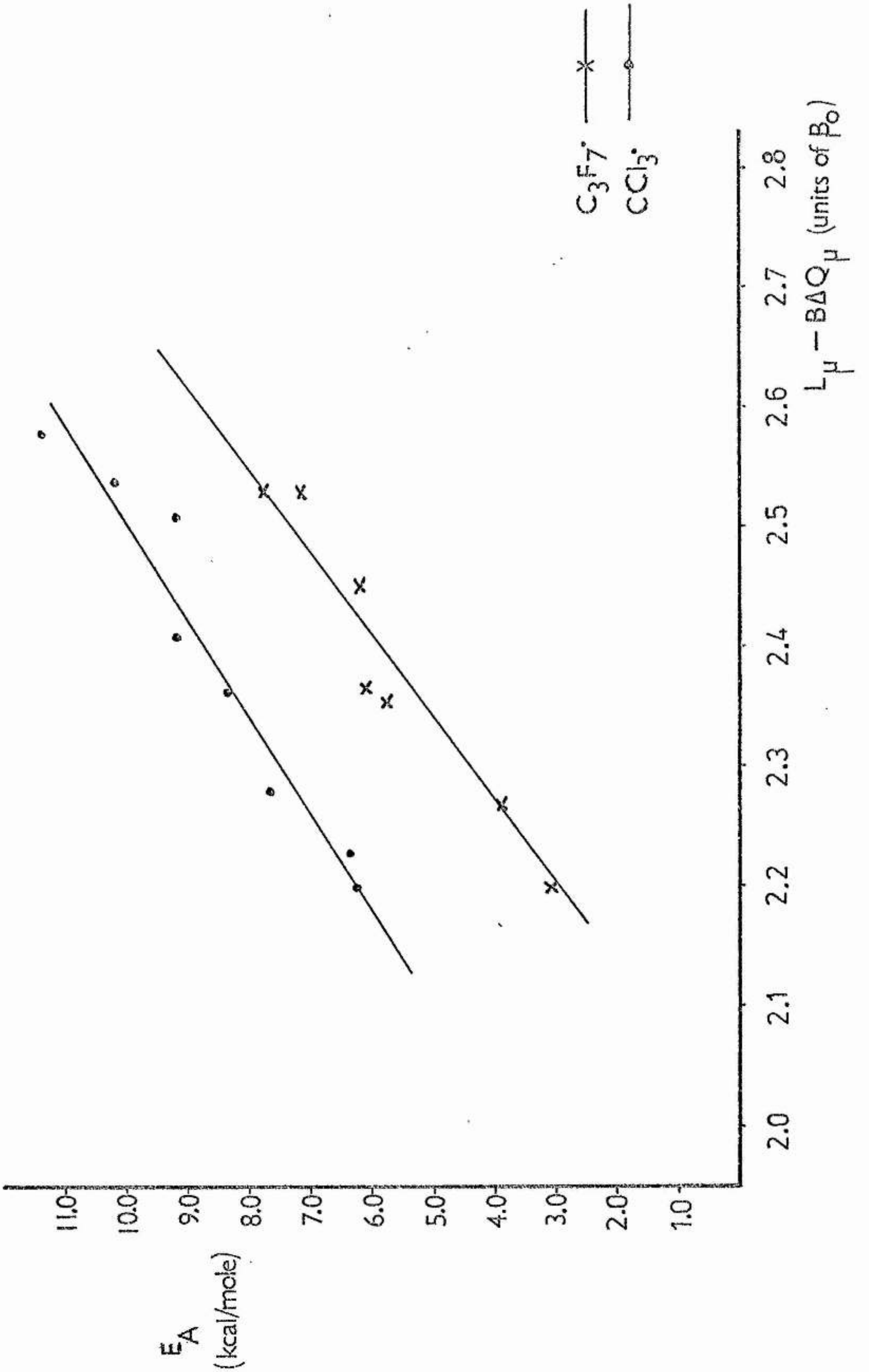
In principle, this equation should be applicable to all radicals. The polar nature of each radical should be represented by the value of B.

An equation of this form has been previously noted,[46] in which the second term is a constant. However, Yang's correlation was restricted to alternant hydrocarbon olefins in which the net charge density at each carbon atom is zero. Thus the results of Yang and those of Kooyman and Farenhorst and of Szwarc and his co-workers are special cases of the more general equation.

The improved correlations for both trichloromethyl and n-heptafluoropropyl radicals are shown in figure I-4. The values of B are those which give the lowest percentage error in the gradient. The point for addition to $CF_2=$ in 1,1-difluoroethylene by n-heptafluoropropyl radicals has been omitted since the activation energy alone is not representative of the rate of addition, the pre-exponential factor differing quite considerably from the values for the other olefins.

The Mayo-Walling theory of radical addition is completely inadequate to describe the addition of the

Figure I-4. Correlation of activation energy with $L_\mu - B\Delta Q_\mu$ for addition of $C_3F_7^\cdot$ (B =.9) and $CCl_3^\cdot$ (B =.7) radicals to fluoro-ethylenes.



electrophilic radicals, $CCl_3^{\cdot}$ and $C_3F_7^{\cdot}$, to the fluoro-ethylenes. It does succeed in predicting the orientation within one molecule, the breakdown comes in the comparison of two molecules. The consideration of both the strength of the new bond formed and electrostatic repulsive forces in the transition state seems to form a better basis for a theory. A semi-quantitative theory seems to be approachable using localisation energies and net atom charges, and it would appear that polar forces in radical reactions are much more important than has hitherto been believed.

Both the trichloromethyl and n-heptafluoropropyl radicals might be expected to have electrophilic character. This similar polar nature is reflected in similar values of B in equation (D). Many authors have suggested that alkyl radicals are slightly nucleophilic. If this is the case, then, if equation (D) holds, the value of B should be quite different for addition of alkyl radicals. The strengths of the new bonds formed should also show some differences from those in the above radicals and, if this is also the case, further departure from the Mayo-Walling theory might not be unexpected.

To investigate these points, the addition of methyl and ethyl radicals to the fluoro-ethylenes was studied. The results are to be found in Part II.

PART II

The Addition of Methyl and Ethyl Radicals to Fluoro-ethylenes

PART II

INTRODUCTION

In a very naïve approach, the reactions of free radicals should be free of any polar influences, due to the lack of any charged species. However, polar and solvent effects are often very much in evidence in radical reactions. And the polar effects are not just seen in the substrates but also in the radicals themselves. This can be illustrated by considering hydrogen abstraction from propionic acid. The relative selectivities for abstraction by methyl are 1 : 7.8 (primary : secondary), while for abstraction by chlorine, the figures are 30 : 1(primary : secondary).[47] The very different natures of the radicals are apparent. While the chlorine atom is electrophilic, the methyl radical is relatively nucleophilic. But the position is not as clear cut as this.

In its reactions with substituted toluenes, methyl radicals have been classed as being slightly electrophilic.[48] The Hammett equation for the abstraction reactions was found to give a value of ρ^+ of about -0.1 which is similar to that given by the correlation for phenyl radicals. This contrasts with the work of Kalatzis and Williams[49] who concluded that there were no polar influences on the rate of α-hydrogen abstraction from toluenes.

Minisci and his co-workers have extensively studied the reactions of alkyl radicals produced in redox systems.[50] They come to the conclusion that alkyl radicals are nucleophilic and the order of increasing nucleophilicity is given as: $\dot{C}H_2Cl < CH_3\dot{C}HCl < \dot{C}H_3 < ClCH_2CH_2\dot{C}H_2 < C_2H_5^{\bullet} < n\text{-}C_4H_9^{\bullet} < C_6H_{11}^{\bullet} < i\text{-}C_3H_7^{\bullet} < sec\text{-}C_4H_9^{\bullet}$. They find that, in agreement with the polar character of the groups bonded to the radical carbon, secondary alkyl radicals are more nucleophilic than primary alkyl radicals.[50c]

It has been pointed out that the ethyl radical, the methyl radical and also the hydrogen atom belong to a class of radicals having low electron affinities.[51] In fact, it would seem reasonable to expect these radicals to have predominantly nucleophilic character since the cations are formed more readily than the anions. The electron affinities are shown in table II-1. It is apparent that ethyl, methyl and hydrogen atoms are likely to show similar properties and these different from the properties of trichloromethyl and n-heptafluoropropyl. It is interesting to note, in passing, that on the basis of electron affinity, n-heptafluoropropyl should have greater electrophilic character than trichloromethyl. This is reflected in the value of the constant B as found in Part I.

Table II-1. Electron Affinities of Radicals

Radical	$H^{\bullet}$	$CH_3^{\bullet}$	$C_2H_5^{\bullet}$	$CCl_3^{\bullet}$	$C_3F_7^{\bullet}$
E.A. (eV)	0.75[52a]	1.13[52b]	1.0[52c]	1.7[52c]	2.4[52d]

If the accepted nucleophilic character of alkyl radicals has not been rigorously established, it is at least clear that methyl and ethyl radicals have different polar characteristics from trichloromethyl or n-heptafluoropropyl. With the intent of studying the polar factors in addition reactions, methyl and ethyl radicals were added to the fluoroethylenes and it is this work which is described in this part of the thesis.

The kinetics of reactions of alkyl radicals constitutesone of the most studied fields of free radical chemistry. Although abstraction reactions have been studied primarily, the results of kinetic studies on additions are not few. Compilations of data[32] show that, of the alkyl radicals, methyl and ethyl show the greatest availability of data.

The sources of alkyl radicals are analagous to those mentioned in Part I for the fluorinated radicals. The most convenient sources are azo-alkanes and ketones, photolyses of which, at 3130 Å, produce two alkyl radicals and a molecule of nitrogen or carbon monoxide for each initiator molecule. The measurement of the nitrogen or carbon monoxide provides an internal actinometer.

$$R.N{=}N.R \xrightarrow{h\nu} R. + N_2 + R.$$

$$R.CO.R \xrightarrow{h\nu} R. + CO + R.$$

Other sources include, aldehydes, biacetyl, di-t-butyl peroxide and acetyl peroxide.

The addition of methyl radicals to unsaturated substrates has been the subject of a comprehensive study by Szwarc and his co-workers.[53,54,55] Their source has been thermal decomposition of acetyl peroxide and the reactions were carried out in iso-octane solution. The unsaturated substrates have been aromatics,[53] polyenes and dienes[54] and aliphatics.[55] In one study,[56(d)] azomethane was used as a source to check some of their own results. In none of their studies, however, were rates determined absolutely. All rate parameters were determined competitively with abstraction from the solvent. The quantity determined

$$CH_3^\cdot + i\text{-}C_8H_{18} \longrightarrow CH_4 + i\text{-}C_8H_{17}^\cdot \qquad (1)$$

$$CH_3^\cdot + \text{Olefin} \longrightarrow CH_3\text{-Olefin}^\cdot \qquad (2)$$

was k_2/k_1 at each temperature. By arbitrarily setting this to unity for benzene, a scale of "methyl affinities" was determined for the unsaturated compounds studied. These methyl affinities were found to correlate well with some theoretically derived quantities. In particular, in the case of addition to aromatics, the log(methyl affinity) correlated very well with the singlet to triplet excitation energy for the aromatic.[53(b),(c)]

Mandelcorn and Steacie[56] used photolysis of acetone to study the addition to ethylene, as did Endrenyi and le Roy.[57] Di-t-butyl peroxide has been used by several workers[58,59] including Hogg and Kebarle[60] who also measured the rate of methyl addition to vinyl chloride.

The use of aldehydes has been shown for methyl radicals by Raal and Danby,[61] but this method has been more extensively developed by Trotman-Dickenson and his co-workers.[62] Cvetanović and Irwin[63] have used photolysis of biacetyl in their studies as have Sangster and Thynne[64] in studying methyl addition to tetrafluoroethylene.

Two general methods have been used to measure rates of methyl addition to olefins. The first involves strict identification and quantitative determination of all the products coupled with an analysis of a postulated mechanism. The second method is analytically less demanding and entails measuring the "methane deficiency" found when the radicals are added competitively with abstraction from another solvent. The first of these two methods could be used for measuring the rates of addition at the opposite ends of unsymmetrical olefins, although it would be very tedious. The second, however, cannot be so used because no strict product identification or determination is effected. In fact, no previous investigation has attempted to find the Arrhenius parameters for the addition to the opposite ends of an unsymmetrical olefin. There are, however, some qualitative date.[65,66]

The addition reactions of ethyl radical have been studied using similar methods to those for methyl. Propionaldehyde has been used to study addition to ethylene[67] and also azoethane.[68,69] Pinder and le Roy, however, have used a less direct route to ethyl radical formation.[70] Hydrogen atoms were produced by the mercury photosensitised decomposition of molecular hydrogen, the atoms then added to ethylene and the ethyl radicals produced subsequently added to ethylene to study their kinetics.

The kinetics of the ethyl radical additions have been studied using analysis of the products due to the reactions of the adduct radicals - a method analogous to the first one mentioned above for methyl radicals. This method has the advantage that the kinetics of the addition of propyl and butyl radical addition can also be studied (for methyl and ethyl cases respectively).

As in the case of methyl radicals, no activation parameters have been determined for addition of ethyl radicals to each end of unsymmetrical double bonds.

PART IIa

EXPERIMENTAL

1. Materials

Commercial iodomethane (Fisons) was purifed by distillation and stored over copper wire in the dark to keep it iodine free. sym-Dimethylhydrazine dihydrochloride was prepared by the method of Hatt via hydrazine sulphate, dibenzoyl hydrazine and dibenzoyldimethylhydrazine.[71] The sym-dimethylhydrazine dihydrochloride was dissolved in an excess of sodium hydroxide solution to yield the free base. This solution was then used to prepare azomethane by oxidation with yellow mercuric oxide.[72] The azomethane was distilled through calcium chloride and collected in a trap at -78°C. It was stored on the line at liquid nitrogen temperature. The ethylenes were treated as previously described. All reactants were trap-to-trap distilled and thoroughly degassed before use.

2. Apparatus and Procedure

The apparatus and procedure were as described in Part I with the following modifications:

a) prior to distilling the reaction mixture into a small tube on the line for subsequent analysis, the mixture was frozen down using liquid nitrogen and the nitrogen formed in the primary photolysis of azomethane was pumped off (failure to do this prevented quantitative distillation of the other products);

b) analysis was on a 6 ft, 20% dinonyl phthalate on 60/100 mesh 'Embacel', column.

3. Identification of products

Mass spectra were recorded on an A.E.I. MS 12 with g.l.c. inlet from a Perkin-Elmer F11 gas chromatograph (reaction with trifluoroethylene) or on an A.E.I. MS 902 with g.l.c. inlet from a Pye 104 instrument. The principal identifying peaks with assignments and intensities are shown in table II-2.

These spectra served to identify the suspected adduct peaks. However, while this was reasonably good evidence, it could not be regarded as unequivocal evidence as to the identity of the two isomeric adducts. To provide such evidence, it was necessary to obtain an n.m.r. spectrum of at least one of the adducts which, in each case where two isomers were formed, would be quite distinctive. There was never sufficient adduct formed in the kinetic runs and either special preparative runs were made or the adduct was synthesised by an unambiguous route. The n.m.r. spectra were obtained on a Varian HA-100 spectrometer at 100 Hz, the solvent was carbon tetrachloride and the internal reference was tetramethylsilane.

TABLE II-2. MASS SPECTRA OF FLUOROPROPYL IODIDES

CH_3CHFCF_2I			CH_3CF_2CFHI		
m/e	%	assignment	m/e	%	assignment
47	61.4	CH_3CHF^+	47	25.3	CH_3CHF^+
51	46.0	CF_2H^+	51	30.3	CF_2H^+
77	100	$C_3H_3F_2^+$	65	33.4	$CH_3CF_2^+$
97	82.8	$C_3H_4F_3^+$	77	100	$C_3H_3F_2^+$
127	52.8	I^+	97	14.9	$C_3H_4F_3^+$
142	18.1	CH_3I^+	127	18.5	I^+
177	4.0	CF_2I^+	142	3.8	CH_3I^+
224	15.3	M^+	159	4.6	$CHFI^+$
			224	25.0	M^+

$CH_3CH_2CF_2I$			$CH_3CF_2CH_2I$		
29	9.5	$CH_3CH_2^+$	33	13.0	CFH_2^+
33	6.4	CH_2F^+	39	12.6	$C_3H_3^+$
39	8.6	$C_3H_3^+$	45	4.8	$C_2H_2F^+$
45	2.1	$C_2H_2F^+$	51	12.6	HCF_2^+
51	40.0	CF_2H^+	59	100	$CH_2CFCH_2^+$
59	78.6	$C_3H_4F^+$	60	15.0	$CH_3CFCH_2^+$
64	5.7	$CH_2CF_2^+$	64	16.7	$CH_2CF_2^+$
77	11.4	$C_3H_3F_2^+$	65	30.0	$CH_3CF_2^+$
79	100	$CH_3CH_2CF_2^+$	77	9.3	$C_3H_3F_2^+$
80	7.1	$C_3H_6F_2^+$	79	11.1	$CH_3CF_2CH_2^+$

Table II-2 continued

m/e	%	assignment	m/e	%	assignment
127	2.7	I^+	127	12.6	I^+
128	0.6	HI^+	128	0.7	HI^+
177	1.0	CF_2I^+	141	2.6	CH_2I^+
206	0.7	M^+	206	10.0	M^+
CH_3CFHCH_2I			CH_3CH_2CFHI		
42	11.0	$C_3H_3^+$	29	19.4	$CH_3CH_2^+$
43	24.2	C_2F^+	42	100	$C_3H_6^+$
45	18.8	$C_2H_2F^+$	45	15.2	$C_2H_2F^+$
46	7.1	$C_2H_3F^+$	46	10.3	$C_2H_3F^+$
47	8.4	CH_3CHF^+	60	26.1	$C_3H_4F^+$
57	15.7	$C_3H_2F^+$	61	12.7	$C_3H_6F^+$
59	17.7	$C_3H_4F^+$	127	8.5	I^+
61	100	$C_3H_6F^+$	128	12.1	HI^+
127	16.1	I^+	159	96.4	$CFHI^+$
128	25.9	HI^+	188	6.7	M^+
141	4.3	CH_2I^+			
142	39.2	CH_3I^+			
188	54.9	M^+			

Preparation of $CH_3CF_2CH_2I$

Iodoacetone was prepared from chloroacetone by the method of Scholl and Matthaiopoulos.[73] 8 ml of iodoacetone and 15 ml of liquified sulphur tetrafluoride were put into a cooled high pressure stainless steel reactor. The mixture was heated at 45°C for 18 hr, the reactor was then cooled. The excess sulphur tetrafluoride was released and the reactor opened. The tarry liquid was removed, anhydrous potassium fluoride added and the liquid distilled on a vacuum line. Iodine was removed by washing with sodium metabisulphite solution. The liquid was then washed several times with water and dried over anhydrous sodium sulphate.

The liquid contained one major component which had the same retention as one of the adducts formed from 1,1-difluoroethylene and an n.m.r. spectrum which confirmed it as $CH_3CF_2CH_2I$. The spectrum showed a triplet at τ 8.18 with a proton-fluorine splitting of 18 Hz and a triplet at τ 6.63 with a proton-fluorine splitting of 13 Hz.

Preparation of CH_3CHFCF_2I and CH_3CF_2CFHI

A series of high pressure runs were carried out photolytically in a quartz cell between methyl iodide and trifluoroethylene. The combined reaction mixtures were then separated by preparative g.l.c. (Pye 105 preparative gas chromatograph) and n.m.r. spectra obtained in microcells on the two adduct peaks.

The first eluted adduct (CH_3CFHCF_2I) showed a quartet at τ8.55 with a proton-fluorine splitting of 22 Hz and a proton-proton splitting of 6 Hz, and a complex doublet at τ5.66 with a proton-fluorine splitting of 48 Hz.

The second eluted adduct (CH_3CF_2CFHI) showed a triplet of doublets at τ8.13 with a proton-fluorine splitting of 18 Hz and a long range proton-fluorine splitting of 1.5 Hz, and a doublet of triplets at τ3.28 with a proton-fluorine splitting of 49 Hz and another proton-fluorine splitting of 7.5 Hz.

Preparation of CH_3CH_2CHFI

A cooled high pressure stainless steel reactor was charged with 20 ml of CH_3I, 1 ml of t-butyl perbenzoate and 10 ml of liquified vinyl fluoride. The reactor was sealed and was heated at 130^oC for 24 hr. The reactor was cooled, the excess pressure released and the residual liquid removed. G.l.c. analysis of this mixture showed that only one adduct had been prepared in isolable quantity, the other was present only in trace amount. The mixture was separated by preparative g.l.c. and the n.m.r. spectrum of the adduct obtained in a microcell.

The spectrum showed a triplet at τ8.96 with a proton-proton coupling of 7 Hz, a multiplet at τ7.80 and a doublet of triplets at τ3.24 with a proton-fluorine coupling of 50 Hz and a proton-proton coupling of 5 Hz.

All spectra were found to integrate correctly.

4. Details of reactions

Table II-3. VARIATION OF TEMPERATURE ON ADDITION TO $CFH:CF_2$

Temp (^oC)	No. of Runs	$[CH_3CF_2CFHI] / [CH_3CFHCF_2I]$	
180±1	4	6.70;6.14;6.14;6.14	ave = 6.24
153±1	3	6.68;7.16;6.68	ave = 6.84
137±1	3	6.70;9.00;8.07	ave = 7.93
120±1	4	9.80;9.84;9.73;7.85	ave = 9.27
108±1	3	10.12;10.12;10.12	ave = 10.12
102±1	4	11.51;10.79;10.00;10.00	ave = 10.57

$Me_2N_2 = 7.31 \times 10^{-5}$ m; $MeI = 7.31 \times 10^{-4}$ m; $CF_2:CFH = 2.77 \times 10^{-4}$ m; photolysis time = 7200 s.

Least squares plot of $\log\{[CH_3CF_2CFHI] / [CH_3CFHCF_2I]\}$ against $10^3/T$ gave gradient 0.53 ± 0.12 and intercept -0.38 ± 0.05.

Table II-4 VARIATION OF TEMPERATURE ON ADDITION TO $CF_2:CH_2$

Temp (°C)	No. of Runs	$[CH_3CH_2CF_2I]/[CH_3CF_2CH_2I]$	
185±2	3	3.35;2.71;2.93	ave = 2.99
170±2	5	3.01;2.85;3.04;2.67;2.60	ave = 2.91
150±2	4	2.36;2.15;2.16;2.17	ave = 2.21
125±2	4	1.61;1.63;1.81;1.81	ave = 1.75
105±2	4	1.38;1.57;1.64;1.69	ave = 1.57

$Me_2N_2 = 7.31 \times 10^{-5}$ m; MeI = 1.74×10^{-3} m; $CF_2:CH_2 = 2.77 \times 10^{-4}$ m; photolysis time = 7200 s.

Least squares plot of $\log\{[CH_3CH_2CF_2I]/[CH_3CF_2CH_2I]\}$ against $10^3/T$ gave gradient -0.66 ± 0.12 and intercept 1.92 ± 0.05.

Table II-5 VARIATION OF TEMPERATURE ON ADDITION TO $CFH:CH_2$

Temp (°C)	No. of Runs	$[CH_3CH_2CHFI]/[CH_3CFHCH_2I]$	
207±2	2	1.47;1.54	ave = 1.50
175±2	5	1.65;1.56;1.55;1.70;1.59	ave = 1.61
134±2	5	1.81;1.64;1.81;1.84;1.94	ave = 1.80
116±2	4	1.82;1.98;1.81;1.68	ave = 1.82
94±2	5	2.13;2.00;2.10;1.95;2.12	ave = 2.06
77±2	3	2.25;2.25;2.49	ave = 2.33

$Me_2N_2 = 1.22 \times 10^{-4}$ m; MeI = 1.34×10^{-3} m; $CFH:CH_2 = 2.77 \times 10^{-4}$ m; photolysis time = 14 400 s.

Least squares plot of $\log\{[CH_3CH_2CHFI]/[CH_3CHFCH_2I]\}$ against $10^3/T$ gave gradient 0.22 ± 0.05 and intercept -0.29 ± 0.02.

Table II-6 VARIATION OF TEMPERATURE ON THE COMPETITIVE ADDITION TO $CHF:CH_2 + CH_2:CH_2$

Temp. (^oC)	No. of Runs	$[CH_3CH_2CH_2I] / [CH_3CH_2CHFI]$	
181±2	5	6.05;5.78;5.83;5.86;6.03	ave = 5.91
161±2	4	6.05;6.46;6.58;6.32	ave = 6.34
135±2	5	6.76;6.37;6.55;6.49;6.71	ave = 6.58
115±2	5	7.11;6.75;6.90;6.56;7.06	ave = 6.88
91±2	5	7.94;8.20;7.83;7.80;7.41	ave = 7.83

$Me_2N_2 = 1.22 \times 10^{-4}$ m; $MeI = 1.46 \times 10^{-3}$ m; $CHF:CH_2 = CH_2:CH_2 = 2.08 \times 10^{-4}$ m; photolysis time = 14 400 s

Least squares plot of log $\{[CH_3CH_2CH_2I] / [CH_3CH_2CHFI]\}$ against $10^3/T$ gave gradient 0.20 ± 0.04 and intercept 0.32 ± 0.02.

Table II-7 VARIATION OF TEMPERATURE ON THE COMPETITIVE ADDITION TO $CF_2:CF_2 + CF_2:CHF$

Temp. (^oC)	No. of Runs	$[CH_3CF_2CF_2I] / [CH_3CF_2CHFI]$	
187±2	4	2.53;2.87;2.64;2.64	ave = 2.67
156±2	3	2.75;2.36;2.48	ave = 2.58
148±2	3	2.11;2.33;2.53	ave = 2.32
109±2	4	2.25;2.53;1.96;1.79	ave = 2.13
92±2	2	1.83;1.74	ave = 1.79

$Me_2N_2 = 1.22 \times 10^{-4}$ m; $MeI = 1.46 \times 10^{-3}$ m; $CF_2:CF_2 = CF_2:CHF = 2.77 \times 10^{-4}$ m; photolysis time = 7200 s.

Least squares plot of log $\{[CH_3CF_2CF_2I] / [CH_3CF_2CHFI]\}$ against $10^3/T$ gave gradient 0.23 ± 0.05 and intercept -0.32 ± 0.02.

Table II-8 VARIATION OF TEMERATURE ON THE COMPETITIVE ADDITION TO $CHF:CF_2$ + $CHF:CH_2$

Temp. (^oC)	No. of Runs	$[CH_3CF_2CHFI] / [CH_3CH_2CHFI]$	
187±1	4	0.62;0.66;0.66;0.66	ave = 0.65
144±1	4	0.79;0.79;0.81;0.81	ave = 0.80
127±1	4	1.10;1.05;1.05;1.05	ave = 1.06
112±1	3	1.18;1.12;1.14	ave = 1.15
93±1	4	1.31;1.31;1.34;1.33	ave = 1.32
82±1	5	1.45;1.51;1.52;1.46;1.46	ave = 1.47

$Me_2N_2 = 1.22 \times 10^{-4}$ m; $MeI = 1.56 \times 10^{-3}$ m; $CHF:CF_2 = CHF:CH_2 = 4.94 \times 10^{-4}$ m; photolysis time = 10 400 s.

Least squares plot of $\log\{[CH_3CF_2CHFI] / [CH_3CH_2CHFI]\}$ against $10^3/T$ gave gradient 0.57 ± 0.05 and intercept -1.43 ± 0.02.

Table II-9 VARIATION OF TEMPERATURE ON THE COMETITIVE ADDITION TO $CH_2:CF_2$ + $CHF:CH_2$

Temp. (^oC)	No. of Runs	$[CH_3CH_2CHFI] / [CH_3CH_2CF_2I]$	
183±1	4	3.53;3.53;3.78;3.42	ave = 3.57
132±1	4	4.88;4.76;4.57;4.39	ave = 4,64
119±1	4	6.08;5.77;5.92;5.62	ave = 5.85
108±1	4	7.00;6.22;6.56;6.74	ave = 6.63
99±1	4	5.56;5.22;5.22;5.48	ave = 5.39
79±1	4	8.19;8.73;8.45;7.60	ave = 8.24

$Me_2N_2 = 1.22 \times 10^{-4}$ m; $MeI = 1.56 \times 10^{-3}$ m; $CHF:CH_2 = CH_2:CF_2 = 4.94 \times 10^{-4}$ m; photolysis time = 10 800 s.

Least squares plot of $\log\{[CH_3CH_2CHFI] / [CH_3CH_2CF_2I]\}$ against $10^3/T$ gave gradient 0.53 ± 0.12 and intercept -0.61 ± 0.05.

Table II-10 VARIATION OF TEMPERATURE ON THE COMPETITIVE ADDITION TO $CH_2:CH_2$ + $CF_2:CF_2$

Temp. (^oC)	No. of Runs	$[CH_3CF_2CF_2I] / [CH_3CH_2CH_2I]$	
210±3	3	1.90;2.01;2.08	ave = 2.00
159±2	3	2.08;2.62;2.52	ave = 2.41
140±2	3	3.70;2.75;3.54	ave = 3.33
118±2	3	4.86;4.06;3.56	ave = 4.16
105±2	3	3.99;3.86;3.47	ave = 3.77
97±2	3	5.00;3.39;3.16	ave = 3.85

$Me_2N_2 = 1.22 \times 10^{-4}$ m; MeI = 1.56×10^{-3} m; $CH_2:CH_2 = CF_2:CF_2 = 4.94 \times 10^{-4}$; photolysis time = 2700 s

Least squares plot of $\log\{[CH_3CF_2CF_2I] / [CH_3CH_2CH_2I]\}$ against $10^3/T$ gave gradient 0.57 ± 0.2 and intercept -0.92 ± 0.09.

Table II-11 VARIATION OF TEMPERATURE ON THE COMPETITIVE ADDITION TO $CH_2:CH_2$ + $CH_2:CF_2$

Temp. (^oC)	No. of Runs	$[CH_3CH_2CH_2I] / [CH_3CH_2CF_2I]$	
197±2	5	9.14;10.02;10.02;8.32;7.64	ave = 9.02
179±2	5	9.59;9.14;8.71;9.40;8.89	ave = 8.95
165±2	5	12.16;11.64;12.56;11.99;12.11	ave =12.09
144±2	4	22.28;23.17;20.80;19.77	ave =21.50
113±2	3	23.28;24.95;26.00	ave =24.74
100±2	6	26.42;29.85;29.85;30.06;34.51; 33.73	ave =30.74

$Me_2N_2 = 1.83 \times 10^{-4}$ m; MeI = 3.47×10^{-3} m; $CH_2:CH_2 = CH_2:CF_2 = 4.94 \times 10^{-4}$ m; photolysis time = 10 800 s.

Least squares plot of $\log\{[CH_3CH_2CH_2I] / [CH_3CH_2CF_2I]\}$ against $10^3/T$ gave gradient 1.04 ± 0.2 and intercept -1.31 ± 0.08

Table II-12 VARIATION OF TEMPERATURE ON THE COMPETITIVE ADDITION TO $CH_2:CH_2$ + $CH_2:CHCl$

Temp. (^oC)	No.of Runs	$[CH_3CH_2CH_2I] / [CH_3CH_2CHClI]$	
150±1	3	2.85;2.72;2.55	ave = 2.70
131±1	2	2.86;2.91	ave = 2.89
110±1	2	3.41;3.01	ave = 3.21
93±1	3	3.44;3.70;3.95	ave = 3.63
89±1	3	4.01;4.48;4.23	ave = 4.24

$Me_2N_2 = 1.22 \times 10^{-4}$ m; $MeI = 1.56 \times 10^{-3}$ m; $CH_2:CH_2 = CH_2:CHCl = 4.94 \times 10^{-4}$ m; photolysis time = 5400 s.

There was a single adduct peak in addition to the C_3H_7I peak which had the following identifying peaks in its mass spectrum: m/e 206, 204 ($CH_3CH_2CHClI^+$); 177, 175 ($CHClI^+$); and 29 ($CH_3CH_2^+$). Least squares plot of $\log\{[CH_3CH_2CH_2I] / [CH_3CH_2CHClI]\}$ against $10^3/T$ gave gradient 0.41 ± 0.10 and intercept -0.55 ± 0.04.

Table II-13 VARIATION OF TEMPERATURE ON THE COMPETITIVE ADDITION TO $CH_2:CH_2$ + $CH_3CH:CH_2$

Temp. (^{o}C)	No. of Runs	$[CH_3CH_2CH_2I] / [CH_3CH_2CHICH_3]$	
151±2	3	4.46;4.46;4.41	ave = 4.44
130±2	3	4.52;4.40;4.12	ave = 4.35
111±1	3	4.09;4.65;3.86	ave = 4.20
85±2	2	3.90;3.68	ave = 3.79
62±1	3	3.52;3.60;3.45	ave = 3.53

$Me_2N_2 = 1.22 \times 10^{-4}$ m; MeI = 1.45×10^{-3} m; $CH_2:CH_2 = 1.83 \times 10^{-4}$ m; $CH_3CH:CH_2 = 3.12 \times 10^{-4}$ m; photolysis time = 7200 s; the values of the adduct ratios have already been corrected to allow for the different initial concentrations of the olefins.

Least squares plot of $\log\{[CH_3CH_2CH_2I]/[CH_3CH_2CHICH_3]\}$ against $10^3/T$ gave gradient -0.16 ± 0.08 and intercept -1.04 ± 0.03. There was a single adduct peak, in addition to the C_3H_7I peak, which had a retention time identical to that of 2-iodobutane.

Table II-14 VARIATION OF $[MeI]_i$ ON ADDITION TO $CH_2:CF_2$

Press. of MeI in 286 ml (mm of Hg)	Temp. (^{o}C)	No. of Runs	$[CH_3CH_2CF_2I] / [CH_3CF_2CH_2I]$	
120.0	100±2	3	1.45;1.55;1.44	ave = 1.48
100.0	97±3	4	1.62;1.46;1.55;1.41	ave = 1.51
70.0	96±3	4	1.33;1.58;1.63;1.60	ave = 1.54
50.0	96±2	4	1.48;1.33;1.57;1.34	ave = 1.43
30.0	99±2	5	1.60;1.31;1.54;1.45;1.27	ave = 1.43
15.0	98±2	4	1.38;1.45;1.46;1.44	ave = 1.43

$Me_2N_2 = 7.31 \times 10^{-5}$ m; $CH_2:CF_2 = 1.98 \times 10^{-4}$ m; photolysis time = 7200 s.

Table II-15 VARIATION OF $[MeI]_i$ ON ADDITION TO $CHF:CF_2$

Press. of MeI in 529.5 ml (mm of Hg)	Temp. (^oC)	No. of Runs	$[CH_3CF_2CFHI] / [CH_3CFHCF_2I]$	
100.0	125±1	4	8.70;10.00;7.69;7.14	ave = 8.38
75.0	123±2	4	7.69;7.69;9.09;8.70	ave = 8.29
50.0	126±2	4	8.85;9.09;8.70;8.33	ave = 8.74
25.0	124±2	4	7.69;8.00;8.00;8.00	ave = 7.92
10.0	127±2	4	7.69;9.09;8.00;8.70	ave = 8.37

$Me_2N_2 = 1.22 \times 10^{-4}$ m; $CHF:CF_2 = 2.16 \times 10^{-3}$ m; photolysis time = 7200 s.

Table II-16 EFFECT OF SURFACE AREA ON ADDITION TO $CHF:CH_2$

Surface/area ratio (cm^{-2})	Temp (^oC)	No. of Runs	$[CH_3CH_2CHFI] / [CH_3CHFCH_2I]$	
923.8	108±1	3	3.09;2.94;2.92	ave = 2.98
210.0	108±1	2	2.66;2.37	ave = 2.52

$MeI = 6.80 \times 10^{-4}$ m; $CHF:CH_2 = 2.04 \times 10^{-4}$ m; $Me_2N_2 = 4.93 \times 10^{-5}$ m; photolysis time = 10 800 s; temperature = 108 ± 1.

PART IIb

EXPERIMENTAL

1. Materials

Commercial iodoethane (Fisons) was purified by distillation and stored over copper wire in the dark to keep it iodine free. Azoethane was prepared by a slightly modified method of Stowell[74] (sodium methoxide being used as the base in the conversion of N,N'-diethylsulphamide to azoethane). The yield of pure azoethane was very low ($\sim 10\%$). It was stored on the line at liquid nitrogen temperature. The ethylenes were treated as described in Part I. All reactants were trap-to-trap distilled and thoroughly degassed before use.

2. Apparatus and Procedure

The apparatus and procedure were as described in Part I with the same modifications as used in the study of methyl radical addition.

3. Identification of Products

By analogy with the identification of the adducts from methyl addition, the products could be sensibly identified. G.l.c. retention times were compared and corresponding ratios of retention times for isomeric methyl adducts and isomeric ethyl adducts were very similar.

The identity of the adduct peaks was confirmed by mass spectrometry. (The spectra were measured on an A.E.I. MS 902 instrument with g.l.c. inlet from a Pye 104 gas chromatograph). The identifying peaks are shown in table II-17.

TABLE II-17 MASS SPECTRA OF FLUOROBUTYL IODIDES

$EtCH_2CHFI$			$EtCHFCH_2I$		
m/e	intensity	assignment	m/e	intensity	assignment
29	44.4	Et^+	29	91.3	Et^+
39	16.1	$C_3H_3^+$	39	21.1	$C_3H_3^+$
46	13.6	CH_2CHF^+	42	20.7	$EtCH^+$
47	47.8	CH_3CHF^+	46	7.6	CH_2CHF^+
55	50.0	$EtCHCH^+$	47	92.4	CH_3CHF^+
59	14.2	$C_3H_4F^+$	55	49.9	$EtCHCH^+$
75	100	$EtCH_2CHF^+$	60	18.7	$EtCF^+$
127	15.3	I^+	75	100	$EtCHFCH_2^+$
128	9.4	HI^+	127	14.5	I^+
159	1.9	$CHFI^+$	128	7.5	HI^+
202	26.7	M^+	141	2.1	CH_2I^+
			202	23.1	M^+

Table II-17 (continued)

$EtCF_2CHFI$			$EtCHFCF_2I$ (very weak spectrum)		
m/e	intensity	assignment	m/e	intensity	assignment
29	53.1	Et^+	29	48.6	Et^+
39	18.4	$C_3H_3^+$	41	45.0	EtC^+
40	25.5	$C_3H_4^+$	44	38.2	C_2HF^+
41	33.7	$C_3H_5^+$	51	37.4	CF_2H^+
44	23.0	C_2HF^+	61	64.0	$EtCHF^+$
47	100	$C_2H_4F^+$	71	14.0	$C_4H_4F^+$
51	78.6	CF_2H^+	77	11.3	$C_3H_3F_2^+$
64	8.2	$CH_2CF_2^+$	82	41.9	CF_2CHF^+
65	38.3	$CH_3CF_2^+$	91	100	$C_4H_5F_3^+$
77	24.5	$C_3H_3F_2^+$	127	24.0	I^+
79	71.4	$EtCF_2^+$	128	14.3	HI^+
82	30.6	CF_2CHF^+	177	36.1	CF_2I^+
91	96.9	$C_4H_5F_3^+$	238	70.0	M^+
127	28.1	I^+			
128	11.5	HI^+			
159	15.5	$CHFI^+$			
238	99.0	M^+			

$EtCF_2CF_2I$ showed peaks at m/e 256 (12.5%; M^+), 177 (4%;CF_2I^+), 129 (21%; $EtCF_2CF_2^+$), 109 (29%, $MeCHCFCF_2^+$), 79 (17%;$EtCF_2$) $EtCF_2CF_2CH_2CH_2I$ showed a similar spectrum but with additional peaks at m/e 284 (7%; M^+), 157 (79%; $M^+ - I$), 141 (32%, CH_2I^+).

4. Details of reactions

Table II-18 VARIATION OF TEMPERATURE ON ADDITION TO $CFH:CF_2$

Temp. (^oC)	No. of Runs	[$EtCF_2CFHI$] / [$EtCFHCF_2I$]	
200±3	3	8.18;9.10;9.10	ave = 8.79
184±2	4	9.10;10.53;11.10;10.00	ave = 10.18
170±4	3	11.75;12.48;12.10	ave = 12.12
145±3	4	13.35;14.30;13.88;12.50	ave = 13.56
130±2	3	14.90;15.68;16.30	ave = 15.68

Et_2N_2 = 4.93 x 10^{-5}m; EtI = 3.95 x 10^{-4}m; CF_2:CHF = 2.34 x 10^{-4}m; photolysis time = 15 hr.

Least squares plot of log{[$EtCF_2CFHI$] / [$EtCFHCF_2I$] against 10^3/T gave gradient 0.65 ± 0.12 and intercept -0.41 ± 0.05.

Table II-19 VARIATION OF TEMPERATURE ON ADDITION TO $CFH:CH_2$

Temp. (^oC)	No. of Runs	[$EtCH_2CHFI$]/[$EtCHFCH_2I$]	
194 2	3	3.00;3.39;2.89	ave = 3.09
174 2	3	3.11;3.28;3.21	ave = 3.20
162 2	4	3.54;3.00;2.62;3.35	ave = 3.13
144 2	3	3.31;3.36;3.66	ave = 3.44
138 2	3	3.86;3.74;3.55	ave = 3.72
111 2	3	3.68;3.76;3.79	ave = 3.74

Et_2N_2 = 6.16 x 10^{-5} m; EtI = 4.74 x 10^{-4} m; $CFH:CH_2$ = 3.51 x 10^{-4} m; photolysis time = 16 hr.

Least squares plot of log{[$EtCH_2CHFI$] / [$EtCHFCH_2I$] against 10^3/T gave gradient 0.21 ± 0.13 and intercept 0.02 ± 0.05

Table II-20 VARIATION OF TEMPERATURE ON THE COMPETITIVE ADDITION TO $CH_2:CH_2$ + $CF_2:CHF$

Temp. (^oC)	No. of Runs	$[EtCH_2CH_2I]/[EtCF_2CHFI]$	
188±2	4	3.45;2.86;3.48;3.36	ave = 3.29
170±3	4	3.49;3.40;3.40;3.69	ave = 3.49
140±2	3	3.40;3.92;3.30	ave = 3.55
125±2	4	3.59;3.79;3.70;3.79	ave = 3.72
98±2	3	3.92;3.92;3.60	ave = 3.81

$Et_2N_2 = 4.93 \times 10^{-5}$ m; $EtI = 4.74 \times 10^{-4}$ m; $CH_2:CH_2 = 2.34 \times 10^{-4}$ m; $CF_2:CHF = 2.34 \times 10^{-4}$ m; photolysis time = 15 hr.

Least squares plot of $\log\{[EtCH_2CH_2I]/[EtCF_2CHFI]\}$ against $10^3/T$ gave gradient 0.12 ± 0.08 and intercept 0.26 ± 0.03.

Table II-21 VARIATION OF TEMPERATURE ON THE COMPETITIVE ADDITION TO $CH_2:CH_2$ + $CFH:CH_2$

Temp. (^oC)	No. of Runs	$[EtCH_2CH_2I]/[EtCH_2CHFI]$	
195 2	4	5.78;4.78;5.50;5.11	ave = 5.39
174 2	4	6.86;6.86;6.10;5.78	ave = 6.41
145 2	4	6.86;6.86;7.19;7.33	ave = 7.08
127 2	3	9.14;8.93;8.15	ave = 8.74
117 2	4	9.98;8.43;8.75;8.75	ave = 8.99

$Et_2N_2 = 7.39 \times 10^{-5}$ m; $EtI = 6.32 \times 10^{-4}$ m; $CH_2:CH_2 = 2.91 \times 10^{-4}$ m; $CFH:CH_2 = 2.93 \times 10^{-4}$ m; photolysis time = 16 hr.

Least squares plot of $\log\{[EtCH_2CH_2I]/[EtCH_2CHFI]\}$ against $10^3/T$ gave gradient 0.54 ± 0.11 and intercept -0.42 ± 0.05.

Table II-22 VARIATION OF TEMPERATURE ON THE COMPETITIVE ADDITION TO $CH_2:CH_2 + CF_2:CF_2$

Temp. (^oC)	No. of Runs	$[EtCF_2CF_2I] / [EtCH_2CH_2I]$	
170±2	3	3.48;4.10;4.05	ave = 3.88
146±2	3	4.80;6.33;5.63	ave = 5.59
143±2	3	4.62;4.60;4.60	ave = 4.61
121±2	3	7.00;7.00;7.35	ave = 7.12
111±2	3	6.71;7.88;8.34	ave = 7.64
99±1	3	10.02;10.84;10.08	ave = 10.31

$Et_2N_2 = 1.23 \times 10^{-2}$ m; $EtI = 7.90 \times 10^{-2}$ m; $CF_2:CF_2 = 2.93 \times 10^{-2}$ m; $CH_2:CH_2 = 2.91 \times 10^{-2}$ m; photolysis time = 16 hr.
Least squares plot of $\log\{[EtCF_2CF_2I] / [EtCH_2CH_2I]\}$ against $10^3/T$ gave gradient 0.96 ± 0.18 and intercept -1.60 ± 0.07.

In this series, the telomer, $Et(CF_2CF_2)_2I$, was found in appreciable quantity. To find the Arrhenius parameters for addition of ethyl radicals to $CF_2:CF_2$, the value $[EtCF_2CF_2I]$ is equated to $[Et(CF_2CF_2)_2I] + [EtCF_2CF_2I]$. This assumes that k_2 for addition of $EtCF_2CF_2^{\bullet}$ to $CF_2:CF_2$ is greater than that for addition of $Et^{\bullet}$, i.e. addition of $EtCF_2CF_2^{\bullet}$ is not rate determining. Consideration of the rates calculated from part I for $C_3F_7^{\bullet}$ shows that the rates of addition of $C_3F_7^{\bullet}$ and $Et^{\bullet}$ to $CF_2:CF_2$ are very similar. If the values proposed by Kerr and Ratajczak[75] are used, then the addition of $C_3F_7^{\bullet}$ is faster. In either case, the value found for the rate of ethyl addition to $CF_2:CF_2$ is, at least, a very good approximation.

PART II

DISCUSSION

Methyl iodide is not suitable as a source of methyl radicals for competitive reaction kinetics. Its absorption maximum in the range of frequencies emitted by a medium pressury mercury arc is at 2500 Å, there being a continuous absorption band centred round this maximum. The photolysis of methyl iodide has been studied by Goodeve and Porret[76] and by Schultz and Taylor.[77] The primary process for photolysis at 2537 Å is represented by (1).[76] If the strength of the carbon-iodine bond in methyl iodide, $D(CH_3-I) = 54$ kcal mole^{-1},

$$CH_3I \xrightarrow{h\nu} CH_3{}^{\bullet *} + I^{\bullet}({}^2P_{\frac{1}{2}}) \qquad (1)$$

is assumed and the excitation energy of the iodine atom $({}^2P_{\frac{3}{2}} \longrightarrow {}^2P_{\frac{1}{2}})$ is 22 kcal mole^{-1}, then the conservation of momentum requires that the absorption of 112 kcal mole^{-1} by methyl iodide yields methyl radicals which are "hot" to the extent of 32 kcal mole^{-1}. These hot radicals are then found to give rise to methane and methylene iodide by reactions (2) and (3). Reaction (2) does not proceed very easily with

$$CH_3{}^{\bullet *} + CH_3I \longrightarrow CH_4 + {}^{\bullet}CH_2I \qquad (2)$$

$${}^{\bullet}CH_2I + CH_3I \longrightarrow CH_2I_2 + CH_3{}^{\bullet} \qquad (3)$$

unexcited methyl radicals.[77] The reactions of "hot" radicals are independent of temperature and so meaningful kinetics cannot be derived from their use.

To overcome the difficulties encountered in the photolysis of methyl iodide and yet to still use its advantages in a chain propogation, a method of photolysis of azomethane in presence of methyl iodide and a substrate has been used.[78] The method was used successfully to study hydrogen abstraction from n-butane by methyl radicals.

The photolysis of azomethane has been extensively studied, in some cases to determine its usefulness as a source of methyl radicals. Much of the earlier work has been summarised by Steacie.[79] However, the more important points can be noted: (a) the decomposition is unimolecular, (b) the quantum yield of 1.0 ± 0.1 has been reported for the formation of nitrogen,[79] (c) the quantum yield is unaffected by a fourfold variation in light intensity[80] and (d) the quantum yield is unaffected by temperature up to 218°.[81] The primary process of photolysis at 3650 Å is represented in equation (4).

$$CH_3.N{=}N.CH_3 \xrightarrow{h\nu} 2CH_3^{\bullet} + N_2 \qquad (4)$$

The points (a)-(d) would appear to make azomethane an eminently suitable source of methyl radicals.

There are, however, two other reactions which should be considered, (5) and (6). These reactions are faster than the addition reactions studied[82] but by keeping the concentrations of azomethane small, these reactions were minimised.

$$CH_3^{\bullet} + CH_3.N{=}N.CH_3 \longrightarrow CH_4 + \dot{C}H_2{-}N{=}N{-}CH_3 \qquad (5)$$

$$CH_3^{\bullet} + CH_3.N{=}N.CH_3 \longrightarrow (CH_3)_2N{-}\dot{N}{-}CH_3 \qquad (6)$$

The photolysis of azomethane and methyl iodide in the presence of ethylene was found to produce propyl iodide. The reaction conditions and products were consistent with a free radical chain mechanism:

$$CH_3.N{=}N.\,CH_3 \xrightarrow{h\nu > 2800\,Å} 2CH_3^{\bullet} + N_2 \qquad (1)$$

$$CH_3^{\circ} + E \longrightarrow CH_3E^{\bullet} \qquad (2)$$

$$CH_3E^{\bullet} + CH_3I \longrightarrow CH_3EI + CH_3^{\bullet} \qquad (3)$$

(E represents olefin)

Possible terminations are:

$$CH_3E^{\bullet} + CH_3E^{\bullet} \longrightarrow CH_3E.ECH_3 \qquad (7)$$

$$CH_3^{\circ} + CH_3^{\circ} \longrightarrow C_2H_6 \qquad (8)$$

The product of reaction (7) was not found, nor were the disproportionation products of CH_3° and CH_3E°. Application of steady state theory to reactions (1),(2),(3) and (8) gives

$$\frac{d[CH_3EI]}{dt} = \frac{k_2[E]}{2k_8^{\frac{1}{2}}}$$

When addition to two different sites is considered and if the reaction is taken only to small conversion, this equation becomes:

$$\frac{[CH_3EI]_f}{[CH_3E'I]_f} = \frac{k_2[E]}{k_2'[E']}$$

where $[CH_3EI]_f$ and $[CH_3E'I]_f$ are the final concentrations of the two adducts, be they isomeric or from two different olefins.

The biggest source of error is the possible reversibility of reaction (3). The reaction is approximately themoneutral and hence almost certainly reversible. To minimise the reverse reaction, a high concentration of methyl iodide was used in all the kinetic experiments. Tables II-14,15 show the effect on adduct ratios for 1,1-difluoroethylene and trifluoroethylene of varying the concentration of methyl iodide. At the temperatures studied, there appeared to be little difference in the adduct ratios which could not be accounted for by experimental errors. The reversible nature of reaction (3), therefore, did not seem to be of great importance. Table II-16 shows that reaction at the surface was not of importance, certainly in the case of vinyl fluoride. The results of the experiments on methyl iodide concentration and temperature were assumed to be applicable to all the olefins studied.

The results of kinetic experiments on the addition to fluoroethylenes are shown in tables II-3 to II-1b. Some of the kinetic parameters can be determined through more than one route and the similarity in values so found is good evidence as to the validity of the method.

From the results in table II-6 the differences in the Arrhenius parameters for addition of methyl radical to ethylene and to the CH_2- end of vinyl fluoride are found to be $\Delta \log A_2 = -0.14 \pm 0.03$ and $\Delta E_2 = -0.93 \pm 0.2$.† If the results of Cvetanović and Irwin for addition to ethylene are used,[63] then $\log A_2$ and E_2 for addition to CH_2- in vinyl fluoride become 9.04 ± 0.03 and 8.8 ± 0.2 respectively. Combining these results with those of table II-5, gives $\log A_2 = 9.5 \pm 0.03$ and $E_2 = 9.9 \pm 0.2$ for addition to CHF- in vinyl fluoride. From tables II-8 and II-3 and using these figures for vinyl fluoride, the Arrhenius parameters for addition to trifluoroethylene can be determined as $\log A_2 = 8.2 \pm 0.8$ and $E_2 = 8.6 \pm 0.06$ (for addition to CHF-) and $\log A_2 = 7.8 \pm 0.04$ and

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† A_2 is measured in ℓ $mole^{-1}$ s^{-1} and E_2 in kcal $mole^{-1}$

E_2 = 6.2 ± 0.3 (for addition to CF_2-).

Arrhenius parameters for methyl addition to tetrafluoroethylene can be obtained from table II-7 and the figures computed for trifluoroethylene (i.e. via the sequence $CH_2{:}CH_2$ against $CHF{:}CH_2$, $CHF{:}CH_2$ against $CHF{:}CF_2$ and $CHF{:}CF_2$ against $CF_2{:}CF_2$) or directly from table II-10. The former three step comparison gives log A_2 = 8.9 ± 0.06 and E_2 = 4.8 ± 0.5 which is in reasonable agreement with the direct competition values of log A_2 = 8.0 ± 0.09 and E_2 = 5.3 ± 1.1.

Absolute data for the addition to the CH_2: end of 1,1-difluoroethylene can be obtained from table II-9, using the Arrhenius parameters for vinyl fluoride calculated above. Alternatively, they can be obtained more directly from table II-11. The two step computation via vinyl fluoride yields log A_2 = 9.8 ± 0.06 and E_2 = 11.2 ± 0.5 while the direct competition values are log A_2 = 10.2 ± 0.11 and E_2 = 12.2 ± 1.0. The agreement between the two pairs of figures is reasonable but the former are to be preferred. The difference in reactivity between ethylene and 1,1-difluoroethylene towards methyl radicals is so great that accurate measurement of adduct ratios is difficult.

Although there has been no previous study of the kinetic parameters for addition at each end of these olefins, Szwarc and Stefani have obtained overall rates for addition at one temperature (65°C).[83] The values of the rate constants at 65°C calculated from the above parameters for the total rate of addition (i.e. the sum of the rate constants for addition at each end) and the values of Szwarc and Stefani are shown in table II-23. (The rate constants are relative to unity for ethylene.)

TABLE II-23 RELATIVE OVERALL RATES OF ADDITION OF METHYL RADICALS TO FLUOROETHYLENES

Olefin	Overall Rates of Addition	
	This work	ref 83
$CH_2{:}CH_2$	1.00	1.00
$CH_2{:}CHF$	0.70	0.53
$CH_2{:}CF_2$	0.11	0.65
$CHF{:}CF_2$	1.06	1.50
$CF_2{:}CF_2$	≃6.30	10.1

The agreement between this work and that of Szwarc and Stefani is very good, only in the addition to vinylidene fluoride is there a considerable deparature.

The addition of methyl radicals to tetrafluoroethylene has been previously studied and Arrhenius parameters determined.[64] The values found were log $A_2 = 8.95 \pm 0.23$ (l $mole^{-1}s^{-1}$) and $E_2 = 5.7 \pm 0.4$ kcal $mole^{-1}$. The agreement with the values found from this work with those of Sangster and Thynne is very good, moreover a consistency is apparent in going from the work of Cvetanović and Irwin through this work to that of Sangster and Thynne. Buckley and Szwarc have also studied the addition to ethylene and tetrafluoroethylene in solution[55a] and find that the differences in activation parameters are $\Delta\log A_2 = 0.6$ and $\Delta E_2 = 2.2$, values which are very similar to those found from table II-10.

Table II-13 gives the data for the competitive reaction with ethylene and propylene. No evidence for addition to the CH_3CH- end of the double bond in propylene could be detected i.e. addition was exclusively at the terminal carbon atom. The observed values for the differences in Arrhenius parameters are $\Delta\log A_2 = 1.04 \pm 0.02$ and $\Delta E_2 = -0.75 \pm 0.4$. These values agree well with those of Cvetanović and Irwin of $\Delta\log A_2 = 0.42$ and $\Delta E_2 = -0.5$. According to Mandelcorn and Steacie, to Cvetanović and Irwin and to this work, the activation energies are slightly lower for addition to propylene and the reduced rate is almost entirely due to a lower pre-exponential factor. The data of Szwarc and of Brinton and co-workers gives virtually the same activation energy for addition to both ethylene and propylene but again the slower rate is attributable to a lower pre-exponential factor. In fact, the differences between all five sets of work are probably within experimental error, and an extremely coherent picture is represented.

As with propylene, evidence was found only for addition at one end of vinyl chloride, the CH_2 end. This observation is in line with studies on CF_3.[84] and CCl_3[85] addition. It is a possibility that the 2-chloropropyl radical resulting from addition to the CHCl- end decomposed before taking part in reaction (3). However, attack at this end is likely to have been small and may be neglected. The differences in Arrhenius parameters calculated from table II-12 are $\Delta\log A_2 = -0.54$ and $\Delta E_2 = -1.87 \pm 0.5$ These values agree well with the differences observed by Hogg and Kebarle of $\Delta\log A_2 = -1.33$ and $\Delta E_2 = -1.23$. At 64°C, the observed parameters give a rate of addition relative to ethylene of 3.98, agreeing favourably with the values of 2.7 (Hogg and Kebarle) and 5.7 (Szwarc).

Although no previous attempt has been made to find the Arrhenius parameters for addition of methyl radicals to each end of unsymmetric olefins, there are sufficient data on total rates with which this study may be compared. The agreement between this work and previous studies is very good and increases confidence in the method. Although no absolute rates have been determined, steps have been made between four sets of absolute determinations and all appear to be mutually consistent. The calculated Arrhenius parameters are shown in table II-24. The values are all relative to the values of Cvetanović and Irwin for addition to ethylene. (These values are close to the preferred values suggested by Kerr and Parsonage.[32]) The trends in table II-24 show marked differences from those in tables I-11 and I-12 (p 30) which are very similar to each other. In both tables I-11 and I-12, moving along the first row shows a marked increase in activation energies but in table II-24, the activation energies are all very similar. The first columns of tables I-11 and I-12 show much slower increases in the activation energies, while for addition to the fluoroethylenes in table II-24, a very marked increase is apparant. It can also be pointed out that for addition of methyl radicals, the highest activation energy occurs for the CH_2- end of vinylidene fluoride but that for addition of n-heptafluoropropyl or trichloromethyl radicals the highest activation energy is for the CF_2- end of vinylidene fluoride.

The differences in behaviour of these radicals can also be shown by the orientation ratios for the unsymmetrical fluoroethylenes - table II-25. Addition to the more fluorinated

Table II-24 Addition of Methyl Radicals in the Gas Phase

Addn. to CH_2:	log A_2	E_2	Addn. to CFH:	log A_2	E_2	Addn. to CF_2:	log A_2	E_2
CH_2:CH_2	8.6	7.9	CFH:CH_2	9.5	9.9	CF_2:CH_2	7.9	8.2
CH_2:CHF	9.2	8.8				CF_2:CHF	7.8	6.2
CH_2:CF_2	9.8	11.2	CFH:CF_2	8.2	8.6	CF_2:CF_2	7.7	5.3
CH_2:CHCl	8.4	9.8						
CH_2:$CHCH_3$	7.9	7.1						

E_2 in kcal $mole^{-1}$

A_2 in l $mole^{-1}$ s^{-1}

end of the olefin is increased by at least a factor of ten. This is totally consistent with the previous observations that addition of methyl radicals to tetrafluoroethylene was much faster than to ethylene. The most important consequence of this increased reactivity towards the more fluorinated ends of the olefins is the reversal of the preferred orientation in trifluoroethylene. This is the first occasion that radical addition has gone in a reverse manner to that suggested by the simple Mayo-Walling theory. Haszeldine and co-workers have, however, in a preparative system observed reversal of orientation of addition of dimethylphosphine to trifluoroethylene.[86] The ratio of the products was 48 : 52. This compared with 2 : 98 for addition of di-(trifluoromethyl)phosphine and it was concluded that the difference was one of electrophilicity of the radicals. The phosphine radical itself gave the orientation ratio 15 : 85. More recently it has been found that this reversal of orientation is also exhibited by

TABLE II-25 ORIENTATION RATIOS FOR ADDITION TO FLUOROETHYLENES AT 150°C

Radical	CH_2 : CFH	CH_2 : CF_2	CFH : CF_2
CCl_3	1 : 0.077	1 : 0.012	1 : 0.29
C_3F_7	1 : 0.050	1 : 0.009	1 : 0.25
CH_3	1 : 0.588	1 : 0.179	1 : 7.26
C_2H_5	1 : 0.305	-	1 :13.30

monofluoromethyl radicals.[87]

To increase the nucleophilicity of the attacking radical, the addition of ethyl radicals was studied. The results of the study of methyl addition using the photolysis of azomethane were so encouraging that the same method was applied to the analagous ethyl system. The results of the kinetic experiments are shown in tables II-18 to II-22. The cross-checking as carried out on the methyl addition was not done since the applicability of the method had now been established. Combining the results of the kinetic experiments produced the Arrhenius parameters shown in table II-26. The values are all relative to the activation parameters of Watkins and O'Deen for addition of ethyl radicals to ethylene.

Comparing the figures of table II-26 with those of II-24 shows that the olefins are less reactive towards ethyl addition than methyl addition. The decreased reactivity manifests itself in the lack of data for vinylidene fluoride. This olefin, which was the least reactive towards methyl radicals, showed no evidence of adduct formation with ethyl radicals under the conditions used. The decreasing reactivity of alkyl radicals with increasing chain length has been noted by Kerr and Parsonage,[32] but they conclude that present methods of study are not sufficiently accurate to determine if this is due to increased activation energies or lower pre-exponential factors. The figures of table II-26 suggest that it is

Table II-26 Addition of Ethyl Radicals in the Gas Phase

Addn to CH_2:	log A_2	E_2	Addn. to CHF:	log A_2	E_2	Addn to CF_2:	log A_2	E_2
CH_2:CH_2	8.17	7.56	CFH:CH_2	8.57 ±.07	10.99 ± 1.03	C		
CH_2:CHF	8.59 ± .05	10.01 ± .5				CF_2:CFH	7.90 ± .03	8.11 ± .6
			CFH:CF_2	8.31 ±.06	11.07 ± .8	CF_2:CF_2	6.57 ±.07	3.16 ± .8

E_2 in kcal $mole^{-1}$

A_2 in l $mole^{-1}$ s^{-1}

more a function of higher activation energies, although the reason for this is not apparent.

The decreased reactivity can also be seen in the orientation ratios (table II-25). The proportion of attack at the less fluorinated end of vinyl fluoride increases over that for methyl addition and yet for trifluoroethylene, addition is even more favoured at the more fluorinated end than is the case for methyl addition. At first, this behaviour might appear anomalous but the lesser reactivity of ethyl radicals is paralleled by a greater selectivity as shown by the orientation ratios.

There have been many theoretical attempts at interpreting the rates and Arrhenius parameters of methyl and ethyl addition reactions, and hopefully producing a predictive picture. By far the greatest proportion of the early correlations were for rates of addition to aromatic systems. The free valence and localisation energy have been found to correlate well, as has the singlet-triplet excitation energy, with the logarithm of the rate constant. However, in these correlations, an internal energy is effectively being equated with the free energy of the reaction, the constancy of the entropy from one reaction to an other is implied. While this may be true for systems in which there is an identical substitution pattern at the double bond under consideration, it is not generally true. The steric changes in the system will be associated with a corresponding change in the pre-exponential factor. This was recognised by Jennings and Cvetanović[85] who used hydrogen atoms as the attacking species in the expectation that any steric effects would be minimised. They subsequently found that there was a correlation with localisation energies but not with f.v.i. However, it would be more satisfactory to achieve correlations between activation energies and the appropriate molecular property. To this end, Yang[46] studied the addition of hydrogen atoms to similar hydrocarbons and confirmed the studies of Jennings and Cvetanović by finding correlations of the activation energies with localisation energies but not with the f.v.i. (The steric effects in addition of methyl and ethyl radicals had been recognised by Buckley and Szwarc[89] and James and Steacie[90] in reactions with alkyl substituted olefins.)

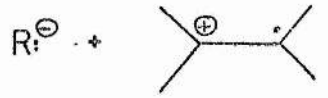
The correlation of rates of ethyl radical addition have been considered by Bloor, Brown and James.[51] A reasonable correlation of localisation energies with rates of addition, but the correlation with activation energy is poor. The correlations of f.v.i. with rates and activation energies are also poor. Those workers conclude that the reactivity index to be considered appropriate to alkyl radical addition is the atom localisation energy.

Using the localisation energies of Part I, no correlation with activation energies for methyl or ethyl addition is apparent. Even introducing the polar term as shown in part I, does not improve either correlation. It is apparent then that, although the simple Mayo-Walling picture is totally inadequate to describe the observations - particularly the reversal of orientation of addition to trifluoroethylene - the correlations which held for the electrophilic radicals, trichloromethyl and heptafluoropropyl, are also inadequate. The lack of correlation may be compared with the observations in oxygen atom addition. Moss[91] has found that the relative rate constants for $O(^3P)$ addition to the fluoroethylenes do not correlate with calculated quantities. It is also interesting to note that as with methyl and ethyl radical addition, the rates of oxygen atom addition decreases from ethylene to 1,1-difluoroethylene and then increase so that addition to tetrafluoroethylene is faster than to ethylene. However, the postulated transition states for addition of oxygen atoms and of alkyl radicals are somewhat different (this point will be clarified in Part IV).

As discussed in part I, the main approaches to considering reactivity in chemical reactions were the static and localisation ideas. The next step was the "delocalisation" approach as developed by Fukui and his co-workers.[92] In this approach, a hyperconjugation is assumed to occur between the π-electron system of the substrate and the quasi π-orbital of the attacking species. The "hyperconjugation energy" is then the stabilisation energy produced by charge transfer in a heterolytic reaction or by the increased delocalisation of the single electron in a radical reaction. The calculation of the hyperconjugation energy, however, has its difficulties in that to obtain a value for it, some value must be fixed for the energy of the quasi π-system.

The reactivity indices developed in this approach are dependent on assuming that only the frontier electrons i.e. those in the highest occupied molecular orbitals are involved in the reaction and that the major contribution to the activation energy is the energy associated with changes in the energies of these electrons. The most commonly encountered indices are the frontier electron density and the superdelocalisability. Both these indices have had success in predicting the relative reactivities in molecules with a definite reagent.[92]

Within the framework of the delocalisation approach, a model for addition to olefins can be suggested involving the frontier orbitals.[93] The model can theoretically be used for any character of radical. The orbitals considered are the highest bonding orbital of the olefin, the lowest anti-bonding orbital of the olefin and the singly occupied orbital of the radical and the electron shifts between these radicals are assumed to make up the major contribution to the activation energy. For addition of electrophilic radicals, the electron which is localised at the site of attack should be captured by the radical giving rise to (in the extreme case):



For addition of a nucleophilic radical, the single electron on the radical is donated to the lowest anti-bonding orbital of the olefin and (again in the extreme case) we get:

The extent of these charge transfers should be dependent on the electron affinities and the ionisation potentials and the pictures only represent the extreme results of electron shifts. The true picture would be one in which only partial charges develop at the reaction centres. The activation energy then becomes dependent on both the localisation energy and the charge transfer energy. In fact, this again is probably an over simplification of the true situation since electron repulsions and steric factors are neglected.

The addition of radicals to monomers in free-radical polymerisation has also been considered by Yonezawa and his co-workers.[94] Again within the delocalisation approach, the interconjugation energy was defined as:

$$\Delta E_{r,s} = 2\left(\sum_{m}^{occ}\sum_{n}^{unocc} - \sum_{n}^{occ-N}\sum_{m}^{unocc}\right)\frac{(a_r^{m})^2(b_s^{n})^2(\Delta\beta)^2}{F_n - E_m} + \left(\sum_{m}^{occ} - \sum_{m}^{unocc}\right)\frac{(a_r^{m})^2(b_s^{N})^2(\Delta\beta)^2}{F_N - E_m}$$

This equation treats the reaction as a perturbation of the orbitals on the olefin and the radical (the a_r^m and b_s^n being orbital coefficients on the olefin and radical respectively and the F_n and E_m being eigenvalues of the molecular orbitals). The activation energy was then related to the interconjugation energy by the equation,

$$E_a = C - (\Delta E)_{r,s}$$

in which C is a constant that relates to the σ-electron part of the activation energy, E_a. Considerable success was obtained in correlating the activation energies for the reaction between several radical-monomer pairs. The application of the equation, however, requires a knowledge of the molecular orbitals of the reactants and products within the Hückel approximation.

PART III

The Addition of Trimethylgermyl Radicals to Fluoro-ethylenes

PART III

INTRODUCTION

Although no other satisfactory general theory of free radical addition has been developed, the Mayo-Walling theory, in its simplest form, has been shown to be totally unacceptable. In Part II of this thesis, the theory was shown not even to be truly predictive in the addition of the relatively nucleophilic alkyl radicals, methyl and ethyl. In order to investigate still further the importance of the polar effect, a study of the addition of trimethylgermyl radicals was made.

Since the other members of group IVb in the periodic table are all more electropositive than carbon, radicals with one of these elements as the radical centre should tend to release electrons more readily to a substrate in the transition state. Thus, these radicals should show some differences from carbon radicals, at least in the polar factors involved, in radical additions. Some evidence has been accumulated in support of such polar effects in reductions by organotin and organosilicon hydrides.

One of the most striking differences between carbon free radicals and radicals of the other group IVb elements is apparent in abstraction reactions. While the former preferentially abstract hydrogen atoms, the latter abstract halogen atoms preferentially. The explanation for this phenomenon is thermodynamic. One of the factors determining the rate of abstraction is the exothermic or endothermic nature of the reaction.[47] This in turn is dependent on the strengths of the bonds made and broken, D(R_3M-X) and D(X-R'). If the R_3M-X bond is strong and the X-R' bond is weak, then the reaction will be fast. For carbon, bonds to hydrogen are stronger than bonds to halogens while for the other group IVb elements, the opposite is true. Thus, the behaviour in abstraction is easily accountable. However, the strengths of the bonds in question must to some extent at least be a function of the polar nature of the R_3M- moiety.

Although considerable kinetic data are available for addition of carbon radicals, our knowledge of the addition of hetero-atom radicals is essentially limited to preparative uses.[95] This is extensive due to the importance of the reaction in that it provides an incursion to organometallic compounds with functional groups present. The first report of an addition of a group IVb radical was the benzoyl peroxide initiated addition of trichlorosilane to 1-octene, when a chain mechanism was proposed.[96] An analogous reaction was found to occur between trichlorogermane and 1-hexene.[97] And two years later, the addition of triphenylstannyl radicals to acrylonitrile was reported.[98] Trimethyllead was reported to add to ethylene[99] at a rate faster than the tin compound, continuing the trend in going from silicon to lead. Only the additions of silicon radicals have subsequently been studied to a great extent, largely due to the industrial importance in polymerisation initiation processes.

Jackson has considered the thermochemistry involved in the addition of group IVb trialkyl radicals to ethylene.[100] The calculated heats of reaction are shown in table III-1. In the additions of methyl and trialkylsilyl radicals, reaction

$$R_3M^\bullet \; + \; CH_2 = CH_2 \;\rightleftharpoons\; R_3MCH_2 - CH_2^\bullet \qquad (1)$$

$$R_3MCH_2CH_2^\bullet \; + \; R_3MH \;\longrightarrow\; R_3MCH_2CH_3 \; + \; R_3M^\bullet \qquad (2)$$

Table III-1 Heats of Reactions in Addition of $R_3M^\bullet$ to Ethylene

(M = Group IVb element)

M	C(methyl)	Si	Ge	Sn	Pb
H for rn. (1)	-26	-18	+3?	+5	+24
H for rn. (2)	+6	-13	-16 ?	-32	-48

(1) is non-reversible, but the additions of trialkyl-germane, -stannane and -plumbane were predicted to be reversible on the basis of the thermochemistry of the addition step. The reversibility of germyl addition was demonstrated in the addition of trimethylgermyl to cis-1-deuterio-1-hexene,[101] the isomerised olefin was detected in reactions above 80°C. The reversible nature of the trimethylstannyl radical at room temperature had already been established by the same method.[102]

The kinetics of reactions of group IVb radicals have not been as extensively studied as is the case for carbon radicals. There are data for abstraction by various silyl radicals[75,103] but only comparatively recently have comprehensive data been obtained for abstraction by trimethylgermyl and trimethylstannyl.[104] The addition reactions, however, appear to have escaped kinetic study.

The addition to fluoro-olefins has been studied by Haszeldine and his co-workers in a semi-quantitative fashion.[105] Their studies have, however, been resticted to silyl radicals, $Cl_3Si\cdot$ [105a,b], $MeCl_2Si\cdot$ [105c], $Me_2HSi\cdot$ [105d] and $Me_3Si\cdot$ [105e,f,g]. Frequently, the adducts were found to decompose after formation. There are no reports of addition of radicals of the other group IVb elements to fluoro-olefins. On the basis of the heats of reaction for the addition and hydrogen abstraction steps shown in table III-1, it was decided the kinetics of reaction of trimethylgermyl radicals might merit study. The source used was the photolysis, in quartz, of trimethylgermane, as previously used in studying halogen abstraction.[104]

PART III

EXPERIMENTAL

1. Materials

Trimethylgermane was prepared by $LiAlH_4$ reduction of trimethylgermanium bromide (Emanuel) in a method analogous to that of van der Kerk for preparation of triorganostannanes.[106] It was stored in the dark at liquid nitrogen temperature. The ethylenes were treated as previously described. All reactants were thoroughly degassed, after trap-to-trap distillation, before use.

2. Apparatus and Procedure

Because the concentration of the termination product, hexamethyldigermanium, was very low and its boiling point is fairly high, compared with the other products of reaction, to ensure its complete distillation into a sample tube, a re-designed reaction vessel was employed (figure III-1). The

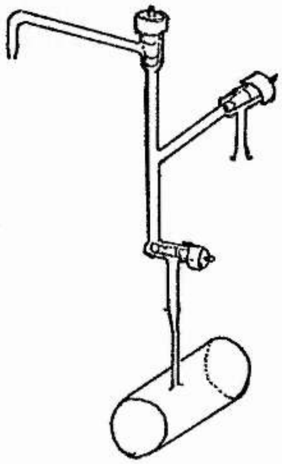


Figure III-1

rest of the apparatus and procedure were as described previously with the exception that instead of distilling the reaction mixture into a tube on the main manifold, it was distilled into a sample tube on the side arm of the reaction vessel. The reaction vessel was cylindrical and made of quartz. Analysis was on a 6 ft, 20% silicone oil on silanised 'Chromosorb' column.

3. Identification of products

The adduct peaks on the g.l.c. trace of the reaction mixtures were identified by g.l.c. coupled mass spectrometry. The mass spectra of tetra-alkylated germanes have been previously recorded.[107] These workers found two different base peaks for tetramethyl- and tetraethyl- germanes, namely, Me_3Ge^+ and $HGeEt_2^+$, respectively. In neither case was the parent ion very large, with the tetramethylated compound showing the smaller parent. In the spectra of the adducts of trimethylgermane and the fluoroethylenes, the parent ions were absent or present in less than 1%. The base peak was Me_3Ge^+, the primary fragmentation appearing to be loss of the fluoroalkyl chain. The rest of the spectra then showed the fragmentation of the Me_3Ge^+ ion. The fluoroethyl ion and its decomposition ions were present. Thus, while the mass spectra could indicate the adduct peaks, it was difficult to ascertain, with certainty, which was which. The additional confirmation came from n.m.r. spectra.

For each fluoroethylene, several high conversion runs were done and the products accumulated. Trap-to-trap distillation on the line could remove most of the remaining hydride, leaving the adducts in sufficient concentration for the n.m.r. spectra to be obtained in microcells. The spectra were recorded at 100 Hz in carbon tetrachloride solution using chloroform as the internal standard (the chemical shifts are all quoted relative to tetramethylsilane). The absorptions due to the fluoroethyl portions of the adducts are shown in table III-2. The absorption due to the Me_3Ge- group in the adducts is not recorded since in each case, this signal will be contaminated by the absorption by the residual hydride present.

Hexamethyldigermanium was identified by g.l.c. coupled mass spectrometry, the spectrum being identical to that reported by de Ridder and Dijkstra.[108]

4. Details of reactions

The results of the runs conducted under kinetic conditions are shown in tables III-3 to III-6.

Table III-2. N.M.R. Spectra of Adducts

Adduct	Spectrum
$Me_3GeCF'H'CF_2H$	triplet of doublets centred at τ4.02 with coupling constants: J_{HF} = 57 Hz; $J_{HF'}$ = 9 Hz; $J_{HH'}$ = 4 Hz. The signal due to H', which would be very complex, was not resolvable from the signal due to the Me_3Ge- group.
$Me_3GeCF_2CF'H_2$	doublet of triplets centred at τ 5.64 with coupling constants: $J_{HF'}$ = 47 Hz; J_{HF} = 15 Hz.
$Me_3GeCH_2CF_2H'$	triplet of triplets, due to H', centred at τ4.36 with couploing constants: $J_{H'F}$ = 58 Hz; $J_{H'H}$ = 4.5 Hz; triplet of doublets, due to H, centred at τ 8.94 with coupling constants : J_{HF} = 22 Hz; $J_{H'H}$ = 4.5 Hz.
$Me_3GeCH_2CH_2'F$	doublet of triplets, due to H', centred at τ 5.47 with coupling constants: $J_{H'F}$ = 51 Hz; $J_{H'H}$ = 8 Hz; doublet of triplets, due to H, centred at τ 8.76 with coupling constants: J_{HF} = 21 Hz; $J_{H'H}$ = 8 Hz.

(All spectra were found to integrate correctly).

Table III-3 Effect of varying $[Me_3GeH]_i$ and temperature on addition to 1,1-difluoroethylene.

Temp (^oC)	$[Me_3GeH]_i$ (mole l^{-1} x 10^3)	$[Ge_2Me_6]/[Me_3GeCH_2CF_2H]$		$[Ge_2Me_6]/[Me_3GeCF_2CH_3]$	
68	2.55	.0078;..0100; .0095	ave = .0091	.4547; .5348; .4765	ave = .4887
	2.05	.0123; .0127; .0082	ave = .0111	.4164; .4248; .3571	ave = .3994
	1.79	.0127; .0142; .0100	ave = .0123	.3228; .3263; .3598	ave = .3363
	1.53	.0137; .0129; .0145	ave = .0137	.5507; .4695; .5013	ave = .5072
	1.28	.0198; .0162; .0153; .0164	ave = .0169	.6383; .7287; .4789; .4315	ave = .5694
98	2.55	.0104; .0094; .0076	ave = .0091	.4164; .4172; .3695	ave = .4010
	2.13	.0117; .0141; .0109; .0122	ave = .0122	.4162; .4065; .3556; .4173	ave = .3989
	2.05	.0152; .0138; .0147	ave = .0146	.7400; .5984; .6397	ave = .6594
	1.70	.0106; .0158; .0145	ave = .0136	.4805; .6706; .5583	ave = .5698
	1.36	.0128; .0185; .0214	ave = .0206	1.0922; .7563; .7582	ave = .8689
	1.28	.0186; .0199; .0217; .0218	ave = .0205	.5808; .6075; .6716; .6218	ave = .6204
	1.02	.0237; .0252; .0218	ave = .0236	.9474; .7629; .7031	ave = .8045
115	2.55	.0076; .0093; .0077	ave = .0082	.2915; .3060; .2600	ave = .2858
	2.13	.0116; .0114; .0125	ave = .0118	.3728; .3929; .4295	ave = .3984

	2.05	.0138; .0130; .0125	ave = .0131	.5108; .4472; .4096	ave = .4559
	1.70	.0149; .0168	ave = .0159	.5237; .5904	ave = .5571
	1.36	.0222; .0190; .0185	ave = .0199	.7961; .7331; .7380	ave = .7557
136	2.55	.0099; .0105; .0097	ave = .0100	.5066; .4548; .4423	ave = .4679
	2.13	.0133; .0130; .0113	ave = .0125	.5474; .6502; .4728	ave = .5568
	2.05	.0130; .0167; .0157	ave = .0151	.9296; .8133; .7558	ave = .8329
	1.70	.0210; .0273; .0237	ave = .0240	1.2518; 1.4955; 1.1291	ave = 1.2921
	1.36	.0207; .0270	ave = .0238	1.2522; 1.7420	ave = 1.4971

$[CH_2{:}CF_2] = 1.25 \times 10^{-3}$ mole l^{-1} ;   photolysis time = 1800 s .

Table III-4 Effect of Temperature on Adduct Ratios for Addition to Vinyl Fluoride

Temp (°C)	No. of Runs	$[Me_3GeCH_2CH_2F] / [Me_3\overset{Ge}{\wedge}CHFCH_3]$	
80±2	3	3.57;3.33;3.03	ave = 3.31
104±°2	3	3.03;2.86;2.86	ave = 2.92
124±2	3	2.23;2.56;2.44	ave = 2.41

$[Me_3GeH] = 5.12 \times 10^{-4}$ mole l^{-1}; $[CH_2{:}CHF] = 2.15 \times 10^{-4}$ mole l^{-1}; photolysis time = 3600 s.

Table III-5 Effect of Temperature on Adduct Ratios for Addition to Trifluoroethylene

Temp. (°C)	No. of Runs	$[Me_3GeCHFCF_2H] / [Me_3GeCF_2CH_2F]$	
82±2	3	1.96;2.08;2.08	ave = 2.04
114±2	3	2.04;2.20;2.17	ave = 2.13
125±1	3	2.20;2.30;2.25	ave = 2.25
144±2	3	2.33;2.22;2.12	ave = 2.22

$[Me_3GeH] = 1.02 \times 10^{-3}$ mole l^{-1}; $[CHF{:}CF_2] = 4.31 \times 10^{-4}$ mole l^{-1}; photolysis time = 1800 s.

Table III-6 Variation of Light Intensity on Addition to 1,1-Difluoro-ethylene

Light Intensity	No. of Runs	$[Me_6Ge_2]_f/[Me_3GeH]_i$	
1.000	4	.00199; .00207; .00240; .00226	ave = .00218
0.650	4	.00131; .00127; .00190; .00181	ave = .00157
0.460	4	.00077; .00068; .00077; .00081	ave = .00076
0.320	4	.00054; .00036; .00041; .00059	ave = .00038
0.0		0.0	

$[CH_2:CF_2]_i = 2.15 \times 10^{-4}$ mole l^{-1}; $[Me_3GeH]_i = 5.11 \times 10^{-3}$ mole l^{-1}; photolysis time = 1800 s; (light intensity is expressed as a fraction of the total output of the unfiltered lamp)

Least squares plot of light intensity against $[Me_6Ge_2]_f / [Me_3GeH]_i$ gave gradient 0.00230 ± 0.00008

PART III

DISCUSSION

The products and reaction conditions were consistent with a free radical chain mechanism. The most likely photolysis of trimethylgermane is represented by equation (a),

$$\mathrm{Me_3GeH} \xrightarrow[(=2537\,\text{Å})]{h\nu} \mathrm{Me_2\dot{G}eH} + \mathrm{Me^{\bullet}} \qquad \text{(a)}$$

rather than the homolysis of the Ge-H bond. The fates of the radicals produced in the initial photolysis step can then be represented by the equations :

$$\mathrm{Me^{\bullet}} + \mathrm{Ol} \longrightarrow \mathrm{Me\text{-}Ol^{\bullet}} \qquad \text{(b)}$$

$$\mathrm{Me^{\bullet}} + \mathrm{Me_3GeH} \longrightarrow \mathrm{MeH} + \mathrm{Me_3Ge^{\bullet}} \qquad \text{(b')}$$

$$\mathrm{(Me)_2HGe^{\bullet}} + \mathrm{Ol} \longrightarrow \mathrm{(Me)_2HGe\text{-}Ol^{\bullet}} \qquad \text{(c)}$$

$$\mathrm{Me\text{-}Ol^{\bullet}} + \mathrm{Me_3GeH} \longrightarrow \mathrm{Me\text{-}Ol\text{-}H} + \mathrm{Me_3Ge^{\bullet}} \qquad \text{(d)}$$

$$\mathrm{(Me)_2HGeOl^{\bullet}} + \mathrm{Me_3GeH} \longrightarrow \mathrm{(Me)_2HGeOlH} + \mathrm{Me_3Ge^{\bullet}} \qquad \text{(e)}$$

$$\mathrm{(Me)_2HGe^{\bullet}} + \mathrm{Me_3GeH} \longrightarrow \mathrm{Me_2GeH_2} + \mathrm{Me_3Ge^{\bullet}} \qquad \text{(c')}$$

(where Ol represents the olefin).

Whether each of the radicals produced in the primary step proceeds by abstracting a proton from the trimethylgermane or by adding to the olefin and the addend radical then abstracting a proton from the trimethylgermane, for each light quantum absorbed, two trimethylgermyl radicals are produced. The absorbance of trimethylgermane at the wavelength of the principal line in the light from the mercury arc, 2537 Å, is very low so that the chains involved in the propogation of the adduct formation appear to be very long. Thus the complicated initiation process may be capable of representation by equation (1),

$$Me_3GeH \xrightarrow[(\approx 2537\text{Å})]{h\nu} 2\ Me_3Ge^{\bullet} \qquad (1)$$

The rest of the reaction then can be accounted for by the equations:

$$Me_3Ge^{\bullet} + Ol \longrightarrow Me_3Ge\text{-}Ol^{\bullet} \qquad (2)$$

$$Me_3GeOl^{\bullet} + Me_3GeH \longrightarrow Me_3GeOlH + Me_3Ge^{\bullet} \qquad (3)$$

$$Me_3Ge^{\bullet} + Me_3Ge^{\bullet} \longrightarrow Me_6Ge_2 \qquad (4)$$

(where Ol represents olefin).

In preliminary experiments with each of the unsymmetrical fluoro-ethylenes, it was found that the adduct ratios did not appear to change uniformly with temperature as was the case in the addition of n-heptafluoropropyl, methyl and ethyl radicals. Also, the amount of the termination product, hexamethyldigermanium, increased with increasing temperature. This could be explained in three ways, (a) the recombination of trimethylgermyl radicals had an activation energy, (b) the reaction (2) was reversible or (c) in the initiation, ϕI_a was, in some way, temperature dependent. The first explanation seemed unlikely in view of the fact that trimethylsilyl radicals are known to recombine without an activation energy.[109] In view of the fact that the chains were very long, explanation (c) seemed also to be unlikely to be a major contributor.

This left (b) as the most likely explanation for the observed effects.

If reaction (2) is considered to be an equilibrium and reaction (1) is a valid representation of the initiation process, then application of steady state theory to the proposed mechanism gives:

$$\frac{d[Me_6Ge_2]}{dt} = \phi I_a/4 \qquad \text{——— (A)}$$

$$\frac{d[Me_3GeOlH]}{dt} = \frac{k_3k_2(\phi I_a/4k_4)^{\frac{1}{2}}[Ol]\,[Me_3GeH]}{k_{-2} + k_3[Me_3GeH]} \qquad \text{—(B)}$$

$$\text{and} \quad \frac{[Me_6Ge_2]_f}{[Me_3GeOlH]_f[Me_3GeH]_i^{\frac{1}{2}}} = \frac{k_4^{\frac{1}{2}}(\phi I_o\beta l)^{\frac{1}{2}}}{2k_2[Ol]_i}\left(1 + k_{-2}/k_3[Me_3GeH]_i\right) \qquad \text{——(C)}$$

(the derivation of these equations is shown in appendix III)

Equation (A) implies that the concentration of hexamethyldigermanium should be linearly related to light intensity. This was found to be the case (table III-6) and so reaction (1) appears to be a reasonable approximation. From the slope of the plot of $[Me_6Ge_2]/[Me_3GeH]$ against I_a, a value of 2.616×10^{-9} mole l^{-1} quantum^{-1} was obtained for ϕ for the initiation. Actinometry using potassium ferrioxalate gave the light intensity just inside the front window of the cell as 2.820×10^{19} quanta s^{-1}.

From equation (C), a plot of $[Me_6Ge_2]_f/\left\{[Me_3GeOlH]_f\,[Me_3GeH]_i^{\frac{1}{2}}\right\}$ against $1/[Me_3GeH]_i$ should be a straight line with gradient

$Ck_4^{\frac{1}{2}}k_{-2}/k_2k_3$ and intercept $Ck_4^{\frac{1}{2}}/k_2$ where $C = (\phi I_0\beta l)^{\frac{1}{2}}/[Ol]_i$ when experiments are carried out at constant temperature and initial olefin concentration. (The value of C for the experiments of table III-3 is 3.71×10^9.) Such experiments were carried out in which the olefin was 1,1-difluoro-ethylene (table III-3) and straight line plots were obtained (figure III-2). If it is assumed that C is temperature independent, that is, that ϕI_0 is not temperature dependent, then, with a knowledge of the rate constant for the recombination of trimethylgermyl radicals, estimates can be made of the Arrhenius parameters for the addition reaction and of the ratio, k_{-2}/k_3.

Although the recombination and cross combination rate constants have been determined for many carbon radicals, there are few such studies for radicals of the other group IVb elements. The only radicals studied in the gas phase have been those of silicon. Recently, Watts and Ingold measured the recombination rate constants for a variety of group IVb radicals in solution using electron paramagnetic resonance.[110] They found that the rate constants decreased as the molecular weight of the radical increased, and that a good correlation was obtained between log $2k_t$ and molecular weight. A similar effect was found by Bertrand et al for the combination of alkyl and halogenated alkyl radicals in the gas phase.[111] Figure III-3 shows the correlations found by both sets of workers. From this figure, an estimate for the recombination rate constant of trimethylgermyl radicals in the gas phase would be $10^{9.72}$ l mole^{-1} s^{-1}

Figure III-2a Plot of Equation (A) for Addition of Me_3GeH to CH_2- in 1,1-Difluoroethylene at 68° and 98°.

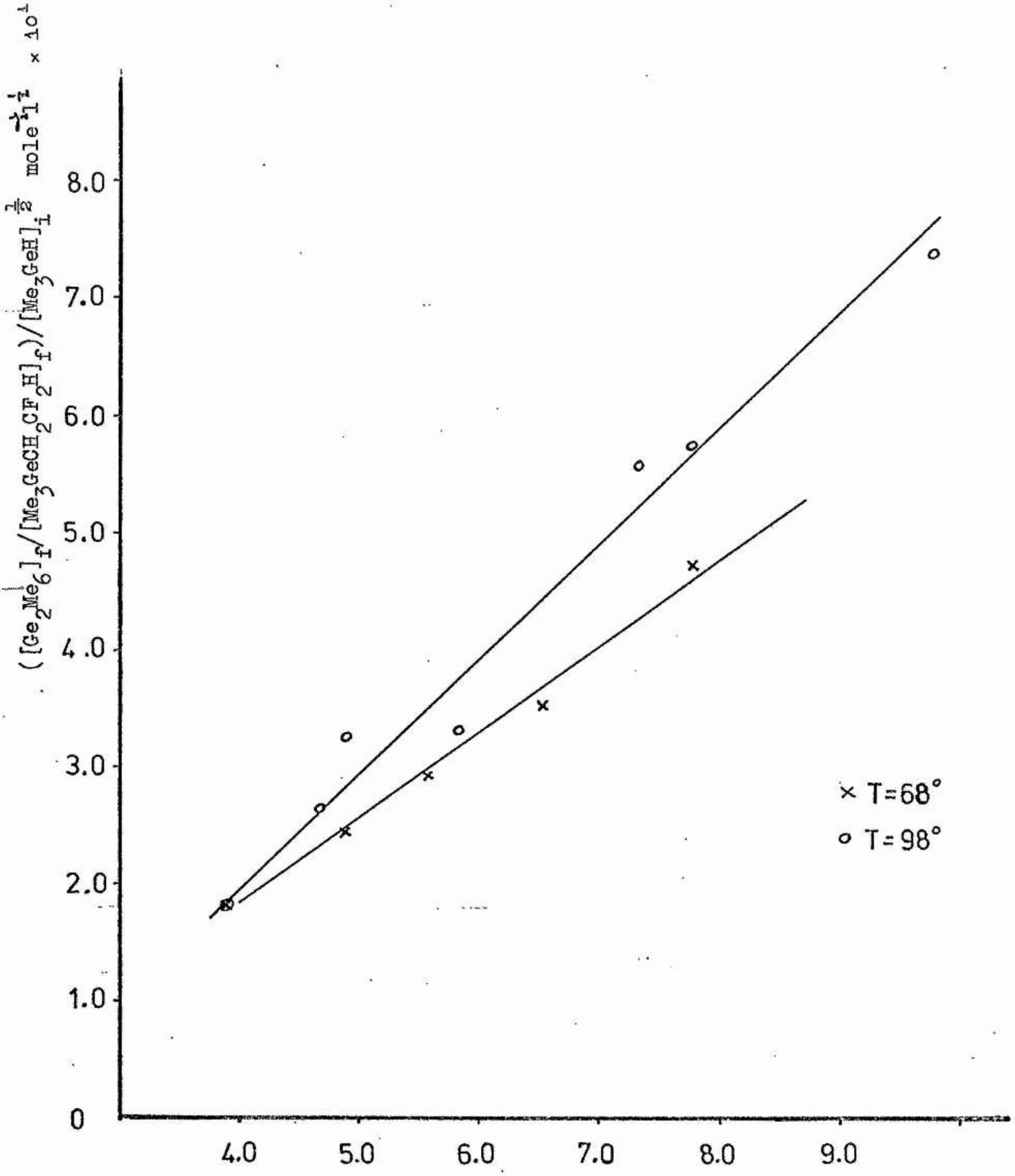


Figure III-2b Plot of Equation (A) for Addition of Me_3GeH to CH_2- in 1,1-Difluoroethylene at 115° and 136°.

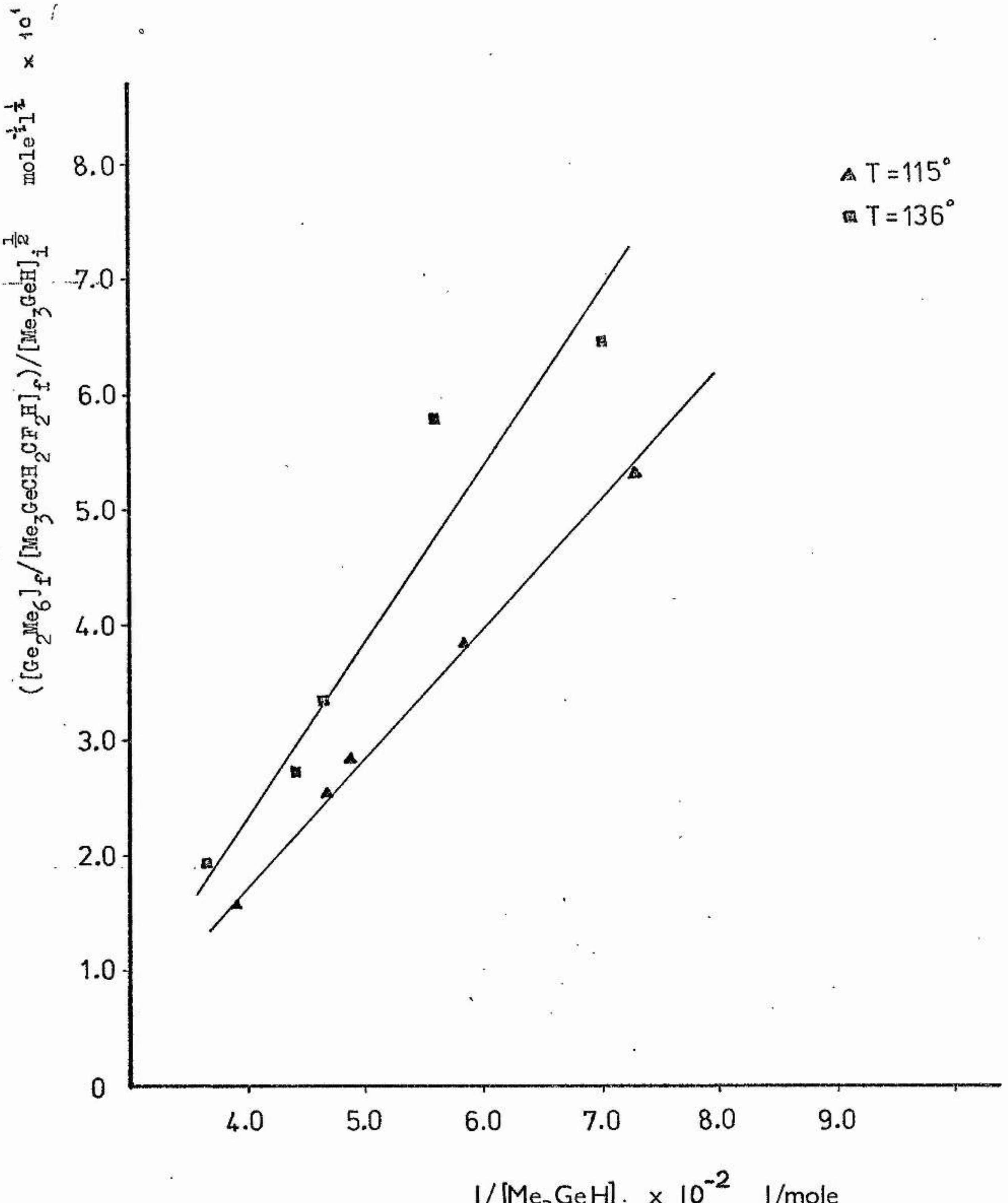
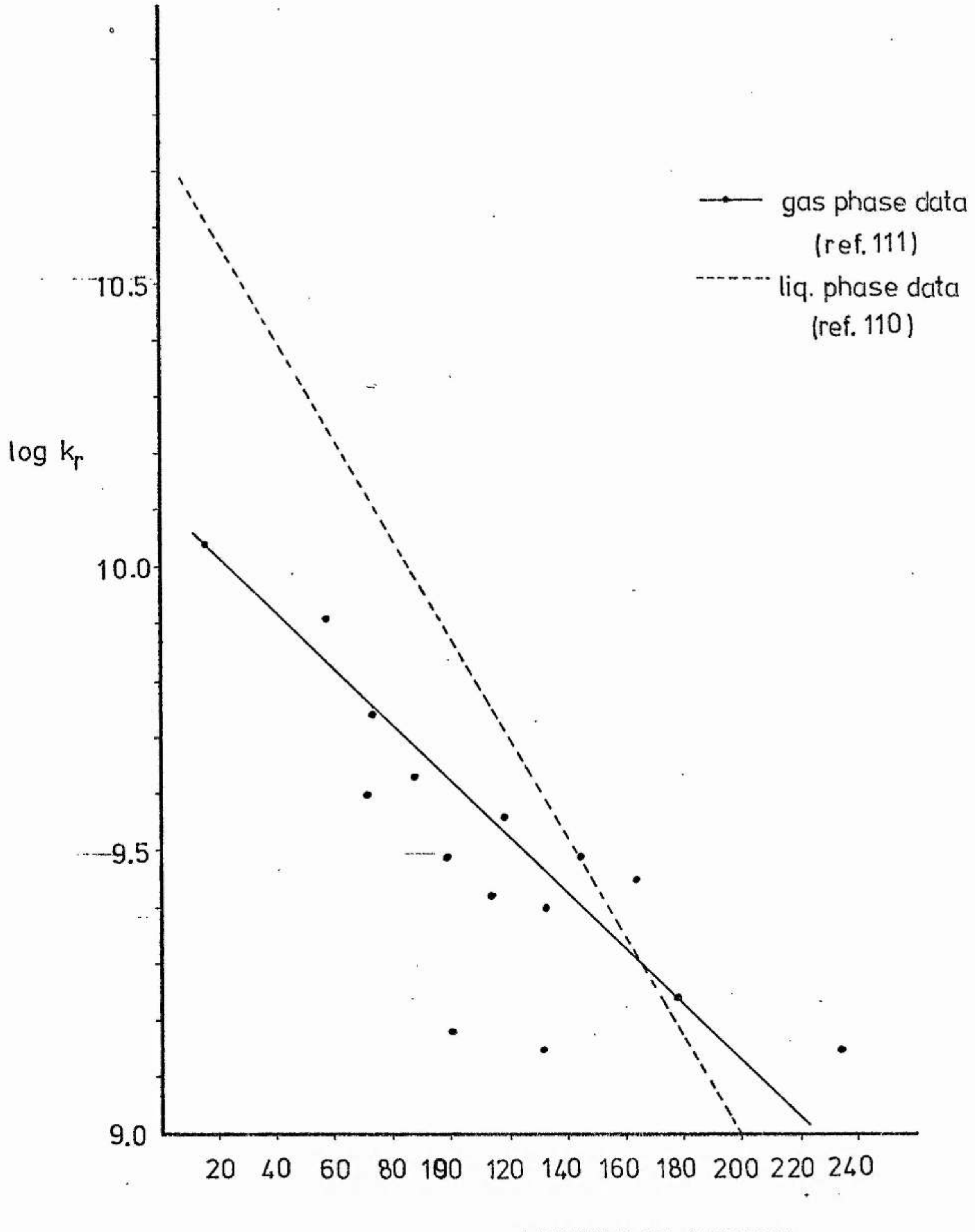


Figure III-3 Correlation of logarithm of rate constants for recombination of group IVb radicals in the liquid phase with molecular weights.



with the assumption that the activation energy is approximately zero. (This is very close to the assumed value of 10^{10} for recombination of $SF_5^{\cdot}$ radicals as used in the study of their addition to fluoro-ethylenes[112])

The gradients and intercepts found from table III-3 using equation C are shown in table III-7.

Table III-7. Gradients and Intercepts of Plots of $[Me_6Ge_2]_f / \{[Me_3GeOlH]_f [Me_3GeH]_i^{\frac{1}{2}}\}$ against $1/[Me_3GeH]_i$ for Addition to 1,1-Difluoroethylene

Temp.	$^{\searrow}CH_2{:}CF_2$		$^{\searrow}CF_2{:}CH_2$	
(°C)	Gradient	Intercept	Gradient	Intercept
68	.000678	-.0875	.00236	11.925
98	.000954	-.1807	.0277	- 2.4305
115	.001082	-.2517	.0429	-11.976
136	.001481	-.3811	.100	-31.041

For attack at the CH_2: end of the olefin, plotting log(gradient) against 1/T (T = temperature in °K) gives a gradient of -0.67×10^3 and intercept -1.21. From these values we find:

$$-\tfrac{1}{2}E_4 - E_{-2} + E_2 + E_3 = 3.06 \text{ Kcal mole}^{-1}$$

——(D)

and $$\log \frac{A_4^{\frac{1}{2}} A_{-2}}{A_2 A_3} = -10.78$$

For attack at the CF_2: end of the olefin, the same treatment gives a gradient of -0.33×10^4 and intercept 7.13 and

$$-\tfrac{1}{2}E_4 - E_{-2} + E_2 + E_3 = 15.05 \text{ Kcal mole}^{-1} \qquad \text{——(E)}$$

and $$\log \frac{A_4^{\frac{1}{2}}A_{-2}}{A_2A_3} = -2.44$$

For attack at the CH_2: end, plotting log (1.0 + intercept) against 1/T gives gradient 0.33×10^3 and

$$\tfrac{1}{2}E_4 - E_2 = -1.51 \text{ Kcal mole}^{-1} \qquad \text{——(F)}$$

For attack at the CF_2: end, plotting log (32.0 + intercept) against 1/T gives gradient 0.31×10^4 and

$$\tfrac{1}{2}E_4 - E_2 = -13.8 \text{ Kcal mole}^{-1} \qquad \text{——(G)}$$

Using the estimates for log k_4 and E_4 already derived, and assuming that A_{-2} is about 10^{13}, equations (D), (E), (F) and (G) give, for addition to the CH_2: end:

$$E_2 = 1.51 \text{ Kcal mole}^{-1}$$

$$E_3 - E_{-2} = 1.55 \text{ Kcal mole}^{-1}$$

$$\log A_2 + \log A_3 = 28.64$$

and for addition to the CF_2: end:

$$E_2 = 13.8 \text{ Kcal mole}^{-1}$$

$$E_3 - E_{-2} = 1.25 \text{ Kcal mole}^{-1}$$

$$\log A_2 + \log A_3 = 20.60.$$

The ratios of log $(A_4^{\frac{1}{2}}/A_2)$ cannot be found from the above plots because the intercepts in table III-7 are mostly negative – an observation which seems to have no physical meaning.

The orientation ratios for addition are not too meaningful in view of the reversibility of the reaction. However, it does appear anomalous in that while we might expect germanium radicals to display nucleophilic character to a greater extent than carbon radicals, no reversal of the orientation of addition is observed. The ratios can be compared with the values for the addition of $SF_5^{\bullet}$ radicals, which is also reversible (table III-8).

Table III-8. Orientation of Addition of $SF_5^{\bullet}$ and $Me_3Ge^{\bullet}$ Radicals to Fluoro-ethylenes

	CH_2 : CHF	CH_2 : CF_2	CHF : CF_2
$SF_5^{\bullet}$ [113]	—	>100 : 1[a]	>10 : 1[b]
$Me_3Ge^{\bullet}$	~ 3 : 1[c]	~ 35 : 1[d]	~ 2 : 1

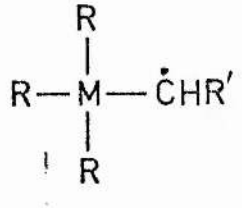
a) at 111°; b) at 92°; c) at 104°; d) at 115°

The addition of sulphur pentafluoride is seen to be more selective than the addition of trimethylgermyl radicals. The values for $SF_5^{\bullet}$ are similar to those found for addition of the fluorinated carbon radicals and it is not surprising to note that the electronegativities of sulphur and carbon are very similar. The more electropositive germanium atom seems to impart at least part of a nucleophilic effect to its radicals as is evident in the ratios of table III -8. However, the radical character appears to be tempered by some other factor which prevents the nucleophilic character coming to the fore.

The geometry of the methyl radical has been considered by many workers using both experimental and theoretical methods. It is generally accepted that the methyl radical is planar, from analysis of its electronic spectrum and its e.s.r. spectrum. Semi-empirical calculations have also shown its planarity, and more recently, ab initio calculations have confirmed these findings and have also shown that the trifluoromethyl radical is pyramidal. In these latter calculations, the C-H bond length was fixed at 1.080 Å.[114] Thus in the gas phase, when free rotation of the methyl radical is possible along all the axes, a sphere of diameter ~2.16 Å will be the time averaged size of the radical. The geometry of the trimethylgermyl radical has not been so well characterised. However, e.s.r. studies indicate that the radical is non-planar.[115] The time averaged size of this radical is going to be much larger. The covalent radius of the germanium atom itself is 1.22 Å and with a C-Ge bond length of about 1.95 Å (as found in CH_3GeH_3), it is quite apparent the much greater size of the trimethylgermyl radical as compared with the methyl radical.

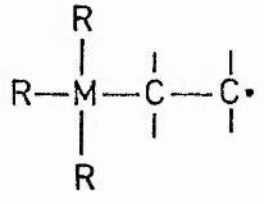
Thus, a very great steric factor is introduced to the addition of the trimethylgermyl radical. However, there is another great difference between carbon radicals and the radicals of the other group IVb elements - the existence of d-orbitals in the valence shell of the element. The extent to which these orbitals play a part in organic reactions and molecules is a matter for conjecture and a topic which has much argument in the literature. Arguments have mainly been centred round organo-sulphur chemistry and the role of the sulphur 3d orbitals in aromaticity since such systems lend themselves well to theoretical treatment.

Recently, the part played by the d orbitals on group IVb elements has stimulated research. Krusic and Kochi have measured the e.s.r. spectra of several alkyl derivatives of silicon, germanium and tin.[116] The radicals were basically of two types, α-substituted (I) and β-substituted (II). The radicals of type (I) appeared to be



$$R-\overset{R}{\underset{R}{M}}-\dot{C}HR'$$

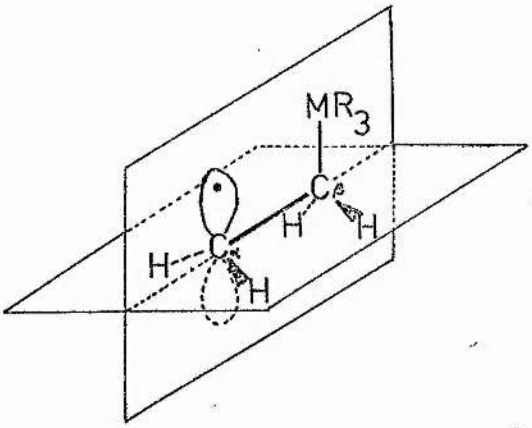
(I)



$$R-\overset{R}{\underset{R}{M}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$$

(II)

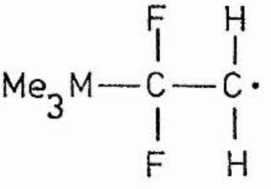
stabilised to some extent and the stabilisation could be attributed to $d_\pi-p_\pi$ electron delocalisation. For radicals of type (II), hindered rotation about the C_α-C_β bond giving rise to a preferred conformational orientation was the interpretation given for abnormally small hyperfine coupling constants. This preferred conformer had the metal atom eclipsing the p-orbital at the trigonal centre (III), and the effect



(III)

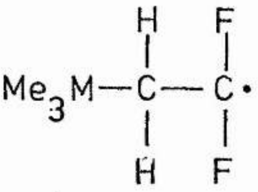
was attributed to incipient 1,3-bonding between the d-orbitals of the metal and the p-orbital of the radical centre. The barrier to rotation has been estimated at 5 kcal mole^{-1} for the radical obtained from addition of trimethylstannyl radical to 1,3-butadiene.[117] However, this area of research is likewise not free from its disagreements and counter-results. Symons[118] has denied the claims of Kochi in his postulated d-p homoconjugative delocalisation of the odd electron into the metal d-orbitals. And n.m.r. studies on stannous containing unsaturated systems indicate that d_π-p_π interactions are small.[119]

Accepting the results of Kochi, there are two ways in which the d-orbitals on the germanium radical can play a part in the addition to fluoroethylenes. Firstly, a repulsive interaction between the d-orbitals and the fluorine p-orbitals and secondly an attractive interaction with the singly occupied p-orbital on the β-carbon atom. It is likely that it is the first of these which will determine the orientation of the addition, the radical being more likely to attack at the least fluorinated end. Once the bond is formed, stabilisation of the radical by d_{π}-p_{π} interaction is likely, but it is difficult to say whether the interaction would be significantly greater in a radical of type (IV) than in type (V) due to the diffuse nature of the d-orbitals.



$Me_3M-CF_2-CH_2\cdot$

(IV)



$Me_3M-CH_2-CF_2\cdot$

(V)

Unfortunately, no e.s.r. studies have been conducted on radicals of this type, other than that formed by addition to ethylene, so that there is no knowledge of their structures. This would be very indicative of the extent of the d-orbital participation, whether there is just interaction or if a bridged radical is likely. As yet, no calculations can be attempted on the radicals in an attempt to determine structures since the available programs have not yet been parameterised to include elements beyond the second row of the periodic table.

It appears, then, that although the trimethylgermyl radical does show orientation ratios closer to those of methyl and ethyl radicals, there is a competitive 'steric' effect which is present. And steric factors may have a significant part to play in many of the addition reactions. The difficulty, however, lies in quantifying the effect.

PART IV

Some Theoretical Considerations on Free Radical Addition to Olefins

The kinetics of reactions in the gas phase has, with the advent of modern calculating powers, become an area rich in theoretical interpretation and study. Attempts have been made by many workers at calculating both activation energies and pre-exponetial factors for a wide range of reactions, comparing the theoretically derived quantities with the experimental data. Many of the calculations use the transition state theory of chemical reactions as developed by Eyring. The fundamental postulate of this theory is that the reactants are always in equilibrium with the activated complex, and the rate of reaction is determined by the rate at which the complex decomposes into products.

The rate of reaction in the theory can be expressed by the equation (1) in which f_A and f_B are the total molecular

$$k = \frac{kT}{h} \cdot \frac{f''_{M^{\neq}}}{f_A \, f_B} \, e^{-E_o/RT} \qquad (1)$$

partition functions for the reactants, A and B, $f''_{M^{\neq}}$ is the molecular partition function for the activated complex, $M^{\neq}$, after the partition function, f_{ν}, for the particular vibration which causes decomposition to products has been factorised out and E_o is the change in zero-point energies in going from reactants to the activated complex. Comparing this equation with the Arrhenius form of the rate equation, we see that the pre-exponential factor, A, is given by:

$$A = \frac{kT}{h}\,\frac{f''_{M^{\ddagger}}}{f_A\,f_B} \qquad (2)$$

Theoretically, then, the rate for any reaction should be capable of calculation with a knowledge of the molecular partition functions and the zero-point energies of the reactants and the activated complex. The stumbling block, however, is the lack of knowledge of the true spatial arrangement of the atoms in the activated complex. The geometry of the complex is a necessary prerequisite to calculation of the partition functions for each degree of freedom which collectively make up the molecular partition function. Estimates have to be made to determine this geometry and to this end, the construction of potential energy surfaces is of great utility, Eyring originally postulated that the activated complex was the highest point of the pass on the potential energy surface.

Potential energy surfaces have been constructed by a variety of methods. The simplest surface is that for the linear attack of an atom on a diatomic molecule, which is a three dimensional surface. For more complicated - and more interesting - reactions the number of degrees of freedom increases so that the complete surfaces can only be constructed in hyperspace. This makes the determination of a reaction path very much more difficult to visualise. Normally, then, a reaction is simplified by considering only those quantities which one would reasonably expect to change significantly during the course of reaction. This drastically reduces the dimensionality of the surface. However, the other atoms whose spatial positions do not change in the approximated reation path must still be accounted for in the theoretical calculations. Thus the major drawback in finding potential energy surfaces has been deficiency in methods of calculation of total energy for a molecular configuration of atoms.

The calculation of molecular orbitals and their energies for any configuration of atoms (and hence many other properties) entails solving the time-independent Schrödinger equation (3) in which H is the total Hamiltonian operator of the system of particles (electrons and nuclei), Ψ_i, which

$$H\Psi_i = E_i\Psi_i \qquad (3)$$

is a function of all space and spin co-ordinates of the particles in the system, is the wave function describing the stationary state and E_i is the energy associated with that state. At the present time, this equation can only be solved explicitly for a relatively few "molecules". (In this context, "molecules" means an agregate of atoms i.e. it can be neutral or charged and not necessarily with recognised bond lengths.) In order to solve this equation for the more interesting cases, several levels of approximation have been made at various stages of the history of molecular orbital theory. The most fundamental approximation to the semi-emperical molecular orbital (M.O.) theories is the Born-Oppenheimer approximation. Using this, ψ becomes a function of a molecular and an electronic part, of which only the electronic part varies and the internuclear distances are used as constants (for a given atomic configuration). The principle of σ-π separability is also of importance, to differing degrees, in these theories.

The first approximate M.O. theory was the well established Hückel theory,[120,42] which invoked some of the most drastic approximations but had as its justification for use that it worked. Hückel theory has been used for the correlations described in Part I. The theory was basically one for π-electron systems although the theory has been extended predominantly by Hoffman to include σ-electrons.[121] In the Hückel theory, each molecular orbital is assumed to be a linear combination of atomic orbitals (LCAO):

$$\psi = \sum_{\nu} c_{\nu} \phi_{\nu} \qquad (4)$$

each of the M.O.'s is assumed to be a solution of a Schrödinger type equation in which H_i is a one-electron operator. Substituting (4) into such an equation gives, the secular equations:

$$\sum_{\nu} c_{\nu} \left(H_{\mu\nu} - S_{\mu\nu} \right) = 0 \qquad (5)$$

in which $H_{\mu\nu} = \int \phi_{\mu} H \phi_{\nu}\, dv$ and $S_{\mu\nu} = \int \phi_{\mu} \phi_{\nu}\, dv$ the coulomb and overlap integrals respectively. The main feature of the Hückel theory is that these integrals are given empirical values and also that the operator, H, is never actually defined. The empirical parameters are generally defined as:

$$\begin{aligned} \alpha_{\mu} &= \int \phi_{\mu} H \phi_{\mu}\, dv \\ \beta_{\mu\nu} &= \int \phi_{\mu} H \phi_{\nu}\, dv \end{aligned} \tag{6}$$

The solution of the secular equations then requires only a solution for the values of c_{ν}. Another major approximation made was the neglect of all electron-electron repulsions (or else they can be averaged out by judicious selection of the empirical parameters). Many workers then toiled to eliminate this approximation until the self consistent field (SCF) method of Roothaan allowed Pariser and Parr[122] and Pople[123] to formulate the now standard method for π-electron calculations.

The Hückel and Pariser-Parr-Pople methods, however, were restricted to planar molecules and π-electron systems. The search was now on to find methods for including all the valence electrons in the calculations. Hoffmann has used, to great effect, an extended Hückel method which was really the next step. The barrier to new methods was essentially one of computation facilities which could allow introduction of, at least, the more important electron repulsion integrals. The currently most widely used methods using SCF theory have been developed since about 1965, due to the rapidly rising calculating powers of the newest generation of computers.

The semi-empirical methods now largely used are all-valence orbital calculations in which the basis set is the set of all atomic orbitals having the same quantum number as the highest occupied orbital of the atom. Thus for hydrogen, only the 1s orbital is considered, for carbon the 2s, 2px, 2py and 2pz orbitals while for the second row elements the d-orbitals are also included. The differences in various methods lie in the extent to which electron repulsion integrals are included.

It is known that many electron repulsion integrals have values very close to zero, especially those involving the overlap distribution $\phi_\mu(1)\phi_\nu(1)$, with $\mu \neq \nu$. So in developing the approximate SCF molecular orbital schemes, it is a good simplification to neglect the electron repulsion integrals with small values. The various semi-empirical methods currently available all show neglect of the repulsion integrals to different levels of approximation. The method used in the following calculations is that of intermediate neglect of differential overlap (INDO). The approximations involved have been well described by Pople and Beveridge.[124] A similar method using parameterisation to reproduce heats of formation and bond lengths (MINDO/2) has been developed by Dewar.[125]

Potential surfaces have been calculated by some of the above semi-empirical methods. Ab initio methods have been used extensively in simple atom-diatomic molecule reactions with great success but some failures to approximate experimentally found values are recorded. For example, Radom and Pople have found a barrier of 138.6 kcal mole^{-1} to rotation in the ethylene molecule,[126] comparing with an experimental value of[127] 65 kcal mole^{-1}. However, the basic problem in the ab initio calculations is that of determining what basis set to use. Hoffman has used his extended Hückel method to calculate many surfaces for simple reactions but Dewar[128] has said that in view of the fact that often results are so unreliable, "calculations of reaction paths by this procedure cannot be taken seriously even in a qualititive sense"!

INDO and CNDO have encouraged some use in surface calculations but the most frequently used method has been MINDO/2 with its parameters chosen to reproduce molecular geometries almost in perfect agreement with experimental observations. Examples of studies of reaction pathways using the MINDO/2 method include conformational iomerisations, ring opening of cyclic ions and radicals, addition of atoms to olefins and carbene reactions. One particularly interesting study has attempted to find the structure of the transition state itself for the cyclobutene-butadiene isomerization,[129] rather than construct a complete surface and postulate the structure that the transition state might have.

There have been a few theoretical studies of addition to olefins. Dewar has used his MINDO/2 method to study carbon atom addition[128] while S atom addition has been studied by other workers.[130] Hoffmann has used his extended Hückel method to study the reaction of methylene and benzyne with ethylene.[131] The CNDO/2 method has been used to study addition of chlorine to ethylene.[132]

The addition of the methyl radical to π-systems has received much attention from Basilevsky and his co-workers. The first calculations used the Pople molecular orbital theory with corrections for molecular repulsions and stabilization energies.[133] In a later calculation, modification was made to the Pariser-Parr-Pople method and an activation energy of 7-10 kcal, which compares very favourably with the experimental values, was found.[134] They have also calculated the pre-exponential factor to be 1.11×10^{-12} $cm^3 mole^{-1} s^{-1}$.[135]

In order to limit the number of degrees of freedom, and hence to reduce the dimensionality of the surface, a simplified molecule of the reaction was used. There were only two variable parameters which were varied to study the surface and which were deemed to be the most important parameters. The model is shown in figure IV-1. When the distance between C_1 and C_2, R, is large, the value of ϕ is zero i.e. the reactants retain their planarity with their planes

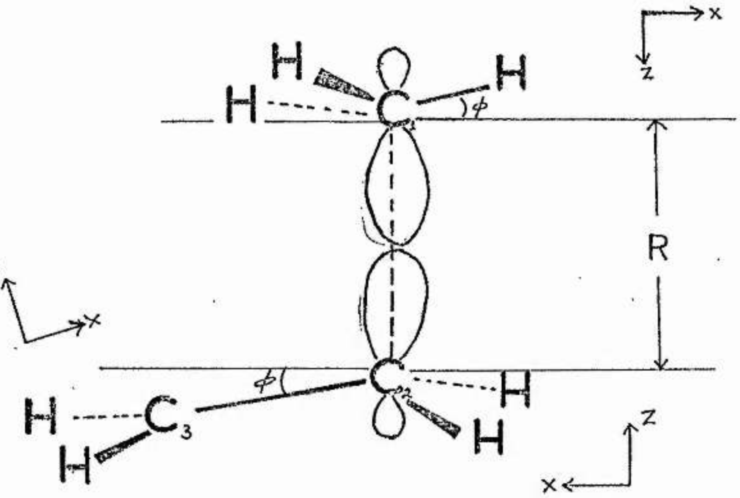


Figure IV-1

parallel. As the addition proceeds, the six σ-bonds adjacent to the reaction centre must be deflected, this can be simulated by varying the angle, ϕ. The potential energy surface obtained by Basilevsky using this model has a saddle point which occurs at the geometry $R = 2.3$ Å and $\phi = 9^\circ$. Although good prediction of the activation energy was obtained, it is interesting to compare this "transition state" with the findings of Szwarc and his coworkers. In a study of the secondary deuterium effect in the addition of $CH_3{}^\bullet$ and $CF_3{}^\bullet$, the relative rates for addition to protonated and deuterated olefins shown in table IV-1 were found.[35] If, in the transition state, the planar sp^2 hybridised carbon atom of the olefin becomes tetrahedrally sp^3 hybridised, the expected k_D/k_H value at 65° is 1.82. If however, the reaction centre remains planar in the transition state, a value close to unity is expected. On the basis of the values in table IV-1. Szwarc concluded that the incipient CH_3-C or CF_3-C bonds are relatively long in the transition

TABLE IV-1

Secondary Deuterium Effect in $CH_3^{\cdot}$ and $CF_3^{\cdot}$ Addition

Olefin	k_D/k_H (at 65°C)	
	$CH_3^{\cdot}$	$CF_3^{\cdot}$
$CD_2:CD_2$	1.05	1.07
$CH_3CH:CD_2$	1.12	1.07
$CD_3CD:CD_2$	1.16	1.09
$PhCD:CD_2$	1.11	1.10
$CD_2:CDCD:CD_2$	1.20	1.09

states and that the groups around the reaction centre essentially retain their planar configuration. This is not consistent with the picture provided by the potential energy surface calculations. A criticism which can be levelled at the calculations is against the use of the P.P.P. method which was developed essentially for planar π-electron systems. In order to remove this partial restriction, calculations have been done on the addition reaction using the all-valence electron INDO method.

The calculations were performed on an IBM 360/44 computer using the program CNINDO.[136] This program, originally written in double precision and requiring about 512K of core storage, was modified to fit the smaller core of the machine. (Some remodifications were implemented when the core of the computer was upgraded to 256K.) Since the program has inbuilt features satisfying the invariance conditions, the model of the addition reaction used by Basilevsky could be slightly simplified to use only one set of co-ordinate axes (figure IV-2). The geometries of the reactants are shown in table IV-2.

Initial calculations showed that, in addition of $CH_3^{\cdot}$ or $CF_3^{\cdot}$ to each of the fluoro-ethylenes (including ethylene), if ϕ were kept constant at zero and R was reduced from about 4.00 Å to 0.50 Å, a curve was every time produced which had a level portion and then dropped

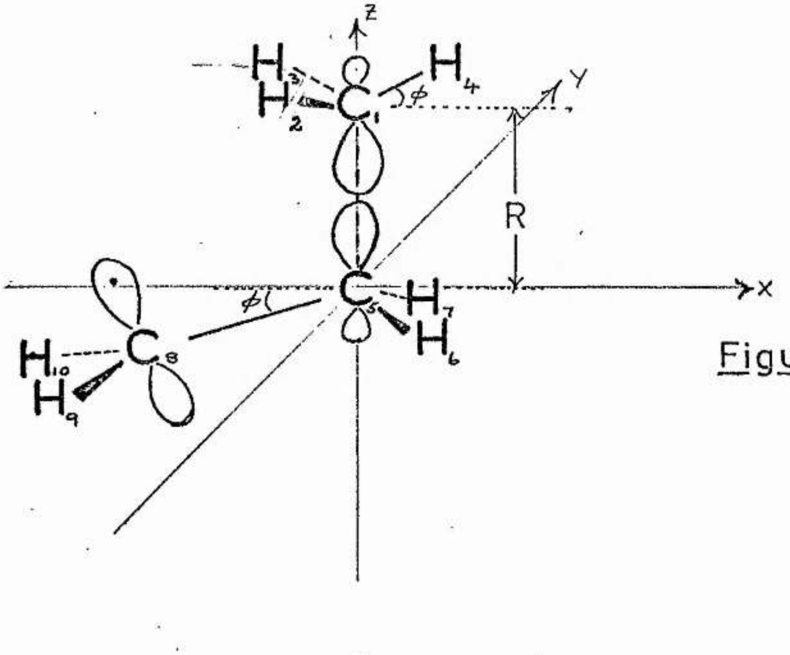


Figure IV-2

TABLE IV-2 GEOMETRIES OF REACTANTS USED IN CALCULATIONS[137]

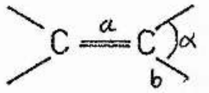
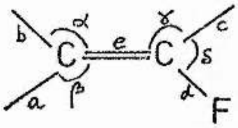
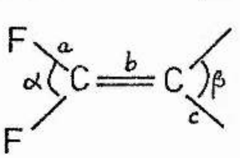
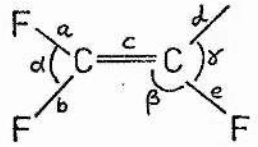
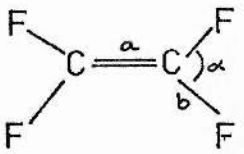
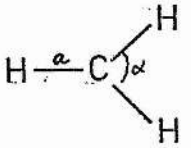
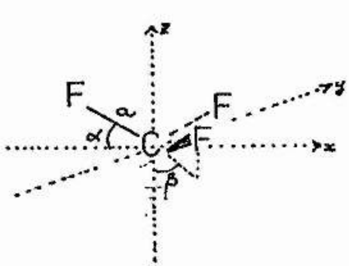
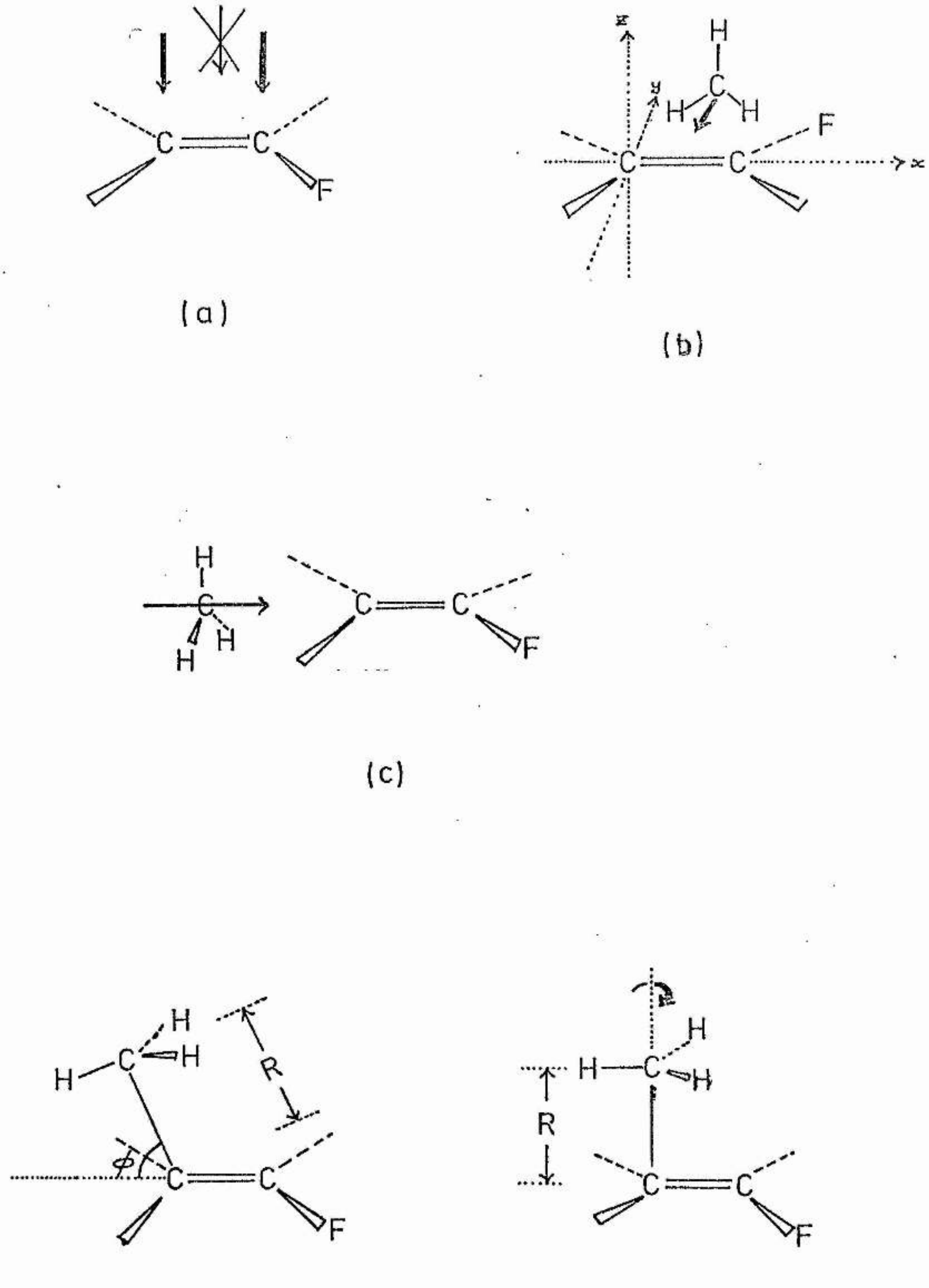
 Ethylene	a = 1.337 Å b = 1.086 Å α = 117.3°
 Vinyl fluoride	a = b = 1.080 Å; α = 118.5° c = 1.073 Å; β = 121.1° d = 1.348 Å; γ = 123.7° e = 1.33 Å ; δ = 113.4°
 1,1-Difluoroethylene	a = 1.321 Å ; α = 110° b = 1.311 Å ; β = 117° c = 1.070 Å
 Trifluoroethylene	a = b = e = 1.31 Å c = 1.33 Å ; α = 112° d = 1.07 Å; β = 120°; γ = 115°
 Tetrafluoroethylene	a = 1.33 Å b = 1.30 Å α = 114°
 Methyl	a = 1.099 Å; α = 120°
 Trifluoromethyl	a = 1.317 Å α = 16.8° β = 30°

Figure IV-3



(a)

(b)

(c)

(d)

(e)

to a minimum about the standard C-C bond length and then rose rapidly as nuclear repulsions grew.

Several important points were then established for the mode of attack of methyl radical at the CH_2: end of vinyl fluoride. It was assumed that the conclusions would be valid for addition to the other olefins and for the addition of trifluoromethyl. They were:

1. Attack was energetically more favourable for attack directly on to the carbon atoms then for attack on the double bond. (figure IV-3a) (Herein lies the difference between addition of methyl radicals and oxygen atoms as alluded to in part II. While the attack of methyl is at the carbon atom, oxygen atoms attack the double bond to form a π-complex in the transition state).

2. The side on approach to the bond (figure IV-3b) was energetically very unfavourable.

3. An 'end-on' approach (figure IV-3c) was also energetically much less favourable.

4. If R is 2.50 or 1.55Å, then the value of ϕ in figure IV-3d giving minimum energy was 90°.

5. For R, (in figure IV-3e) at about the bond length in the

'transition state', rotation of methyl seem to have a negligible effect.

Using the model as shown in figure IV-2, calculation of the surface for methyl addition to ethylene was attempted. The values of R were in the range 1.9 to 4.3 Å and the values of ϕ in the range -6° to 14°. (A negative distortion angle, means that the substituents on C1 and C2 are bent towards each other.) The values of the total energies are shown in table IV-3, (where a total energy is given as 0.0, the energy has not been calculated for that geometry. The figures underlined are those for the minimum energy pathway of the reaction. The figures of table IV-3 can be used to give an impression of the potential energy surface - this is shown in figure IV-4. It should be pointed out that this is not an accurately drawn surface, but is merely meant to give an idea as to its nature.

Unfortunately, the program appears to be incapable of calculation energies of a "molecule" when the values of R are large, hence the apparent continuous valley on the right of figure IV-4. The approximate transition state geometry predicted from the surface is shown by the dotted box in figure IV-4. It is immediately obvious that, although an accurate activation energy cannot be obtained, the transition state predicted does have a long C-C bond between the radical carbon atom and the attacked carbon atom and that there is

Table IV-3. Total Energies (atomic units) for Variation of R and PHI

PHI R	-6.0000	-4.0000	-2.0000	0.0	2.0000	4.0000
1.9	0.0	-25.5465	-25.5613	-25.5745	-25.5861	-25.5956
2.0	-25.5104	-25.5231	-25.5345	-25.5441	-25.5527	-25.5598
2.1	-25.4937	-25.5033	-25.5118	-25.5189	-25.5248	-25.5293
2.2	-25.4800	-25.4871	-25.4935	-25.4985	-25.5028	-25.5055
2.3	-25.4685	-25.4740	-25.4790	-25.4830	-25.4854	-25.4869
2.4	-25.4589	-25.4639	-25.4679	-25.4704	-25.4722	-25.4727
2.5	-25.4518	-25.4560	-25.4589	-25.4608	-25.4620	-25.4618
2.6	-25.4461	-25.4500	-25.4524	-25.4537	-25.4543	-25.4535
2.7	-25.4359	-25.4452	-25.4469	-25.4485	-25.4486	-25.4473
2.8	-25.4384	-25.4414	-25.4434	-25.4446	-25.4442	-25.4430
2.9	0.0	-25.4384	-25.4404	-25.4413	-25.4411	-25.4399
3.0	-25.4343	-25.4366	-25.4386	-25.4391	-25.4387	-25.4375
3.1	-25.4325	-25.4350	-25.4369	-25.4378	-25.4371	-25.4354
3.2	-25.4315	-25.4343	-25.4358	-25.4368	-25.4357	-25.4343
3.3	-25.4306	-25.4333	-25.4350	-25.4355	-25.4345	-25.4336
3.4	-25.4301	-25.4330	-25.4347	-25.4352	-25.4340	-25.4333
3.5	-25.4289	-25.4323	-25.4339	-25.4360	-25.4342	-25.4326
3.6	0.0	-25.4327	-25.4342	-25.4353	-25.4342	-25.4325
3.7	-25.4297	-25.4322	-25.4343	-25.4347	-25.4342	-25.4327
3.8	-25.4296	-25.4324	-25.4338	-25.4344	-25.4342	-25.4322
3.9	-25.4296	-25.4324	-25.4339	-25.4349	-25.4339	-25.4326
4.0	-25.4292	-25.4324	-25.4343	-25.4345	-25.4339	-25.4325
4.1	-25.4296	-25.4321	-25.4336	-25.4346	-25.4334	-25.4327
4.2	-25.4294	-25.4321	-25.4340	-25.4342	-25.4337	-25.4316
4.3	0.0	-25.4319	-25.4343	-25.4334	-25.4345	-25.4329

Table IV-4. Total Energies (atomic units) for Variation of R and PHI

PHI R	-6.0000	-4.0000	-2.0000	0.0	2.0000	4.0000
1.9	0.0	0.0	0.0	0.0	0.0	0.0
2.0	-102.6537	-102.6570	-102.6608	-102.6624	-102.6648	-102.6660
2.1	-102.6308	-102.6329	-102.6361	-102.6381	-102.6386	-102.6393
2.2	-102.6101	-102.6136	0.0	-102.6175	-102.6164	-102.6148
2.3	-102.5944	-102.5975	-102.5987	-102.5984	-102.6002	-102.5975
2.4	-102.5792	-102.5819	-102.5846	-102.5835	-102.5840	-102.5827
2.5	-102.5697	-102.5721	-102.5727	-102.5728	-102.5722	-102.5704
2.6	-102.5612	-102.5637	-102.5654	-102.5655	-102.5646	-102.5636
2.7	-102.5546	0.0	-102.5588	-102.5594	-102.5579	-102.5570
2.8	0.0	0.0	0.0	-102.5551	-102.5545	-102.5521
2.9	-102.5452	-102.5479	0.0	-102.5510	-102.5496	-102.5474
3.0	-102.5430	-102.5480	-102.5489	-102.5490	-102.5496	-102.5469
3.1	-102.5415	0.0	0.0	-102.5466	-102.5472	-102.5424
3.2	-102.5403	-102.5426	-102.5442	-102.5452	-102.5441	-102.5416
3.3	0.0	-102.5406	-102.5426	-102.5434	-102.5414	-102.5396

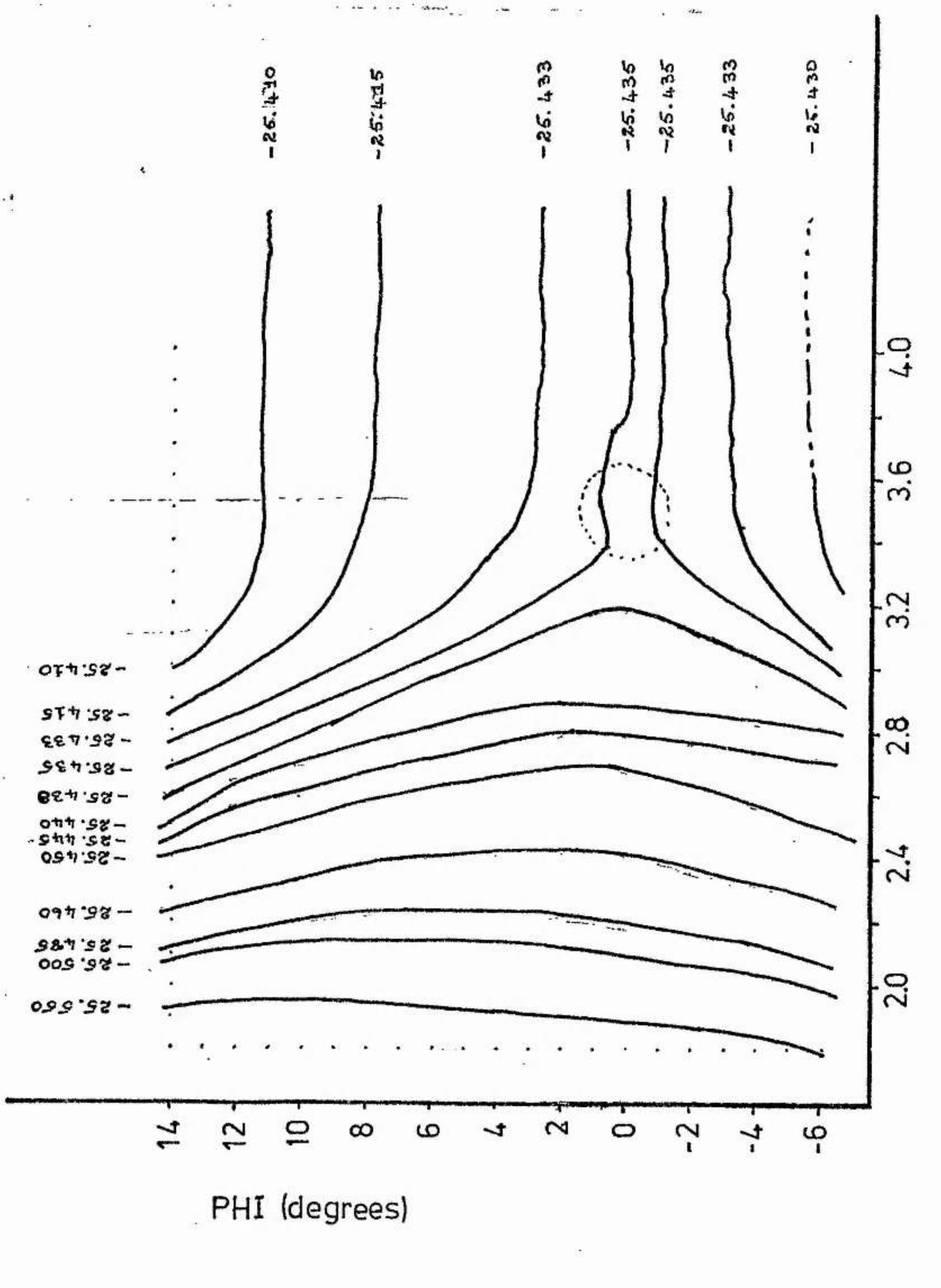
in Addition of Methyl Radicals to Ethylene.

6.0000	8.0000	10.0000	12.0000	14.0000
-25.6039	-25.6100	-25.6148	-25.6175	-25.6178
-25.5654	-25.5695	-25.5719	-25.5725	-25.5711
-25.5329	-25.5350	-25.5354	-25.5349	-25.3248
-25.5072	-25.5074	-25.5066	-25.5037	-25.4990
-25.4875	-25.4861	-25.4840	-25.4798	-25.4742
-25.4721	-25.4704	-25.4664	-25.4617	-25.4549
-25.4603	-25.4578	-25.4537	-25.4479	-25.4409
-25.4516	-25.4484	-25.4442	-25.4384	-25.4303
-25.4452	-25.4420	-25.4371	-25.4308	-25.4230
-25.4408	-25.4371	-25.4323	-25.4258	-25.4170
-25.4371	-25.4336	-25.4287	-25.4214	-25.4133
-25.4349	-25.4312	-25.4256	-25.4191	-25.4107
-25.4330	-25.4290	-25.4236	-25.4169	-25.4092
-25.4318	-25.4277	-25.4223	-25.4158	-25.4074
-25.4303	-25.4265	-25.4224	-25.4147	-25.4065
-25.4302	-25.4266	-25.4214	-25.4140	-25.4056
-25.4299	-25.4258	-25.4209	-25.4141	-25.4051
-25.4301	-25.4256	-25.4208	-25.4141	-25.4044
-25.4302	-25.4263	-25.4210	-25.4138	-25.4052
-25.4298	-25.4259	-25.4202	0.0	-25.4049
-25.4299	-25.4257	-25.4206	0.0	-25.4054
-25.4296	-25.4257	-25.4201	0.0	-25.4048
-25.4289	-25.4251	-25.4199	0.0	-25.4049
-25.4293	-25.4257	0.0	0.0	-25.4055
-25.4302	-25.4254	0.0	-25.4216	-25.4046

in Addition of Trifluoromethyl Radicals to Ethylene.

6.0000	8.0000	10.0000	12.0000	14.0000
0.0	0.0	0.0	0.0	0.0
-102.6659	-102.6659	-102.6634	-102.6616	-102.6566
-102.6374	-102.6361	-102.6325	-102.6297	-102.6248
-102.6136	-102.6109	-102.6089	-102.6037	-102.5984
-102.5962	-102.5915	-102.5885	-102.5830	-102.5784
-102.5791	-102.5758	-102.5723	-102.5661	-102.5592
-102.5684	-102.5642	-102.5598	-102.5544	-102.5482
-102.5603	-102.5563	-102.5507	-102.5462	-102.5392
-102.5528	-102.5485	-102.5462	-102.5390	-102.5314
-102.5500	0.0	-102.5411	-102.5368	-102.5283
-102.5458	0.0	-102.5360	-102.5288	-102.5233
-102.5455	0.0	-102.5347	-102.5288	-102.5215
-102.5423	0.0	-102.5323	-102.5260	-102.5186
-102.5397	0.0	-102.5302	-102.5249	-102.5197
-102.5366	0.0	-102.5297	-102.5234	-102.5165

Figure IV-4. Potential Energy Surface for Addition of Methyl Radicals to Ethylene (energies in atomic units)



little or no angular distortion. This is entirely consistent with the experimental evidence of Szwarc, but not with the surface calculated by Basilevsky. The estimation of a quantitative activation energy from the surface is futile, since it does not truly represent all the bond movements. To be able to make a reasonable estimate, all the bond lengths and angles would have to be varied to minimise the energy for each co-ordinate pair (R, PHI). Such a procedure becomes very costly on computer time. Hoyland[138] has used the MINDO/2 method of Dewar to study the addition of methyl radical to ethylene. He has essentially minimised the geometry of the "molecule" for each of a series of values of R. He has obtained a good estimate of the activation energy, 9.1 kcal mole^{-1}, and also finds that the transition state shows little distortion. The INDO program has, however, been parameterised essentially for e.s.r. data and the use of the MINDO package is probably more advantageous. However, as yet MINDO/2 programs are parameterised only for hydrogen, carbon, oxygen and nitrogen so that their use is excluded from studies on fluorine containing molecules.

Having constructed a surface for addition of methyl radicals it appeared sensible to try to construct one for addition of a radical of different nature, trifluoromethyl. The total energies using essentially the same model as before are shown in table IV-4. In this case, the trifluoromethyl radical is already known to be pyramidal, so that only the olefin shape is changed as the radical approaches. The approximate surface shows a similarity to that for methyl addition. Again the approximate position of the transition state shows a relatively long bond and little distortion of the original reactants, although the tentative bond length is shorter than that in the case of methyl addition. The results do not appear quite as consistent within themselves as the methyl results do, this is largely a product of the loss of accuracy in the modification of the original program to the smaller core storage of the computer used.

Surfaces calculated for addition of methyl radicals to vinyl fluoride have also been calculated and these again appear to be of a similar nature. Further surfaces were not calculated because of the rapidly increasing computation time. This is due to the increasing number of basis functions used, (for addition of methyl radicals to ethylene, 19 basis functions are involved while for addition to tetrafluoroethylene there are 31 basis functions and for addition of trifluoromethyl to tetrafluoroethylene 40 basis functions are used).

It is interesting to consider the electron densities and their changes during the addition reaction for both the methyl and trifluoromethyl radicals. Since the polar natures of these radicals are very different this should be apparent in the electronic effects observed in the reactions. Hoyland[138] has noted that, in keeping with the small geometry changes, there is only slight electronic rearrangement in the transition state, but that the hydrogen atoms on the methyl group gain in charge density giving the methyl group a predicted negative charge of about 0.04 electrons in the T.S. This charge is mostly transferred from the attacked site. Hoÿland, using the MINDO/2 method of Dewar, with his parameterisation, found a transition state closer to the one of Basilevsky than that found in this work. For each minimum geometry as found from tables IV-3 and IV-4, the valence electron densities for each atom were determined using the CNINDO program. The values are shown for addition of methyl and of trifluoromethyl to ethylene in tables IV-5 and IV-6 respectively. (The numbering of the atoms corresponds to that shown in figure IV-2).

The valence electron density at each carbon centre was found by summing the electron densities for each atom attached solely to that carbon atom, and its own electron density giving total valence electron densities for the CH_3-, -CH_2- and -$\dot{C}H_2$ moieties in the case of methyl addition and for CF_3-, -CH_2- and -$\dot{C}H_2$ for the addition of trifluoromethyl. The changes in total valence electron densities for each of the groups, as the reactions proceed along the minimum energy paths, are shown graphically in figures IV-5 and IV-6. If the movement of electron density to or from the attacking radical is a good criterion for judging the transition state, geometries predicted by this method from this work are much closer to the geometry of Hoyland. Again the tentative bond between the trifluoromethyl radical and ethylene in the trans-

Table IV-5. Valence Electron Densities on Each Atom in Addition of Methyl to Ethylene

R	PHI	C(1)	H(2)	H(3)	H(4)	C(5)	H(6)	H(7)	C(8)	H(9)	H(10)
∞	0.0	4.0534	0.9821	0.9821	0.9821	3.9945	1.0028	1.0028	3.9945	1.0028	1.0028
3.7	0.0	4.0537	0.9823	0.9823	0.9822	3.9938	1.0028	1.0028	3.9942	1.0029	1.0029
3.6	0.0	4.0541	0.9822	0.9822	0.9821	3.9937	1.0028	1.0028	3.9941	1.0029	1.0029
3.5	0.0	4.0541	0.9823	0.9823	0.9823	3.9935	1.0028	1.0028	3.9941	1.0028	1.0028
3.4	0.0	4.0544	0.9824	0.9824	0.9823	3.9933	1.0027	1.0027	3.9940	1.0028	1.0028
3.2	0.0	4.0554	0.9827	0.9827	0.9825	3.9924	1.0026	1.0026	3.9938	1.0027	1.0027
3.1	0.0	4.0562	0.9829	0.9829	0.9826	3.9917	1.0025	1.0025	3.9937	1.0026	1.0026
3.0	0.0	4.0574	0.9832	0.9832	0.9828	3.9907	1.0023	1.0023	3.9935	1.0024	1.0024
2.9	0.0	4.0589	0.9836	0.9836	0.9830	3.9891	1.0021	1.0021	3.9932	1.0022	1.0022
2.8	0.0	4.0610	0.9842	0.9842	0.9834	3.9870	1.0018	1.0018	3.9930	1.0019	1.0019
2.7	2.000	4.0620	0.9853	0.9853	0.9843	3.9840	1.0015	1.0015	3.9930	1.0016	1.0016
2.6	2.000	4.0653	0.9863	0.9863	0.9848	3.9793	1.0012	1.0012	3.9935	1.0010	1.0010
2.5	4.000	4.0653	0.9884	0.9884	0.9868	3.9736	1.0090	1.0090	3.9944	1.0060	1.0060
2.4	4.000	4.0692	0.9898	0.9898	0.9878	3.9641	1.0090	1.0090	3.9979	0.9999	0.9999
2.3	6.000	4.0664	0.9925	0.9925	0.9908	3.9527	1.0014	1.0014	4.0033	0.9995	0.9995
2.2	10.000	4.0518	0.9974	0.9974	0.9971	3.9422	1.0027	1.0027	4.0088	0.9999	0.9999
2.1	10.000	4.0467	0.9977	0.9977	0.9982	3.9234	1.0061	1.0061	4.0247	0.9997	0.9997
2.0	12.000	4.0278	0.9995	0.9995	1.0017	3.9106	1.0108	1.0108	4.0378	1.0007	1.0007
1.9	14.000	4.0045	1.0013	1.0013	1.0052	3.9027	1.0163	1.0163	4.0482	1.0022	1.0022
ADDUCT		3.9366	1.0157	1.0157	1.0236	3.9146	1.0250	1.0250	4.0617	0.9910	0.9910

Table IV-6. Valence Electron Densities on Each Atom in Addition of Trifluoromethyl to Ethylene

R	PHI	C(1)	F(2)	F(3)	F(4)	C(5)	F(6)	F(7)	C(8)	F(9)	F(10)
∞	0.0	3.3669	7.2110	7.2110	7.2110	3.9945	1.0028	1.0028	3.9945	1.0028	1.0028
3.5	0.0	3.3670	7.2114	7.2114	7.2113	4.0010	1.0013	1.0013	3.9950	0.9998	0.9998
3.4	0.0	3.3672	7.2116	7.2116	7.2114	4.0016	1.0011	1.0011	3.9948	0.9995	0.9995
3.3	0.0	3.3673	7.2119	7.2119	7.2117	4.0023	1.0008	1.0008	3.9945	0.9992	0.9992
3.2	0.0	3.3675	7.2123	7.2123	7.2121	4.0028	1.0004	1.0004	3.9942	0.9987	0.9987
3.1	2.000	3.3677	7.2127	7.2127	7.2125	4.0054	0.9995	0.9995	3.9925	0.9985	0.9985
3.0	2.000	3.3681	7.2135	7.2135	7.2132	4.0058	0.9989	0.9989	3.9919	0.9979	0.9979
2.9	0.0	3.3688	7.2147	7.2147	7.2143	4.0041	0.9985	0.9985	3.9922	0.9968	0.9968
2.8	0.0	3.3694	7.2162	7.2162	7.2157	4.0039	0.9976	0.9976	3.9914	0.9958	0.9958
2.7	0.0	3.3703	7.2181	7.2181	7.2175	4.0032	0.9963	0.9963	3.9902	0.9947	0.9947
2.6	0.0	3.3713	7.2206	7.2206	7.2198	4.0016	0.9949	0.9949	3.9890	0.9933	0.9933
2.5	0.0	3.3724	7.2238	7.2238	7.2229	3.9986	0.9931	0.9931	3.9884	0.9917	0.9917
2.4	2.000	3.3722	7.2268	7.2268	7.2261	3.9963	0.9910	0.9910	3.9880	0.9906	0.9906
2.3	2.000	3.3717	7.2310	7.2310	7.2306	3.9890	0.9891	0.9891	3.9907	0.9886	0.9886
2.2	0.0	3.3708	7.2366	7.2366	7.2368	3.9970	0.9869	0.9869	3.9965	0.9857	0.9857
2.1	4.000	3.3594	7.2391	7.2391	7.2404	3.9697	0.9863	0.9863	4.0074	0.9859	0.9859
2.0	4.000	3.3443	7.2432	7.2432	7.2459	3.9582	0.9860	0.9860	4.0234	0.9846	0.9846
ADDUCT		3.2419	7.2625	7.2625	7.2668	4.0328	0.9712	0.9712	4.0331	0.9788	0.9788

Figure IV-5. Electron Shifts in Addition of Methyl to Ethylene. Total Valence Electronic Charge on CH_3- (— — —) -CH_2- (———) and -$\dot{C}H_2$ (--------).

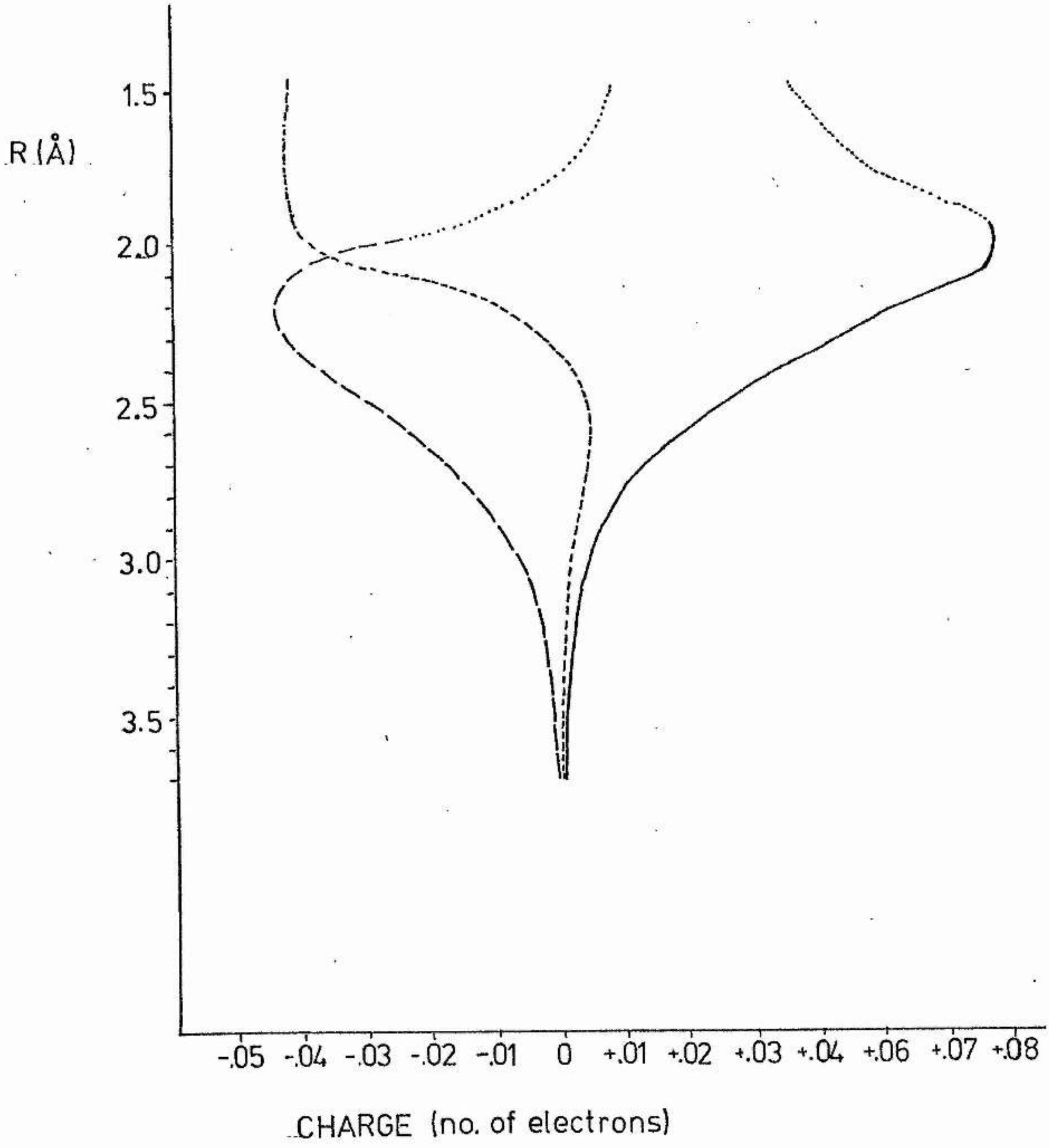
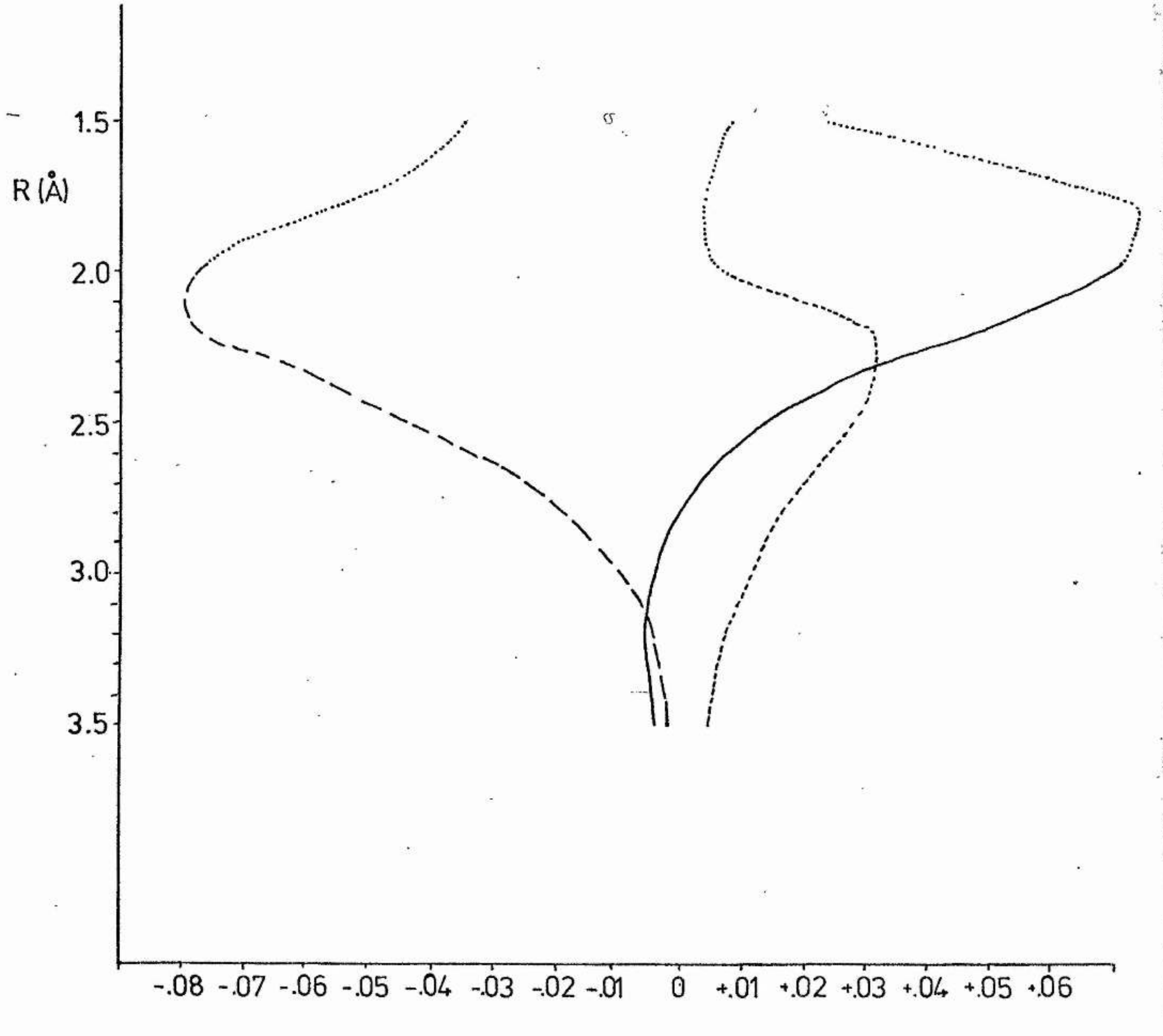


Figure IV-6. Electron Shifts in Addition of Trifluoromethyl to Ethylene. Total Valence Electronic Charge on CF_3- (— — —), $-CH_2-$ (———) and $-\dot{C}H_2$ (--------).



ition state is slightly shorter than the corresponding bond for methyl addition.

Let us consider first the curves for the addition of trifluoromethyl radical to ethylene (figure IV-6). When the radical and olefin are reasonably far apart (3.5 Å), the olefin is considerably polarised due to the electron attracting properties of the radical. As the radical approaches closer to the olefin, this polarisation of the carbon-carbon bond in the olefinic residue increases slightly. As the radical approaches closer, it gains considerably in electron density at the expense mainly of the attacked methylene group. As the molecular configuration moves through the transition state, there is quite a change in the electronic flow. Electrons then start to move away from the attacking radical and the attacked methylene group starts to gain electron density. At some stage past the transition state, the site at which the odd electron is sited in the classical structure starts to regain some of the density which it has been steadily losing. Ultimately, in the addend radical, the trifluoromethyl group shows a net increase in electron density at the expense of both of the carbon atoms of the olefinic residue.

The addition of methyl radical (figure IV-5) is fairly similar but does show distinct differences from the case just considered. Initially the electron density in the olefin is polarised to a much lesser extent, and it is polarised in the opposite manner. The polarisation remains the same throughout the reaction unlike the reaction above in which the polarisation reverses in the region of the transition state. As with the addition of trifluoromethyl, the attacking radical, methyl, takes on electron density, almost totally at the expense of the attacked methylene group. At about the transition state, the electron flow again reverses to start decreasing the density on the radical and increasing the density on the olefinic residue. The excess charge on the CF_3 group in the T.S. is about 0.08 electrons which is larger than the excess charge density on the methyl group in the transition state, as might be expected. The value is about 0.044 electrons, which is in extremely good agreement with the value of Hoyland. It would appear, then, that the question of where the dividing line between electrophilic and nucleophilic character should be drawn again arises. The agreement with the figure of Hoyland is extremely good considering that he optimised the geometry of the system with respect to the other variables keeping one as his variable parameter.

A very recent calculation by Yamabe and his co-workers,[139] using a semi-empirical all valence electron SCF method including configuration interaction, finds that the most dominant configuration is that in which an electron is transferred from the singly occupied MO of the methyl to the lowest unoccupied MO of ethylene. The next most dominant configuration is that in which an electron from the highest occupied MO of ethylene is transferred to the singly occupied orbital of the methyl.

This would suggest that, in the interaction between the two, the methyl takes on a positive charge, while ethylene becomes negatively charged.

While the Mayo-Walling approach in its simplest form has been discounted in part II, the possibility that its extension to considering the stability of the addend radicals as a whole still stands. In order to test the validity of its extension, some energy data are required for the radicals. Using the INDO method and the standard geometries suggested by Pople and Beveridge,[124] the total energies of the radicals formed by adding $CH_3^{\bullet}$ and $CF_3^{\bullet}$ to each of the fluoro-ethylenes were calculated. The results are shown in table IV-7

TABLE IV-7 Total Energies (in hartrees) of the Addend Radicals from $CH_3^{\bullet}$ and $CF_3^{\bullet}$ with Fluoro-ethylenes.

Radical	Total Energy	Radical	Total Energy
$CH_3CH_2CH_2^{\bullet}$	-25.777679	$CF_3CH_2CH_2^{\bullet}$	-102.848190
$CH_3CH_2CHF^{\bullet}$	-51.467056	$CF_3CH_2CHF^{\bullet}$	-128.491364
$CH_3CHFCH_2^{\bullet}$	-51.442017	$CF_3CHFCH_2^{\bullet}$	-128.449326
$CH_3CH_2CF_2^{\bullet}$	-77.162430	$CF_3CH_2CF_2^{\bullet}$	-154.175323
$CH_3CF_2CH_2^{\bullet}$	-77.119415	$CF_3CF_2CH_2^{\bullet}$	-154.095749
$CH_3CHFCF_2^{\bullet}$	-102.819687	$CF_3CHFCF_2^{\bullet}$	-179.799530
$CH_3CF_2CHF^{\bullet}$	-102.802353	$CF_3CF_2CHF^{\bullet}$	-179.765701
$CH_3CF_2CF_2^{\bullet}$	-128.446030	$CF_3CF_2CF_2^{\bullet}$	-205.439896

Table IV-8 Total Energies of Reactants

Ethylene	Total Energy (a.u.)	Radical	Total Energy (a.u.)
$CH_2:CH_2$	-16.559402	$CH_3^{\bullet}$	-8.875416
$CH_2:CHF$	-42.235886	$CF_3^{\bullet}$	-85.987106
$CH_2:CF_2$	-67.916840		
$CHF:CF_2$	-93.583893		
$CF_2:CF_2$	-119.253006		

Table IV-9. Energy Changes Associated with Addition to Fluoro-ethylenes

Position of Attack	Total Energy Changes (a.u.)	
	Addition of $CH_3^{\bullet}$	Addition of $CF_3^{\bullet}$
$\overset{\searrow}{CH_2}:CH_2$	-0.342861	-0.301682
$\overset{\downarrow}{CH_2}:CHF$	-0.355754	-0.268372
$CH_2:\overset{\downarrow}{CHF}$	-0.330715	-0.226334
$\overset{\downarrow}{CH_2}:CF_2$	-0.370174	-0.271377
$CH_2:\overset{\downarrow}{CF_2}$	-0.327159	-0.191803
$\overset{\downarrow}{CHF}:CF_2$	-0.360378	-0.228531
$CHF:\overset{\downarrow}{CF_2}$	-0.343044	-0.194702
$\overset{\downarrow}{CF_2}:CF_2$	-0.317608	-0.199784

The total energies of each of the fluoro-ethylenes and of the two radicals, $CH_3^{\bullet}$ and $CF_3^{\bullet}$ were also calculated using the geometries shown in table IV-2, the results are shown in table IV-8. Using the results from these tables, the change in total energies could be calculated for the reaction of the radical with each site in the olefin. The values are shown in table IV-9.

While the correlations of the energy charges shown in table IV-9 with the corresponding activation energies are not good, in the case of the addition of trifluoromethyl radicals, the correct orientation is always predicted for the addition reaction from the relative stabilities of the two addend radicals. However, as was the case with the simple Mayo-Walling approach, the reversal of orientation of addition of methyl to trifluoro-ethylene is not predicted. So that even the extended Mayo-Walling theory has no adventage over the theory in its simplest form. It can, however, be seen that, for example, in the values for the addition to ethylene and tetrafluoro-ethylene, the energy changes are much closer to each other for methyl addition than for trifluoromethyl addition. The same sort of trend is apparent when considering the addition to the opposite ends of the unsymmetrical olefins. In the addition kinetics, these closer changes are paralled by the proportions of the two addend radicals from methyl radical addition being much closer than in addition of trifluoromethyl addition for the unsymmetrical olefins. Also, the much faster addition of methyl to tetrafluoroethylene than of trifluoromethyl. So that, although no predictions can be drawn, at least one of the contributing factors to a total theory may be radical stability.

APPENDICES

APPENDIX I

$$
\begin{array}{lllll}
C_3F_7I + h\nu & \rightarrow & C_3F_7^{\cdot} + I^{\cdot} & & (1) \\
C_3F_7^{\cdot} + Ol & \rightarrow & C_3F_7Ol^{\cdot} & & (2) \\
C_3F_7Ol^{\cdot} + C_3F_7I & \rightarrow & C_3F_7OlI + C_3F_7^{\cdot} & & (3) \\
C_3F_7^{\cdot} + C_3F_7^{\cdot} & \rightarrow & C_6F_{14} & & (4) \\
I^{\cdot} + I^{\cdot} + M & \rightarrow & I_2 + M & & (5) \\
C_3F_7^{\cdot} + I^{\cdot} & \rightarrow & C_3F_7I & & (-1)
\end{array}
$$

$$\frac{d[C_3F_7OlI]}{dt} = k_3[C_3F_7Ol^{\cdot}][C_3F_7I] \qquad \text{--(A)}$$

$$\frac{d[C_3F_7Ol^{\cdot}]}{dt} = k_2[C_3F_7^{\cdot}][Ol] - k_3[C_3F_7Ol^{\cdot}][C_3F_7I] \fallingdotseq 0$$

$$\therefore [C_3F_7Ol^{\cdot}] = \frac{k_2[C_3F_7^{\cdot}][Ol]}{k_3[C_3F_7I]} \qquad \text{--(B)}$$

$$\frac{d[C_3F_7^{\cdot}]}{dt} = k_1[C_3F_7I] - k_2[C_3F_7^{\cdot}][Ol] + k_3[C_3F_7Ol^{\cdot}][C_3F_7I] - \tfrac{1}{2}k_4[C_3F_7^{\cdot}]^2 - k_{-1}[C_3F_7^{\cdot}][I^{\cdot}]$$

$$= k_1[C_3F_7I] - \tfrac{1}{2}k_4[C_3F_7^{\cdot}]^2 \fallingdotseq 0$$

$$\therefore [C_3F_7^{\cdot}] = (2k_1[C_3F_7I]/k_4)^{\frac{1}{2}}$$

Substituting in (B) :

$$[C_3F_7Ol^{\cdot}] = \frac{2k_1^{\frac{1}{2}}k_2[Ol]}{k_4^{\frac{1}{2}}k_3[C_3F_7I]^{\frac{1}{2}}}$$

Substituting in (A):

$$\frac{d[C_3F_7O1I]}{dt} = \frac{2k_1^{\frac{1}{2}}k_2}{k_4^{\frac{1}{2}}} [O1] [C_3F_7I]^{\frac{1}{2}}$$

$$= \frac{2k_2}{k_4^{\frac{1}{2}}} (\phi I_a)^{\frac{1}{2}} [O1]$$

APPENDIX II

$$CH_3.N{:}N.CH_3 \rightarrow 2CH_3^{\bullet} + N_2 \quad (1)$$

$$CH_3^{\bullet} + E \rightarrow CH_3E^{\bullet} \quad (2)$$

$$CH_3E^{\bullet} + CH_3I \rightarrow CH_3EI + CH_3^{\bullet} \quad (3)$$

$$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_6 \quad (4)$$

$$\frac{d[CH_3EI]}{dt} = k_3[CH_3E^{\bullet}][CH_3I] \quad \text{--(A)}$$

$$\frac{d[CH_3E^{\bullet}]}{dt} = k_2[CH_3^{\bullet}][E] - k_3[CH_3E^{\bullet}][CH_3I] \doteqdot 0$$

$$\therefore [CH_3E^{\bullet}] = \frac{k_2[CH_3^{\bullet}][E]}{k_3[CH_3I]} \quad \text{--(B)}$$

$$\frac{d[CH_3^{\bullet}]}{dt} = \tfrac{1}{2}k_1[CH_3.N{:}N.CH_3] - k_2[CH_3^{\bullet}][E] + k_3[CH_3E^{\bullet}][CH_3I] - 2k_4[CH_3^{\bullet}]^2 \doteqdot 0$$

$$\therefore [CH_3^{\bullet}] = \frac{k_1[CH_3.N{:}N.CH_3]}{4k_4}^{\frac{1}{2}} = \left(\frac{\phi I_a}{4k_4}\right)^{\frac{1}{2}} = \tfrac{1}{2}(k_4)^{-\frac{1}{2}}$$

Substituting in (B):

$$[CH_3E^{\bullet}] = \frac{k_2[E]}{2k_3k_4^{\frac{1}{2}}[CH_3I]}$$

Substituting in (A):

$$\underline{\underline{-\frac{d[CH_3EI]}{dt} = \frac{k_2[E]}{2k_4^{\frac{1}{2}}}}}$$

APPENDIX III

$$Me_3GeH \xrightarrow{h\nu} 2\ Me_3Ge^{\bullet} \qquad (1)$$

$$Me_3Ge^{\bullet} + Ol \longrightarrow Me_3GeOl^{\bullet} \qquad (2)$$

$$Me_3GeOl^{\bullet} + Me_3GeH \longrightarrow Me_3GeOlH + Me_3Ge^{\bullet} \qquad (3)$$

$$Me_3Ge^{\bullet} + Me_3Ge^{\bullet} \longrightarrow Me_6Ge_2 \qquad (4)$$

$$\frac{d[Me_3GeOlH]}{dt} = k_3[Me_3GeOl^{\bullet}][Me_3GeH] \qquad \text{---}(A)$$

$$\frac{d[Me_3GeOl^{\bullet}]}{dt} = k_2[Me_3Ge^{\bullet}][Ol] - k_{-2}[Me_3GeOl^{\bullet}] - k_3[Me_3GeOl^{\bullet}][Me_3GeH] \fallingdotseq 0$$

$$[Me_3GeOl^{\bullet}] = \frac{k_2[Me_3Ge^{\bullet}][Ol]}{k_{-2} + k_3[Me_3GeH]} \qquad \text{---}(B)$$

$$\frac{d[Me_3Ge^{\bullet}]}{dt} = \frac{\phi I_a}{2} - k_2[Me_3Ge^{\bullet}][Ol] + k_{-2}[Me_3GeOl^{\bullet}] + k_3[Me_3GeOl^{\bullet}][Me_3GeH] - 2k_4[Me_3Ge^{\bullet}]^2 \fallingdotseq 0$$

$$[Me_3Ge^{\bullet}] = \left(\frac{\phi I_a}{4k_4}\right)^{\frac{1}{2}}$$

Substituting in equation B

$$[Me_3GeOl^{\bullet}] = \frac{k_2(\phi I_a/4k_4)^{\frac{1}{2}}[Ol]}{k_{-2} + k_3[Me_3GeH]}$$

Substituting in equation A.

$$\frac{d[\mathrm{Me_3GeOlH}]}{dt} = \frac{k_3k_2(\phi I_a/4k_4)^{\frac{1}{2}}[\mathrm{Ol}][\mathrm{Me_3GeH}]}{k_{-2} + k_3[\mathrm{Me_3GeH}]}$$

$$\frac{d[\mathrm{Me_6Ge_2}]}{dt} = k_4[\mathrm{Me_3Ge^{\bullet}}]^2 = \phi I_a/4 \qquad (a)$$

$$\frac{d[\mathrm{Me_6Ge_2}]}{d[\mathrm{Me_3GeOlH}]} = \frac{k_4^{\frac{1}{2}}(\phi I_a/4)^{\frac{1}{2}}(k_{-2} + k_3[\mathrm{Me_3GeH}])}{k_2k_3[\mathrm{Ol}][\mathrm{Me_3GeH}]}$$

$$= \frac{k_4^{\frac{1}{2}}(\phi I_a/4)^{\frac{1}{2}}}{k_2[\mathrm{Ol}]}\left(1 + k_{-2}/k_3[\mathrm{Me_3GeH}]\right)$$

If the extent of reaction is small, and set $\phi I_a = \phi I_o \beta l[\mathrm{Me_3GeH}]$

where $\beta = 2.303\varepsilon$ and l = the length of the cell, then

$$\frac{[\mathrm{Me_6Ge_2}]_f}{[\mathrm{Me_3GeOlH}][\mathrm{Me_3GeH}]_i^{\frac{1}{2}}} = \frac{k_4^{\frac{1}{2}}(\phi I_o \beta l)^{\frac{1}{2}}}{2k_2[\mathrm{Ol}]_i}\left(1 + k_{-2}/k_3[\mathrm{Me_3GeH}]_i\right)$$

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