KINETICS OF GAS PHASE REACTIONS OF PERFLUOROALKYL IODIDES

PART 1: THE EXCHANGE REACTIONS OF PERFLUOROETHYL IODIDE AND PERFLUORO-n-PROPYL IODIDE WITH IODINE

PART 2: GAS-PHASE PHOTOLYSIS OF PERFLUOROETHYL IODIDE

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This thesis contains no material previously submitted for a degree or diploma in any University, and to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text.

G. L. [illegible]

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TABLE OF CONTENTS

Page

PART 1

THE EXCHANGE REACTIONS OF PERFLUOROETHYL IODIDE AND PERFLUORO-n-PROPYL IODIDE WITH IODINE

1. SUMMARY 1

2. INTRODUCTION 2

3. EXPERIMENTAL 4

   3.1 MATERIALS 4

   3.2 APPARATUS 6

   3.3 PROCEDURE 9

4. RESULTS 13

   4.1 THERMAL EXCHANGE 13

   4.2 PHOTOCHEMICAL EXCHANGE 16

5. DISCUSSION 17

   5.1 THERMAL EXCHANGE 17

   5.2 PHOTOCHEMICAL EXCHANGE 22

      (a) Iodine Atom Formation 24

      (b) Iodine Atom Recombination 27

      (c) The Implication of the Formation-Recombination Iodine Atom Mechanisms as Applied to the RI-I_2 Photochemical Exchange Mechanism 33

   5.3 CALCULATION OF THE IODINE ATOM RECOMBINATION RATE CONSTANTS AND THE IODINE ATOM RECOMBINATION ACTIVATION ENERGY 35

Page

(a) Effect of Pressure on the Yield of Products 86

(b) Time Dependence 87

(c) Temperature Dependence 89

(d) Effect of Argon 91

(e) Effect of Iodine 92

(f) Effect of NO 92

(g) Photolysis of CF_3OOCF_3-C_2F_5I Mixtures 96

(h) Fate of the CF_2 Radical 101

(i) Mechanism 104

5. APPENDICES 107

6. REFERENCES 120

TABLE OF CONTENTS

Page

PART 1

THE EXCHANGE REACTIONS OF PERFLUOROETHYL IODIDE AND PERFLUORO-n-PROPYL IODIDE WITH IODINE

1. SUMMARY 1

2. INTRODUCTION 2

3. EXPERIMENTAL 4

 3.1 MATERIALS 4

 3.2 APPARATUS 6

 3.3 PROCEDURE 9

4. RESULTS 13

 4.1 THERMAL EXCHANGE 13

 4.2 PHOTOCHEMICAL EXCHANGE 16

5. DISCUSSION 17

 5.1 THERMAL EXCHANGE 17

 5.2 PHOTOCHEMICAL EXCHANGE 22

  (a) Iodine Atom Formation 24

  (b) Iodine Atom Recombination 27

  (c) The Implication of the Formation-Recombination Iodine Atom Mechanisms as Applied to the RI-I_2 Photochemical Exchange Mechanism 33

 5.3 CALCULATION OF THE IODINE ATOM RECOMBINATION RATE CONSTANTS AND THE IODINE ATOM RECOMBINATION ACTIVATION ENERGY 35

Page

5.4 ARRHENIUS PARAMETERS FOR THE THERMAL EXCHANGE 37

5.5 BOND DISSOCIATION ENERGY OF THE C-I BOND 38

6. APPENDICES 41

7. REFERENCES 50

PART 2

GAS-PHASE PHOTOLYSIS OF PERFLUOROETHYL IODIDE

1. SUMMARY 54

2. INTRODUCTION 56

3. EXPERIMENTAL 63

3.1 MATERIALS 63

3.2 APPARATUS 67

3.3 PROCEDURE 71

3.4 SOURCES OF ERROR 73

4. RESULTS AND DISCUSSION 75

4.1 2537 Å PHOTOLYSIS OF PERFLUOROETHYL IODIDE 75

(a) Effect of Time of Irradiation on ϕ (products) 76

(b) Effect of Pressure on ϕ (products) 76

(c) Effect of NO 77

(d) Mechanism 80

4.2 PHOTOLYSIS OF PERFLUOROETHYL IODIDE WITH UNFILTERED LIGHT 85

Page

(a) Effect of Pressure on the Yield of Products 86

(b) Time Dependence 87

(c) Temperature Dependence 89

(d) Effect of Argon 91

(e) Effect of Iodine 92

(f) Effect of NO 92

(g) Photolysis of CF_3COCF_3-C_2F_5I Mixtures 96

(h) Fate of the CF_2 Radical 101

(i) Mechanism 104

5. APPENDICES 107

6. REFERENCES 120

PART 1

THE EXCHANGE REACTIONS OF PERFLUOROETHYL IODIDE AND PERFLUORO-n-PROPYL IODIDE WITH IODINE

1. SUMMARY

The thermal and photochemical (5461 Å) exchange reactions between I_2 and C_2F_5I or $n\text{-}C_3F_7I$ were investigated in the gas phase between 50 and 170°C. The homogeneous thermal and photochemical reactions are initiated by I atoms and the exchange proceeds by abstraction

$$RI + I \rightarrow R + I_2 \qquad (1)$$

followed by

$$R + I_2 \rightarrow RI + I.$$

The rate constants for (1) are

$$k_{(C_2F_5I)} = 10^{10.0} \exp(-13500 \pm 800/RT) \text{ litre mole}^{-1}\text{sec}^{-1}$$

$$k_{(n\text{-}C_3F_7I)} = 10^{10.2} \exp(-14200 \pm 1200/RT) \text{ litre mole}^{-1}\text{sec}^{-1}.$$

From the activation energy for (1), $D(C_2F_5\text{-}I)$ is 49.5 ± 0.8 kcal mole^{-1} and $D(n\text{-}C_3F_7\text{-}I)$ is 50.4 ± 1.2 kcal mole^{-1}.

2. INTRODUCTION

Probably the simplest reaction that may occur is the interchange of a free atom with a similar bound atom in a molecule. Reactions of this type are called exchange reactions and are accompanied by no chemical change but often by a change in the physical properties of the compound (e.g. optical activity[1] or a change in the dielectric constant[2]) which provides a means of following the reaction. The use of isotopically labelled iodine[3] provides a means of following the behaviour of iodine atoms even in those reactions between iodine and alkyl iodides for which there is no change of physical property on reaction. The first of many exchange experiments between alkyl iodides and labelled iodine was carried out by Hull, Shiflett and Lind.[4]

Bujake, Pratt and Noyes[5] in reporting their own experimental data have reviewed all the available data on the exchange reactions between alkyl iodides and iodine, but were not able to reach any detailed mechanistic conclusion. Many of the studies were hampered by complications such as heterogeneous effects[14] in the gas phase and impurities which act as radical scavengers, in the liquid phase.

Laurence,[6] having collaborated with Stranks[7] on the methyl iodide-iodine exchange induced by the $I^{127}\ (n,\gamma)I^{128}$ reaction (later shown to be heterogeneous[8]) studied the trifluoromethyl iodide-iodine exchange. The gas phase exchange was found to be homogeneous and the thermal and photochemical reactions have the same general mechanism.

The present study is concerned with the exchange reaction between iodine and perfluoroethyl iodide[9] and perfluoro-n-propyl iodide. The rate of thermal exchange has been compared with the rate of exchange initiated by the absorption of 5461 Å light by the iodine. The exchange was initiated by iodine atoms generated thermally or photochemically followed either by abstraction,

$$RI + I^* \rightarrow R + II^*$$

leading to exchange by

$$R + I_2^* \rightarrow RI^* + I^*$$

or direct exchange

$$RI + I^* \rightarrow RI^* + I$$

and according to the rate law the two paths are kinetically indistinguishable.

The homogeneity of the photochemically induced exchange was demonstrated by showing that the rate of exchange depends on the square root of the absorbed light intensity and that the observed activation energy and the rate of exchange in the thermal exchange experiments are unaffected by changing the surface to volume ratio. The latter observation is not however conclusive evidence for homogeneity as both the initiation and termination may occur on the walls of the vessel.[10,11]

3. EXPERIMENTAL

3.1 MATERIALS

PERFLUOROETHYL IODIDE, C_2F_5I, from Columbia Organic Chemicals Ltd. contained a number of impurities as shown by vapour phase chromatography. The low boiling point impurities were removed by fractional distillation at low pressures and the high molecular weight impurities by passing the C_2F_5I through a column containing silica gel (chromatographic grade) under vacuum and operated at 0°C. The purity of the C_2F_5I was checked by vapour phase chromatography and found to be better than 99.99%. The purified C_2F_5I was stored in a darkened bulb.

The apparatus used is described in more detail in Part 2 of this thesis.

PERFLUORO-n-PROPYL IODIDE, n-C_3F_7I, was prepared by the method of Henne and Finnegan.[12] Silver heptafluorobutyrate, obtained by reaction of heptafluorobutyric acid (Koch-Light) with silver oxide, was heated with iodine (mole ratio 1:2).

The perfluoro-n-propyl iodide so formed was shaken with mercury to remove traces of iodine and fractionally distilled, collecting the fraction with boiling point range 39-40°C.[13] The distillate was degassed at -196°C (liquid nitrogen) and further fractionally distilled at low pressures until the purity was greater than 99.9% when checked by vapour phase chromatography. The purified n-C_3F_7I was stored in a dark bulb at -196°C to prevent decomposition.

<u>IODINE-131</u>, was prepared from solutions of carrier-free I-131 in sodium thiosulphate (Radiochemical Centre, Amersham). As trace amounts of water catalyse the exchange[6] labelled I_2 was prepared by a method which ensured the complete removal of water from the system. The method is based on the reaction between PbI_2 and PbO_2 at 200-300°C

$$PbI_2 + PbO_2 \rightarrow 2PbO + I_2.$$

The required amount (approx. 0.4-1.0mg) of PbI_2 was weighed into a small tube and the appropriate amount of iodine-131 solution was added. The exchange of iodide ions with PbI_2 is very rapid. After a further addition of water and ethanol the solution was centrifuged and then evaporated to dryness over a hot plate with nitrogen blown over the surface of the solution to increase the rate of evaporation and to prevent bumping. A five-fold excess of PbO_2 was weighed into the tube which was placed into tube A of the apparatus shown in figure 1. Liquid nitrogen (-196°C) was placed around tube C and the furnace around tube A was raised to 150°C for one hour while the whole system was pumped down. The apparatus was shut off from the vacuum line by means of a stopcock,

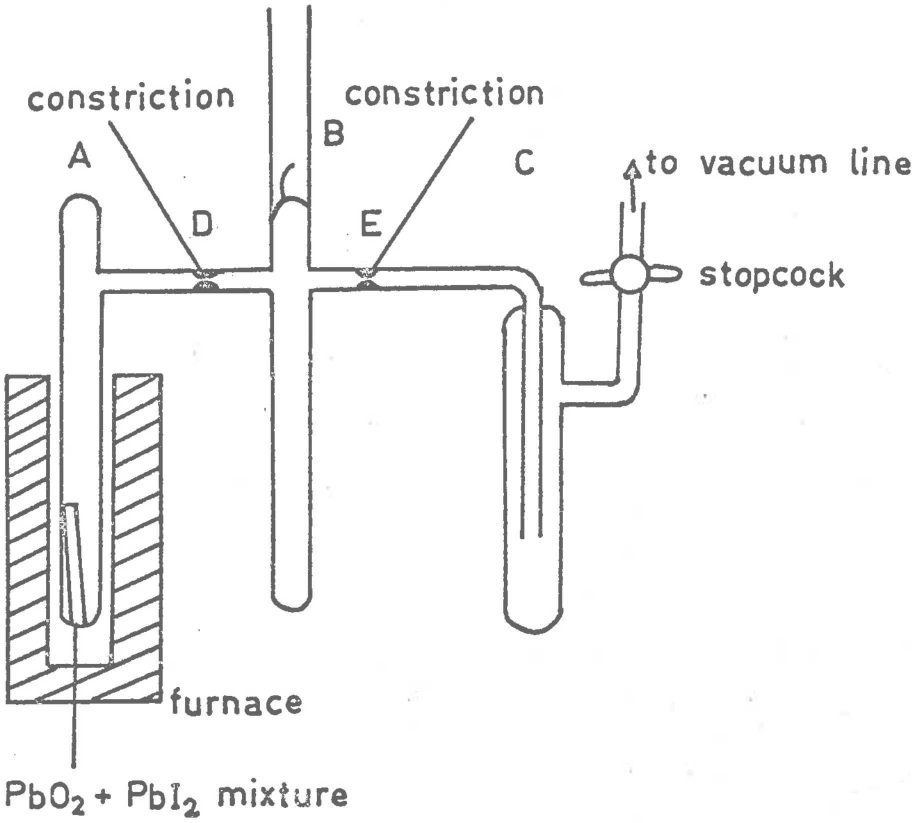


FIG. 1

Apparatus used for preparation of Iodine - 131.

a liquid nitrogen trap was placed around tube B, and the temperature of the furnace raised to 300°C. The iodine liberated condensed in tube B. When all of the iodine had been generated, tube B was sealed off at D, thoroughly pumped down and then sealed off from trap C at E.

The preparation was usually carried out at a specific activity of about 100 μC mg^{-1}, which gave a counting rate in the reaction vessel of 2000-3000 cps.

CARBON TETRACHLORIDE, used in spectrophotometric estimation of iodine was A.R. grade.

3.2 APPARATUS

CELLS

The exchange experiments were carried out in cylindrical Pyrex cells 5 cm diameter and 20 cm long with polished windows. The surface area-to-volume ratio (S/V) of this cell was approximately 1.0. Two additional cells were used to observe the effect of surface area on the rate of thermal exchange. One was 5 cm diameter and 3 cm long, with S/V of 1.6 cm^{-1} ($S = 83$ cm^2, $V = 49$ cm^3), the other was packed with a number of concentric pyrex glass tubes, separated by glass bumps on each end of the tubes. This cell had a S/V of 5.4 cm^{-1}.

In the run in which the effect of glass wool was studied, the glass wool was washed with alocholic KOH, rinsed with distilled water and washed with HNO_3/pot. dichromate mixture. After rinsing thoroughly with distilled water the glass wool was dried in an oven at 150°C. It was placed in an exchange cell and degassed with occasional flaming, for two days before the perfluoroalkyl iodide and iodine-131 were added.

TEMPERATURE CONTROL

The reaction cells were immersed in a bath of paraffin oil (Fauldings Ltd., B.P. grade) and could be illuminated through a pyrex window in the side of the bath. The paraffin oil was clear and transparent to the 5461 Å light. It did however, decompose slowly above 120°C and consequently all the photochemical experiments were performed first.

The bath temperature was held constant to ± 0.05°C by a thermistor operated controller.

LIGHT SOURCE AND OPTICS

The light source used in the photochemical experiments was a 250W medium pressure mercury lamp (ME/D, A.E.I.) run from a solid-state stabilized-current D.C. power supply (the circuit is shown in figure 2). The lamp current was constant to ± 0.1%, but the light intensity was constant to only ± 2% due to arc wander. Light from the lamp was passed through two lenses to give a parallel

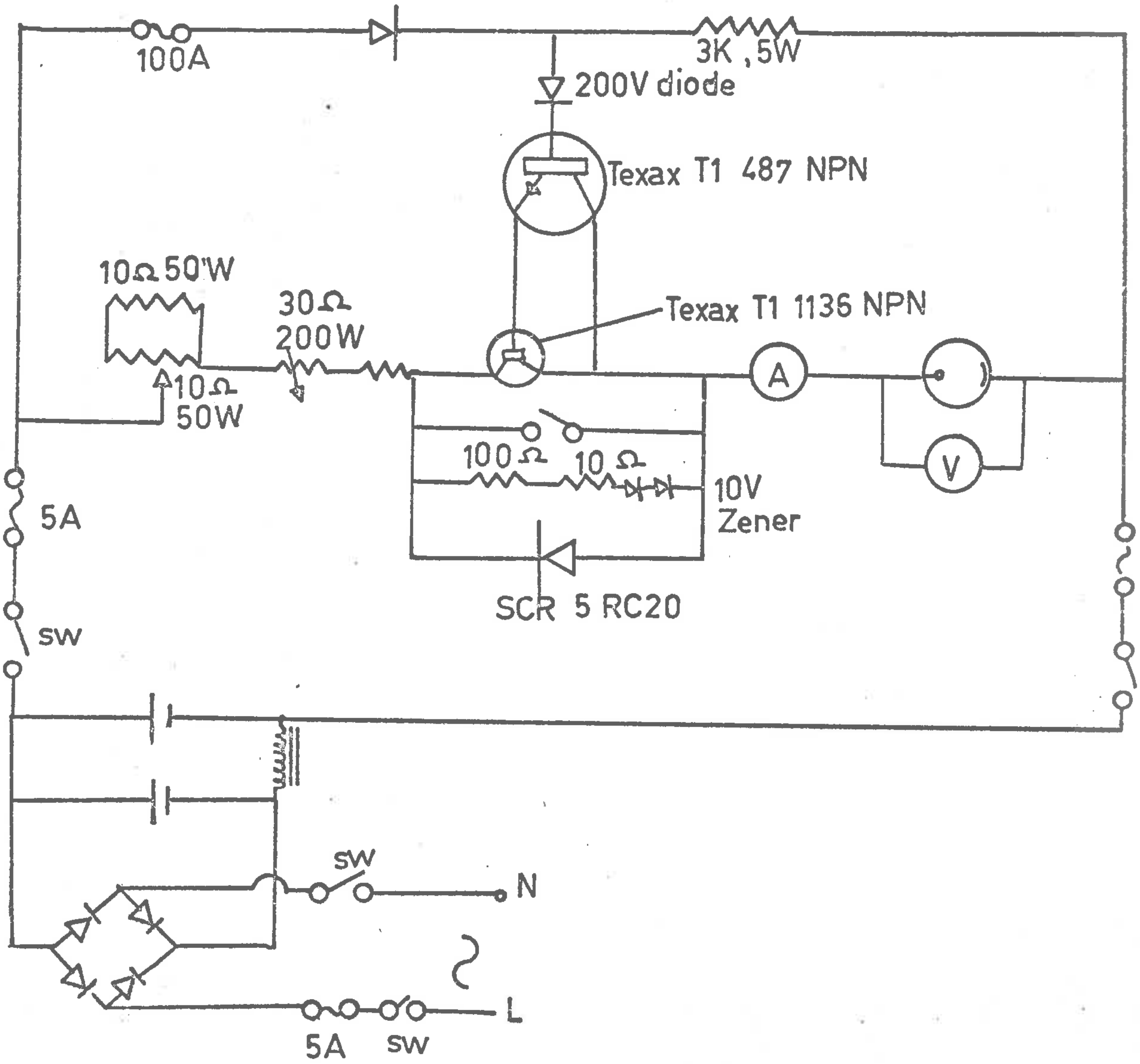


FIG. 2

Circuit for stabilizing the MAZDA ME/D 250W lamp current.

Designed by G.S.Laurence and A.D.Thomas.

beam and then through a Zeiss Monochromat filter to isolate the 5461 Å mercury line. The transmission properties of the filter are shown in figure 3. Although the filter does transmit light at 4990 Å, the net contribution of this wavelength to the total light would be very small as the lamp output at this wavelength is approximately 5% of that at 5461 Å according to the manufacturers specifications.

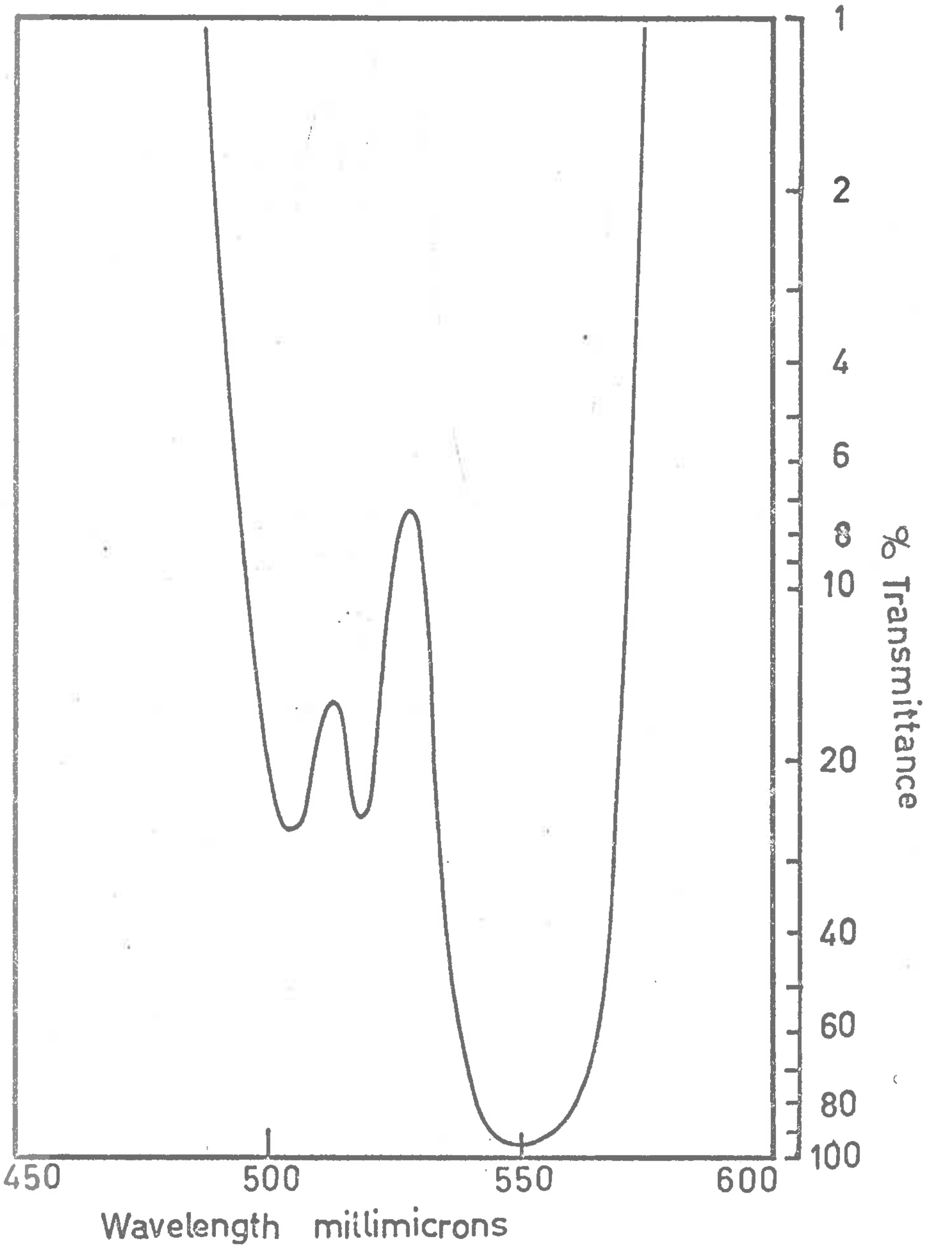
Absolute light intensity measurements were made with a thermopile which had been calibrated by the National Standards Laboratory, Sydney.

For the rotating-sector experiments a metal sector 45 cm diameter was arranged to cut the light beam at a point where the beam diameter was only 2 mm, in order to reduce the rise time of the light pulse and give a rectangular pulse. The sector was driven by an induction motor at a maximum of 1200 revs. per min.

The light intensity in the rotating sector experiments was measured with the thermopile and also calculated from the angle subtended by the slit at various sector settings. The relative light intensities are compared in Table I, and can be seen to agree within 1%.

TABLE I

Relative light intensity	Angular measurements	0.0455	0.0801	0.163	0.248	0.414	0.500
	Thermopile	0.0448	0.0786	0.163	0.247	0.414	0.494



'S' filter used in exchange experiments.

FIG. 3

Transmission characteristic of a Zeiss Monochromat filter used to isolate 5461 A° mercury line.

The values of the relative light intensity used in photochemical experiments are those obtained from the angular measurements.

RADIOACTIVE COUNTER

The iodine-131 activity in the cell was measured with a NaI scintillation counter. The photomultiplier (type 9541S, EMI), cathode follower (type 1430A), EHT unit (type 532/D), amplifier (type 1430A), pulse analyser (type N102) and scalar (type N1009E and N108) were of standard type (Dynatron Radio Ltd.). The photomultiplier was set within a 2 inch lead shield to reduce the background count.

3.3 PROCEDURE

The arrangement of the apparatus used in filling the cell with reactants is given in figure 4. The iodine-131 was condensed down in tube B with liquid nitrogen (-196°C), the break seal broken and the whole system pumped down. The liquid nitrogen trap was replaced by a hexanol slush bath (melting point of hexanol, -52°C) and the system pumped down again to remove the final traces of the gas formed from the decomposition of the thiosulphate during preparation of I_2^{131}. The iodine was distilled into the side arm A kept at -196°C, the perfluoroalkyl iodide (known volume and pressure) was added, and the system pumped down again. The cell was sealed off from the vacuum line at the constriction C and was ready for use. This

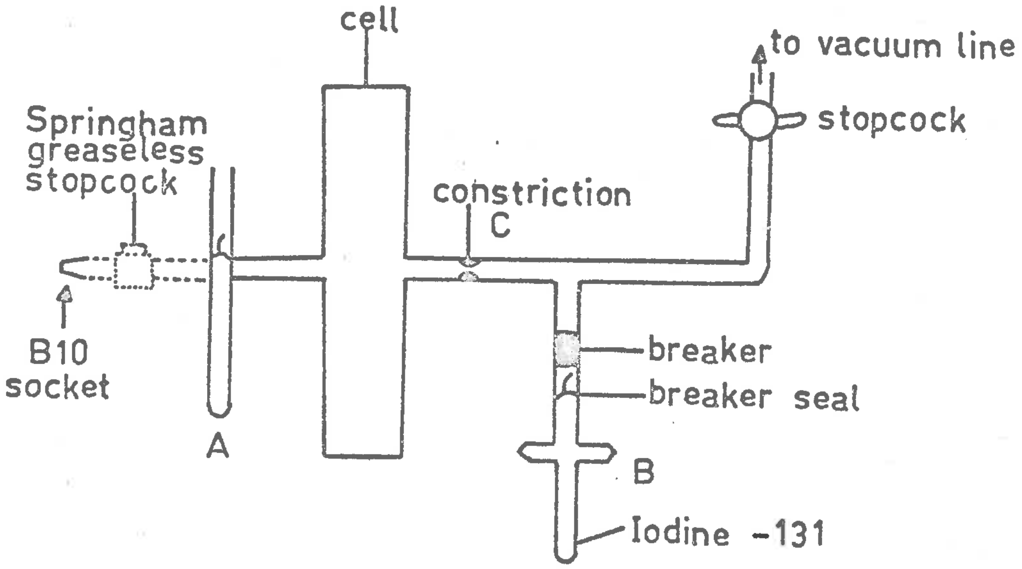


FIG. 4

The arrangement of apparatus for filling the cell with Iodine - 131.

procedure minimised the reaction of iodine with mercury and tap grease.

In the runs in which the pressure dependence of the fluoroalkyl iodide was studied, the iodine was condensed down at -196°C in the side arm A, whilst further amounts of the fluoroalkyl iodide were added through the greaseless stopcock (especially attached to the cell for these runs in the position as shown in figure 4). The pressures of the perfluoroalkyl iodide were read on a mercury manometer.

The iodine concentration in the cell was measured at the end of the exchange run. After condensing the cell contents in the side arm of the cell at -196°C, the cell was opened and the iodine dissolved in AR carbon tetrachloride. The solution was made up to standard volume (usually 10.0 ml) and the optical density of the solution measured at 510 mμ on a Unicam SP600 spectrophotometer (ϵ_{I_2} at 510 mμ was 940 litre moles^{-1} cm^{-1}).

The total volume of the reaction cell including the side arms was measured at the end of each run.

After filling the cell, the perfluoroalkyl iodide (RI) and the iodine (I_2) were condensed into the main body of the cell by placing the cell on paper which had been 'wetted' with liquid nitrogen. The cell was then immersed in hot water, followed by immersion in cold water. This method gave rapid homogeneous mixing of the perfluoro iodide and iodine.

Before the cell was placed in the oil bath, the zero-time fraction exchange was measured. The fraction exchange was then followed as a function of time for a particular set of conditions (e.g. temperature, illumination and RI concentration).

For the formal exchange process

$$I_2^* + RI \rightleftarrows RI^* + II^*$$

the rate of exchange, R_{ex}, is given by

$$R_{ex} = - \frac{2[RI][I_2]}{[RI] + 2[I_2]} \frac{\ln(1-F)}{t} \qquad (i)$$

where F is the fraction exchange at time t. For all the experiments the RI was initially inactive and the fraction exchange, F, was defined as

F = specific activity of I^{131} in RI/specific activity of I^{131} for all iodine in the RI and I_2.

In all of the experiments the RI pressures (C_2F_5I: 3-22 mm Hg, n-C_3F_7I: 3-19 mm Hg) was much greater than I_2 pressure (0.04-0.20 mm Hg) and the pressures were constant during a run, so that the fraction exchange reduced to

F = I^{131} activity in RI/total I^{131} activity in mixture.

Under these conditions, the rate of exchange R_{ex}, becomes

$$R_{ex} = - 2[I_2] \frac{\ln(1-F)}{t} \qquad (ii)$$

MEASUREMENT OF FRACTION EXCHANGE

The fraction exchange was measured without opening the cell by using the difference in the vapour pressures of RI and I_2 to effect the separation of the two reactants. At -52°C (hexanol slush) the vapour pressures of C_2F_5I and I_2 are approximately 25 mm Hg and 10^{-4} mm Hg respectively, whereas for n-C_3F_7I and I_2 at -22°C (CCl_4 slush bath) the vapour pressures are 25 mm Hg and 10^{-3} mm Hg respectively.

The cell was centred over the scintillation counter (figure 5) and the total activity measured. The RI and I_2 were then condensed in the side arm at -196°C and the background activity measured; this provided a check that cell contents were completely condensed. The temperature of the side arm was then raised to -52°C for C_2F_5I or -22°C for n-C_3F_7I and the activity in the RI measured. The shielding of the side trap from the scintillation counter ensured that only about 0.1% of the apparent RI activity was due to the detection of I_2^{131} condensed in the trap. The separation of the RI and I_2, particularly for n-C_3F_7I, is not complete, due to the finite vapour pressure of I_2 at -52°C or -22°C. The effect of the incomplete separation was however equivalent to no more than about 2% exchange and was time independent. Each value of the fraction exchange at a particular reaction time is the average of at least two repetitions of the process of condensing at -196°C, counting, warming the side arm up to -52°C or -22°C and counting again.

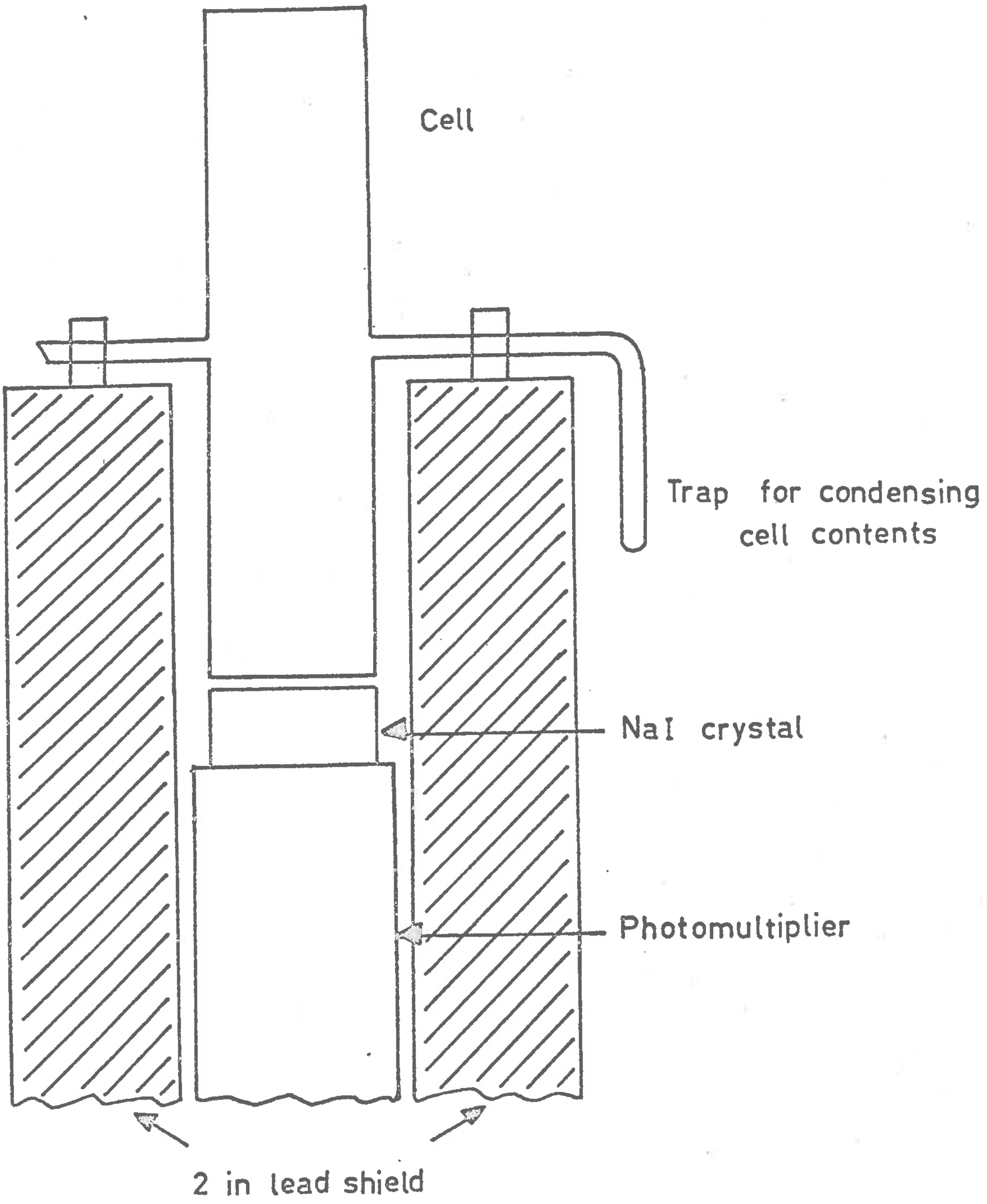


FIG. 5

Arrangement of reaction cell, NaI crystal and photomultiplier for counting.

4. RESULTS

As the results and their interpretation are similar for both C_2F_5I and n-C_3F_7I they will be treated together. Any particular differences will be considered in context.

Diagrams used in illustrating some characteristics of the exchange of C_2F_5I or n-C_3F_7I are given the same figure numbers; those referring to C_2F_5I have the suffix Et and those referring to n-C_3F_7I have the suffix Pr. For example, the temperature dependence of the thermal exchange rate constant is shown in figure 6: - figure 6Et refers to C_2F_5I and figure 6Pr to n-C_3F_7I.

The complete experimental data are given in Appendix 6.1 and 6.2.

4.1 THERMAL EXCHANGE

Although a complete dependence of the thermal exchange rate on the perfluoroalkyl iodide [RI] and the iodine $[I_2]$ concentrations was not carried out, in the case of the $C_2F_5I-I_2$ system for example, there was at least a five-fold variation in the iodine concentration at constant $[C_2F_5I]$. It will be shown that the $C_2F_5I-I_2$ exchanges are very similar to the CF_3I-I_2 exchange. It will be assumed in this analysis that the exchange is first order in [RI], as is the case for CF_3I-I_2 exchange.[6] The exchange is found to be half order in $[I_2]$, (Table II), that is

$$R_{ex} = k_t[C_2F_5I][I_2]^{\frac{1}{2}}$$

TABLE II

Dependence of Thermal Exchange Rate on C_2F_5I and I_2 Concentration at 159.4 ± 0.3°C

$[C_2F_5I]$ mole cm^{-3} x 10^6	$[I_2]$ mole cm^{-3} x 10^9	R_{ex} mole cm^{-3} min^{-1} x 10^{12}	$R_{ex}/[I_2]^{\frac{1}{2}}[C_2F_5I]$ $cm^{3/2}$ $mole^{-\frac{1}{2}}$ min^{-1} x 10^2
1.32	13.03	7.34	4.88
1.27	5.15	7.09	7.76
1.28	3.95	5.16	6.39
1.30	3.76	5.96	7.45
1.34	4.78	7.10	7.65

Although the temperature within the paraffin bath was controlled to within ± 0.05°C by a thermistor controller, however the temperature did vary from run to run by ± 0.3°C because of variations in the thermistor control setting etc. The value of $k_t = 4.08 \times 10^{-2}$ $cm^{3/2}$ $mole^{-\frac{1}{2}}$ min^{-1} in Table II was obtained for the run using the cell whose surface to volume ratio (S/V) was 1.6 cm^{-1}. Only 1/3rd lengthwise of the side arm A (figure 4) is immersed within the paraffin oil, whereas the remaining 2/3rds protrudes above the surface; consequently, the side arm may not be at the same temperature as the body of the cell. As the side arm is approximately 30% of the volume of this cell, it may therefore be responsible for the lower k_t observed.

The exchange rates were measured over the temperature range 125–165°C and the Arrhenius plots are shown in figures 6Et and 6Pr. The apparent activation energy for the exchange of C_2F_5I-I_2 was 31.6 ± 0.8 kcal $mole^{-1}$, and for n-C_3F_7I-I_2 exchange was 32.3 ± 1.2 kcal $mole^{-1}$. The plots do not show any obvious curvature and the relatively high values of the activation energies can be taken to indicate that the exchange is homogeneous in this range. The exchange reactions of the corresponding alkyl iodides with I_2 were found to be heterogeneous in the gas phase.[5] Possible heterogeneous effects in the perfluoroalkyl iodide-iodine system were tested for by carrying out exchange experiments in which S/V ratio of the reaction cell was varied. Three cells were used whose S/V

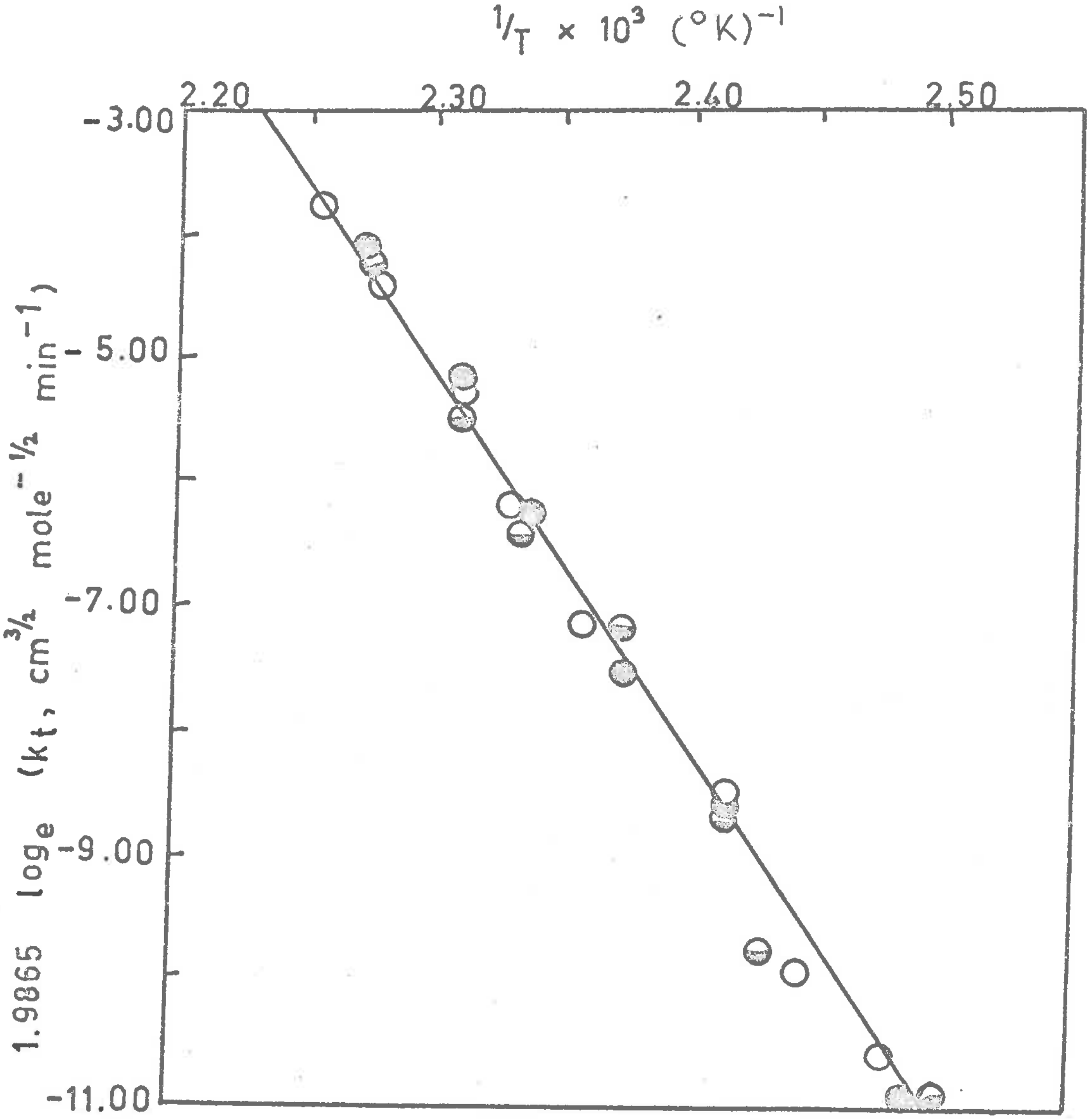


FIG. 6 Et

Temperature dependence of the thermal exchange rate constant.

○ [C_2F_5I] 1.30×10^{-6} mole cm^{-3}, [I_2] 3.76×10^{-9} mole cm^{-3}

⊖ [C_2F_5I] 1.28×10^{-6} mole cm^{-3}, [I_2] 3.95×10^{-9} mole cm^{-3}

● [C_2F_5I] 1.27×10^{-6} mole cm^{-3}, [I_2] 5.15×10^{-9} mole cm^{-3}

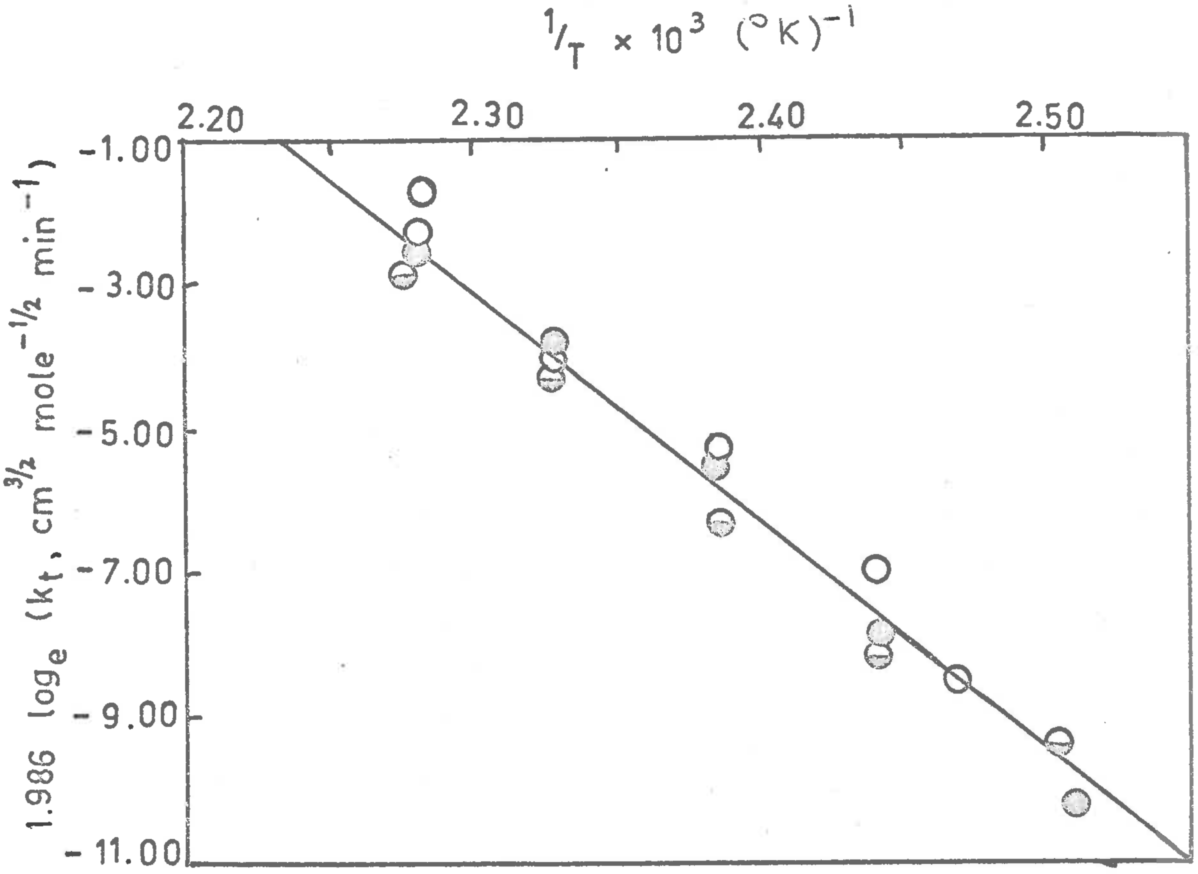


FIG. 6 Pr

Temperature dependence of the thermal exchange rate constant.

○ $[C_3F_7I]$ 9.64×10^{-7} mole cm^{-3}, $[I_2]$ 3.55×10^{-9} mole cm^{-3}

⊖ $[C_3F_7I]$ 9.35×10^{-7} mole cm^{-3}, $[I_2]$ 3.71×10^{-9} mole cm^{-3}

● $[C_3F_7I]$ 10.04×10^{-7} mole cm^{-3}, $[I_2]$ 4.18×10^{-9} mole cm^{-3}

ratios were 1.0, 1.6 and 5.4 cm^{-1}, and the Arrhenius plots for these experiments are given in figure 7Et and 7Pr. The apparent activation energy for $C_2F_5I-I_2$ was 30.7 ± 1.2 kcal $mole^{-1}$, and for n-$C_3F_7I-I_2$ was 31.6 ± 1.2 kcal $mole^{-1}$. These values of the activation energy are the same within experimental error as those obtained from the normal temperature studies of $RI-I_2$ exchange.

In a run with clean, dry glass wool, no exchange could be measured. Apparently, the exchange was completely inhibited, perhaps because the iodine may have reacted with some residual water or was absorbed on the glass due to the enormous surface area.

4.2 PHOTOCHEMICAL EXCHANGE

With the light intensities used in the photochemical exchange runs, the thermal exchange contributed no more than approximately 1% to the overall exchange rate. This is small enough to be insignificant so that the thermal exchange rate was neglected in comparison with the photochemical rate.

The 5461 Å light used in the photochemical exchange experiments is absorbed by the iodine and not the perfluoroalkyl iodides. At the iodine concentration used approximately 10% of the incident light (λ = 5461 Å) was absorbed and light absorption was therefore effectively uniform throughout the cell, ensuring a homogeneous reaction.

The dependence of the exchange rate on the absorbed light

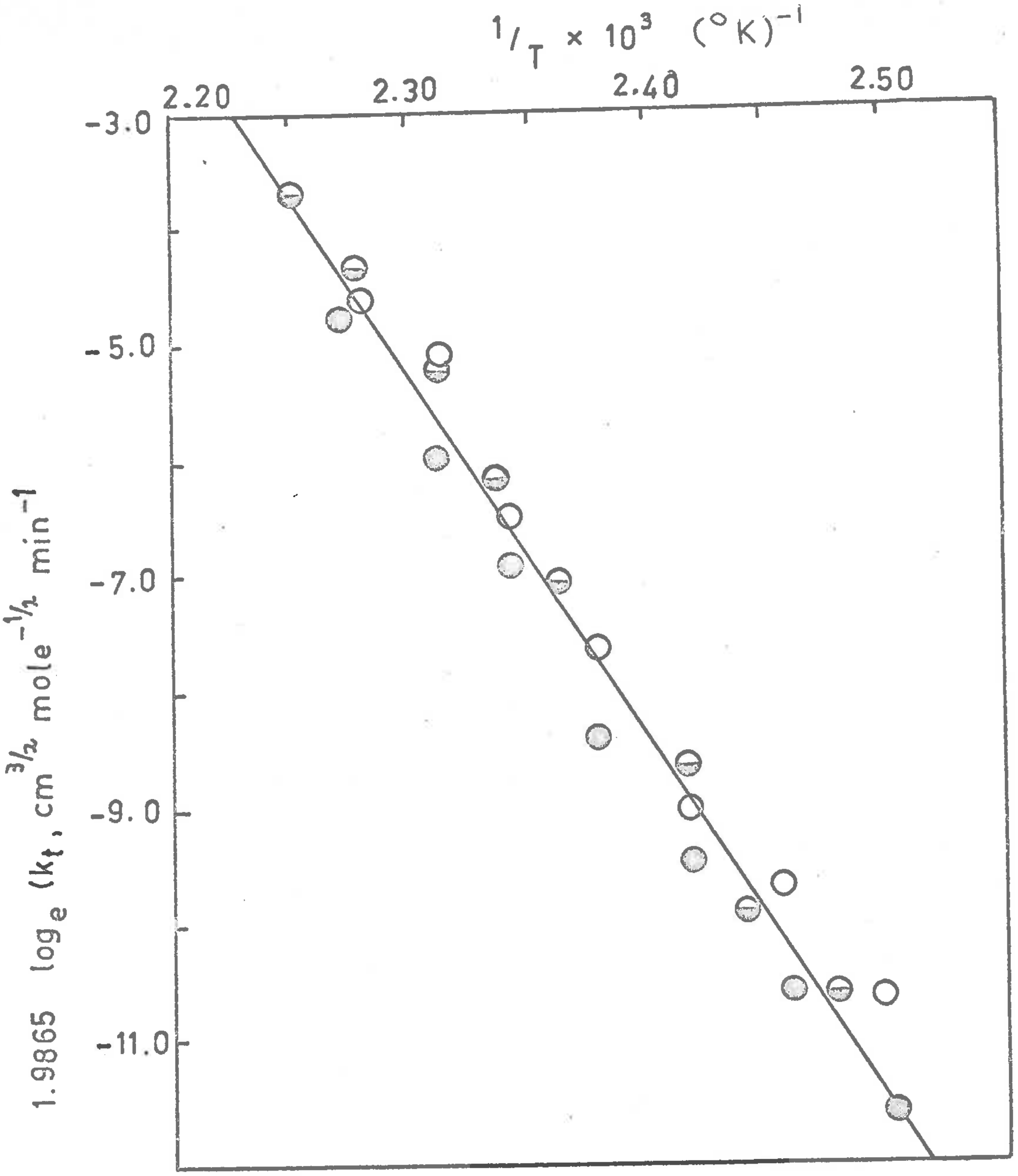


FIG. 7Et

The dependence of the thermal exchange rate constant on the surface area of the reaction vessel.

○ Surface/Volume (S/V) 5.44, [C_2F_5I] 1.34×10^{-6} mole cm^{-3}, [I_2] 4.78×10^{-9} mole cm^{-3}.

⊖ S/V 0.98, [C_2F_5I] 1.30×10^{-6} mole cm^{-3}, [I_2] 3.76×10^{-9} mole cm^{-3}

● S/V 1.59, [C_2F_5I] 1.32×10^{-6} mole cm^{-3}, [I_2] 1.30×10^{-9} mole cm^{-3}

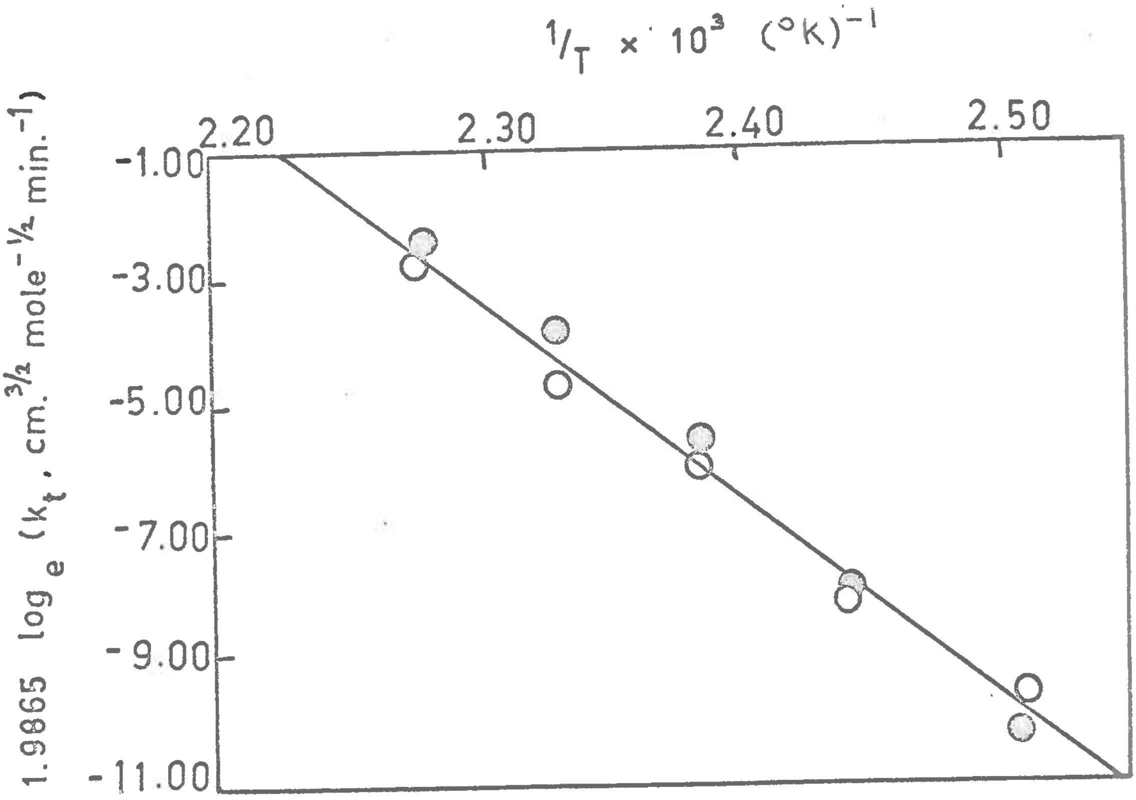


FIG. 7 Pr

The dependence of the thermal exchange rate constant on the surface area of the reaction vessel.

○ S/V = 5.44, $[C_3F_7I]$ 1.12×10^{-6} mole cm^{-3} $[I_2]$
= 4.93×10^{-9} mole cm^{-3}

● S/V = 1.09, $[C_3F_7I]$ 1.00×10^{-6} mole cm^{-3} $[I_2]$
= 4.18×10^{-9} mole cm^{-3}

intensity was determined by varying the incident light intensity with a variable aperture sector run at high speed.[53] Briefly, the high sector speed is essential so that the sector acts as a filter rather than as a 'timer' (i.e. reducing the actual time of exposure to light). To test whether the sector speed was high enough, a run was carried out using a sector with light:dark ratio of 1:3, and it was found that the rate was one half of the rate with full illumination, which meant that sector must have been going fast enough.[6] It was found that the exchange rate for $RI-I_2$ was proportional to the square root of the absorbed light intensity (figures 8Et and 8Pr).

The dependence of the exchange rate on [RI] is shown in figures 9Et and 9Pr. The exchange rate is first order in [RI] at constant absorbed light intensity.

The activation energy, measured over a temperature range 50-120°C, for the photochemical exchanges are $C_2F_5I-I_2$, 14.5 ± 0.8 kcal mole^{-1} and $n-C_3F_7I-I_2$, 17.5 ± 0.8 kcal mole^{-1} obtained from the Arrhenius plots given in figures 10Et and 10Pr.

5. DISCUSSION

5.1 THERMAL EXCHANGE

Experimentally the thermal exchange is first order in [RI] for CF_3-I_2 exchange,[6] and has been assumed to be first order for $[C_2F_5I]$ and $[n-C_3F_7I]$. The exchange is half order in $[I_2]$ and

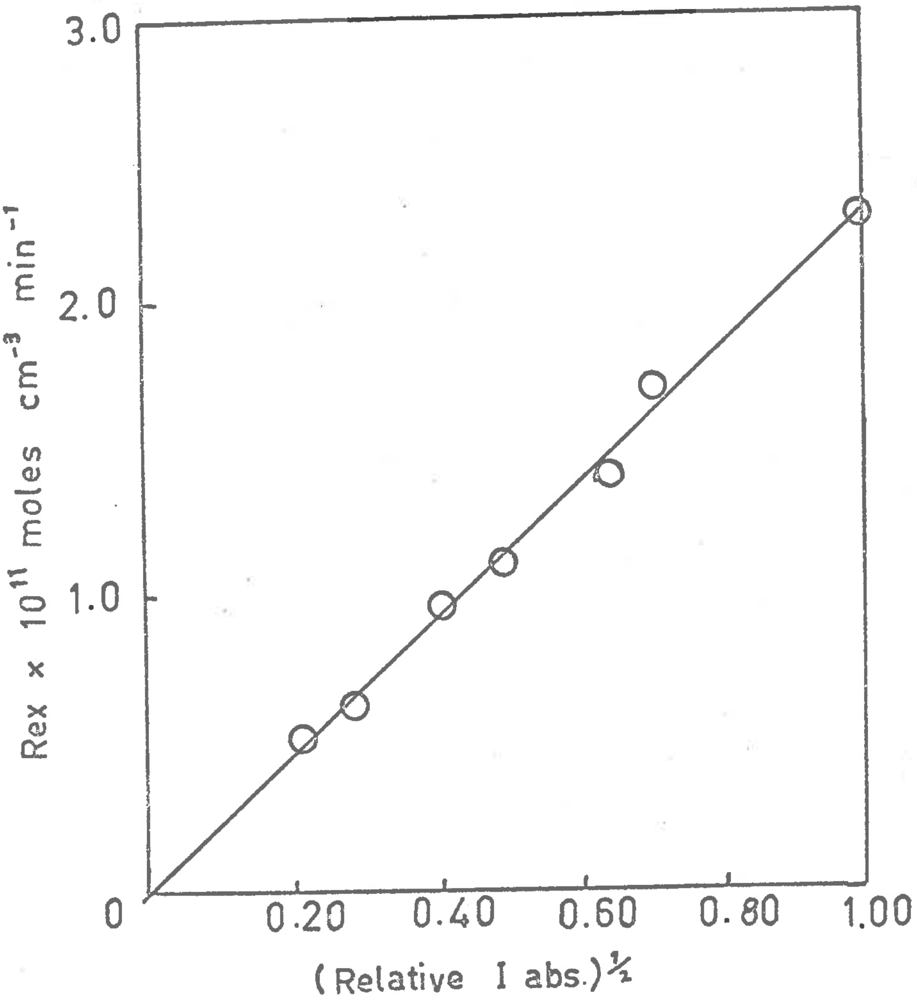


FIG. 8Et

Dependence of the photochemical exchange rate constant upon the square root of the relative absorbed light intensity at 113.5°C.

$[C_2F_5I]$ 1.19×10^{-6} mole cm^{-3}

$[I_2]$ 3.60×10^{-9} mole cm^{-3}

I_o = 1.200×10^{15} hv / cm^2 / min

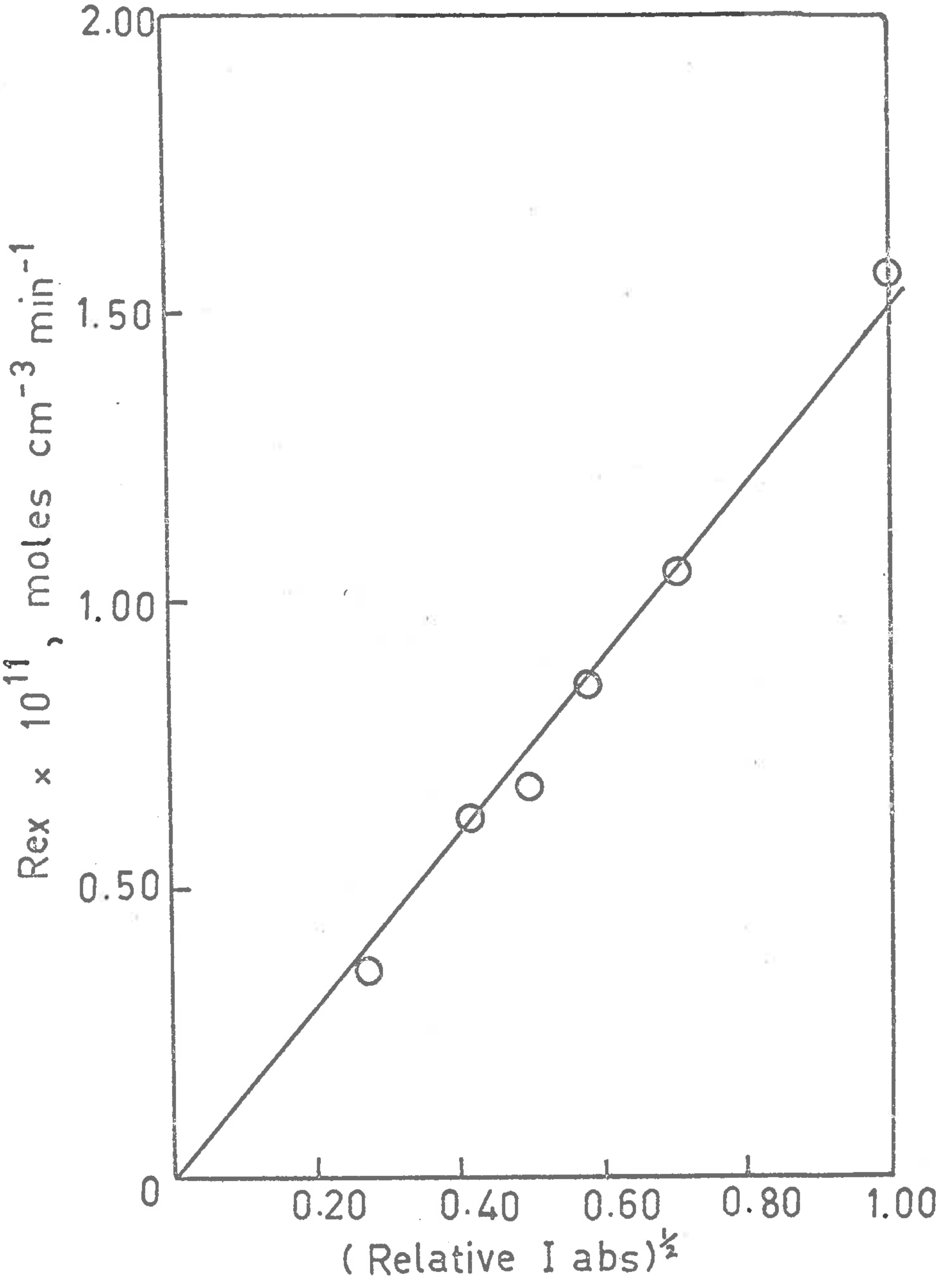


FIG. 8 Pr

The dependence of the photochemical exchange rate constant upon the square root of the relative absorbed light intensity at 80.2 °C.

$[C_3F_7I]$ 9.64×10^{-7} mole cm^{-3},

$[I_2]$ 3.55×10^{-9} mole cm^{-3}.

Note:

In diagrams 9Et, 9Pr, 10Et and 10Pr the relationships R_{ex}/Absorbance or R_{ex}/[RI]Abs are plotted against [RI] or 1/T respectively. The quantity Absorbance or Abs is the factor which takes into account the amount of light absorbed by the iodine in the cell. Absorbance (Abs) is related to the light intensity by

$$I_{Abs} = Abs^2 \, I_o$$

where I_{Abs} = light absorbed

I_o = incident light (constant for each run)

$Abs^2 = (1.0 - 10.0^{-\varepsilon c l})$

where ε = iodine extinction coefficient

= 560 litre moles^{-1} cm^{-1} [96]

c = iodine concentration in moles litre^{-1}

l = path length (cm)

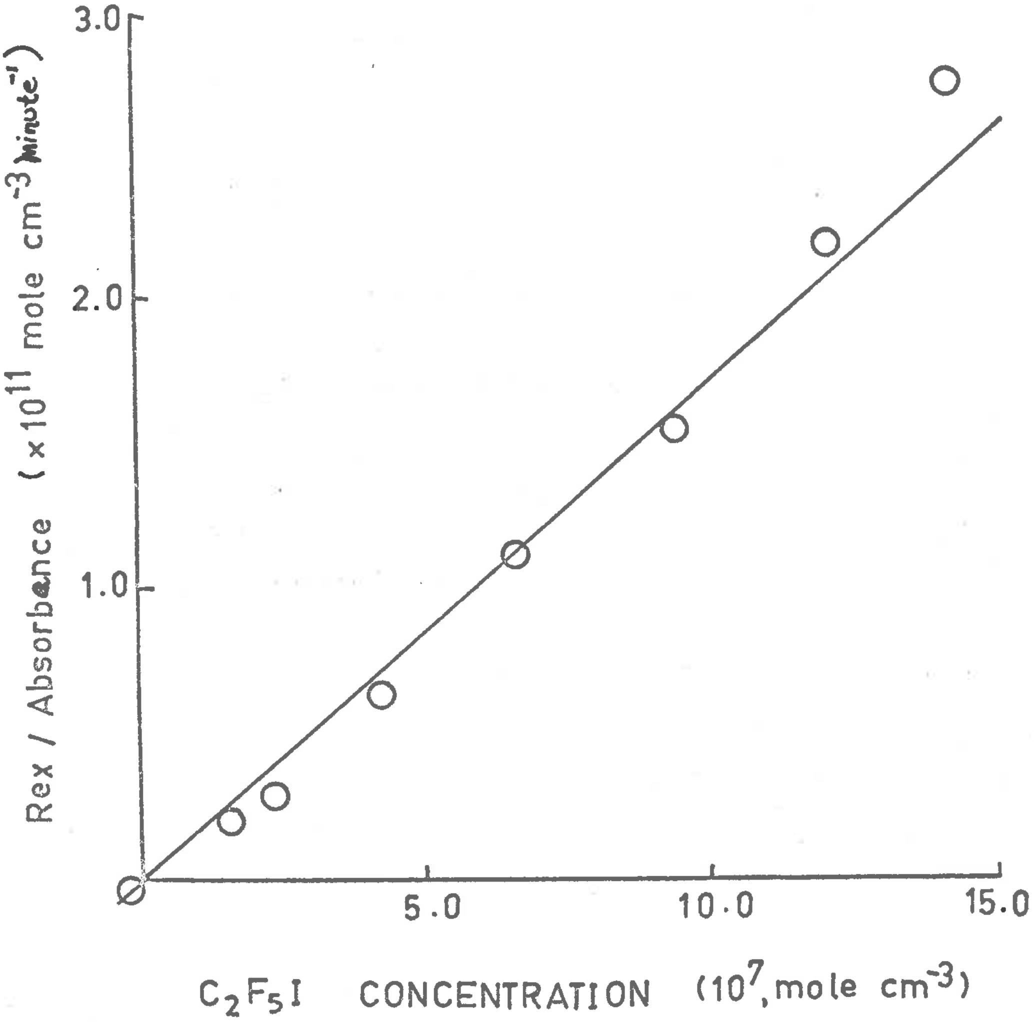


FIG. 9 Et

The dependence of the photochemical exchange rate upon C_2F_5I concentration at 113°C . $[I_2]$ 2.62×10^{-9} mole cm^{-3}

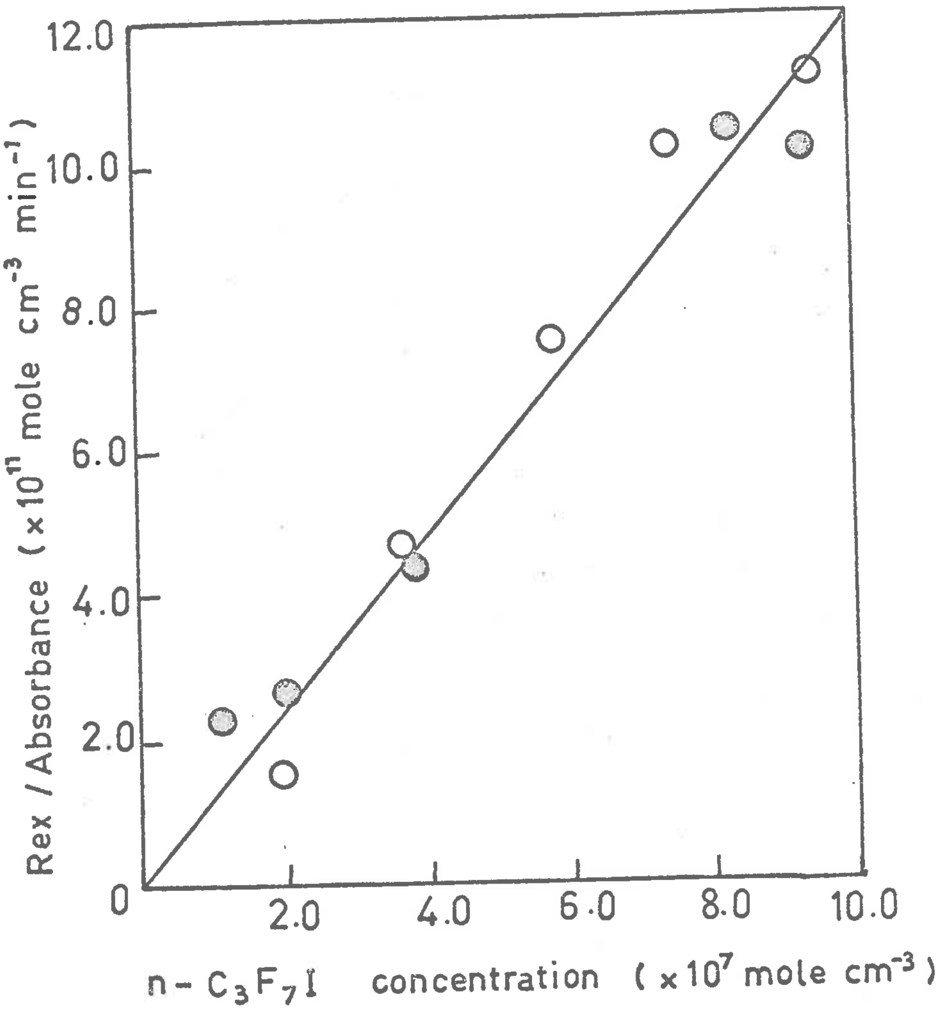


FIG. 9 Pr

The dependence of the photochemical exchange rate upon the n- C_3F_7I concentration at 80 ° C.

● $[I_2]$ 3.47×10^{-9} mole cm^{-3}

○ $[I_2]$ 3.18×10^{-9} mole cm^{-3}

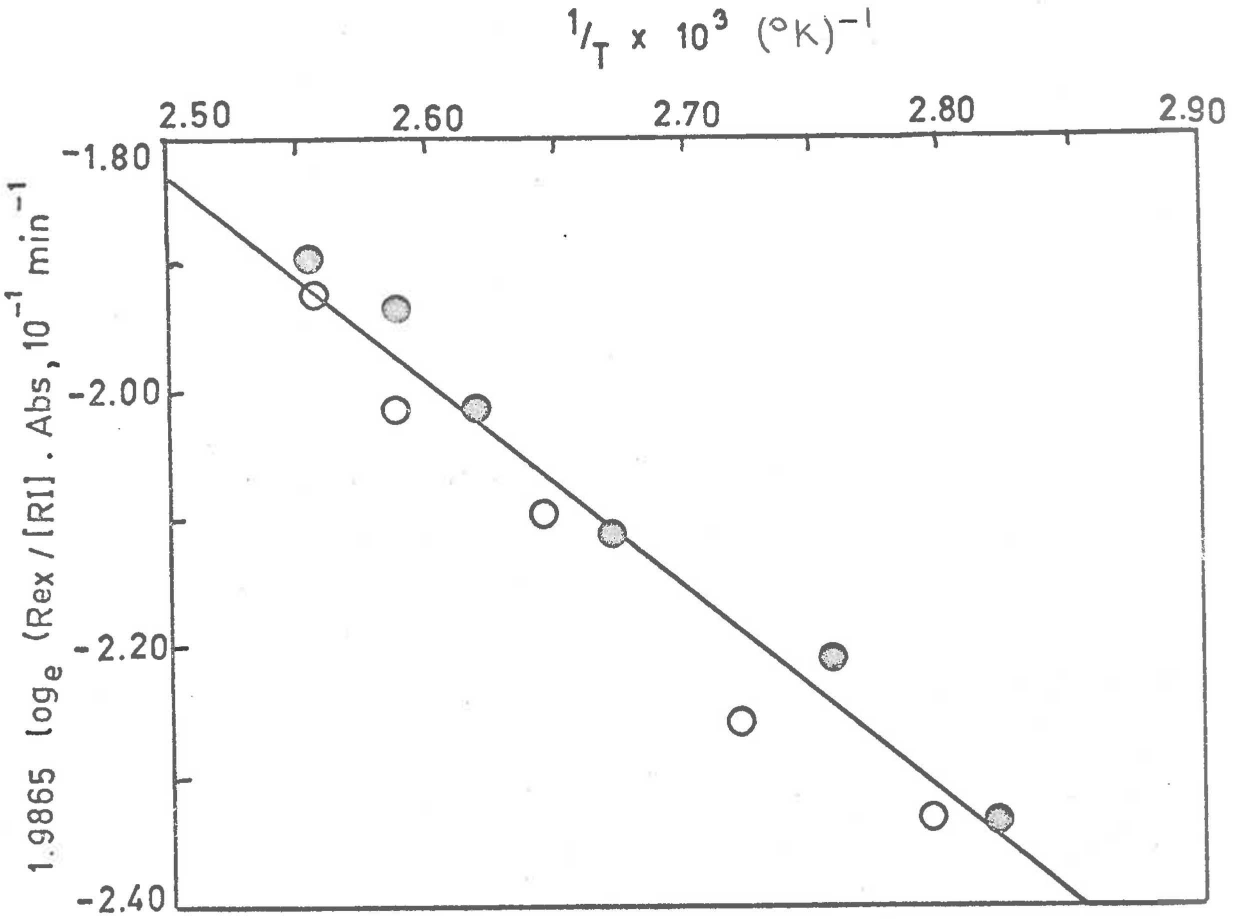


FIG. 10 Et

Temperature dependence of the photochemical exchange rate constant.

○ (C_2F_5I) 1.25×10^{-6} mole cm^{-3}, $[I_2]$ 3.05×10^{-9} mole cm^{-3}

● (C_2F_5I) 1.13×10^{-6} mole cm^{-3}, $[I_2]$ 3.45×10^{-9} mole cm^{-3}

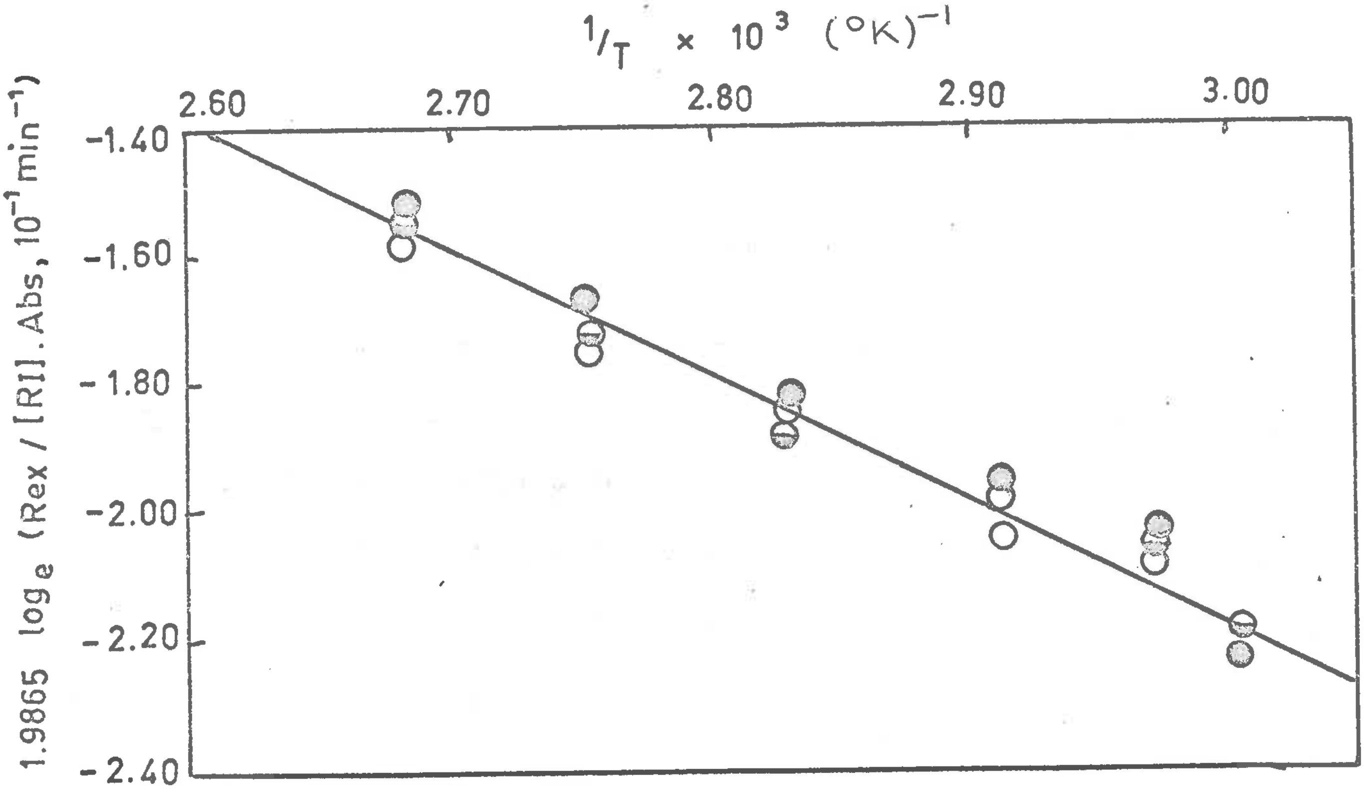


FIG. 10 Pr

Temperature dependence of the photochemical exchange rate constant.

○ n - C_3F_7I 9.59 x 10^{-7} mole cm^{-3}, [I_2] 3.88 x 10^{-9} mole cm^{-3}

⊖ n - C_3F_7I 9.57 x 10^{-7} mole cm^{-3}, [I_2] 3.85 x 10^{-9} mole cm^{-3}

● n - C_3F_7I 9.74 x 10^{-7} mole cm^{-3}, [I_2] 3.85 x 10^{-9} mole cm^{-3}

$I_{Abs} = Abs^2 \, I_o$

appears to be homogeneous, showing no dependence on the S/V ratio of the reaction vessel.

The rate law is

$$R_{ex} = k_t [RI] [I_2]^{\frac{1}{2}}$$

and this is incompatible with the simple bimolecular process

$$I_2^* + RI \rightarrow RI^* + I_2$$

but could result from the reaction initiated by atoms or radicals produced by the thermal decomposition of I_2.

The proposed reaction scheme is

$$I_2 + M \rightarrow 2I + M \tag{1}$$

$$RI \rightarrow R + I \tag{2}$$

$$I^* + RI \rightarrow RI^* + I \tag{3}$$

$$I^* + RI \rightarrow R + II^* \tag{4}$$

$$I_2^* + R \rightarrow RI^* + I^* \tag{5}$$

$$I + I_2^* \rightarrow II^* + I^* \tag{6}$$

$$I + I + M \rightarrow I_2 + M \tag{7}$$

$$R + I \rightarrow RI \tag{8}$$

$$R + R \rightarrow R_2 \tag{9}$$

Reaction (9) is omitted from the ensuing discussion as reaction (5) will be much faster as the steady state concentration of [I] and [I_2] will be much greater than [R]. The ratio of $k_5/k_9^{\frac{1}{2}}$ was measured in the photolysis of C_2F_5I with 2537 Å light (see part 2 of this thesis) and found to be ~7 x 10^4 litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec$^{-\frac{1}{2}}$.

The exchange rate law derived from reactions (1) to (8) is

$$R_{ex} = k_5(R)(I_2) + (k_3(RI)(I) + k_8(R)(I))P \qquad (10)$$

where

$$P = \frac{2k_1(I_2)(M) + k_5(R)(I_2) + k_6(I)(I_2)}{2k_1(I_2)(M) + k_2(RI) + k_3(RI)(I) + k_5(R)(I_2) + k_6(I)(I_2)}$$

The fraction, P, multiplying the terms in brackets is the probability factor that a particular iodine atom was formed from molecular iodine rather than from the organic iodide. The introduction of this probability factor is necessary as the distribution of the radioactivity in the iodine atoms is not necessarily the same as in the iodine molecules. The rate constant for the exchange reaction I-I_2 has been measured by Noyes and Zimmerman[16] and found to be 8 x 10^7 litre mole^{-1} sec^{-1} at 25°C in hexane solutions. The atom-molecule exchange is not subject to solvation effects in the gas phase and therefore the rate constant for the gas-phase atom-molecule exchange is probably much larger than 8 x 10^7 litre mole^{-1} sec^{-1}. The $k_6(I)(I_2)$ term is therefore likely to be much larger than any of the other terms (it has an energy of activation of only about 2-3 kcal mole^{-1} in solution and is virtually diffusion controlled[16]), and therefore the fraction P can be set to unity. Although reactions (5) and (8) have low activation energies, the formation of [R] has a relatively large activation energy of about 50 kcal mole^{-1} by reaction (2), and about 15 kcal mole^{-1} or more by reaction (4) (see below), and so the overall activation energy involving reactions of R will have this inherited activation energy.

As the exchange reaction produces no change in the reactant concentrations (a necessary consequence if reaction (9) is omitted) reactions (1) to (8) will be in equilibrium, so that

$$k_1(I_2)(M) = k_7(I)^2(M)$$

$$k_2(RI) = k_8(R)(I)$$

$$k_4(I)(RI) = k_5(R)(I_2)$$

When these equalities are introduced, equation (10) can be rearranged to give

$$R_{ex} = k_2(RI) + (k_3 + k_4)(k_1/k_7)^{\frac{1}{2}}(RI)(I_2)^{\frac{1}{2}} \qquad (11)$$

This expression (1) is similar to the observed rate law but has an additional term $k_2(RI)$, which corresponds to the exchange initiated by thermal decomposition of RI. The contribution of this term to the rate of exchange may be estimated if it is assumed that $k_2 = 10^{13}\ e^{-E_2/RT}$, where 10^{13} sec^{-1} is the typical magnitude of the pre-expotential term (frequency factor) for unimolecular

dissociation, and E_2 will be at least the C-I bond dissociation energy, if not larger, depending on the exact slope of the potential energy curve for RI at large internuclear distance. The C-Br and C-Cl bond energies show similar trends for alkyl and perfluoroalkyl homologous series,[52] and similar trends in C-I bond energies may be expected for perfluoroalkyl iodides as for alkyl iodides.
If the mean C-I bond energy for C_2F_5I and n-C_3F_7I is approximately 50 kcal mole^{-1}, then k_2 is 10^{-14} sec^{-1} at 125°C and the contribution of reaction (2) to the rate of exchange ($\sim 1.2 \times 10^{-13}$ mole cm^{-3} sec^{-1}) is approximately 10^{-7} the observed rate. Reaction (2) is therefore omitted from the reaction scheme and equation (11) becomes

$$R_{ex} = (k_3 + k_4)(k_1/k_7)^{\frac{1}{2}}(RI)(I_2)^{\frac{1}{2}} \qquad (12)$$

If the experimentally determined value of k_t may be represented by the proposed reaction scheme, then k_t is a composite term containing contributions of the two paths (3) and (4) having identical kinetics, but not necessarily a similar temperature dependence. If reactions (3) and (4) both contribute significantly to the overall exchange over the experimental temperature range (125°-165°C) they probably have comparable activation energies, and over this small temperature range the departure from linearity of the Arrhenius plots, due to the experimental rate constant being the sum of two rate constants, is likely to be within the experimental error. The overall activation energy is therefore written as $E_{3,4}$ and is to be understood to refer to the activation energy for reaction (3), reaction (4) or to some sort of average of both activation energies. The most likely path for exchange and the path therefore to which $E_{3,4}$ refers will be considered below.

The ratio k_1/k_7 is the equilibrium constant for iodine dissociation. This means that the observed activation energy,

$$E_{obs} = E_{3,4} + \frac{1}{2} D.E\ (I-I),$$

where D.E (I-I) is the iodine dissociation energy, and at 126°C has a value of 36.2 kcal $mole^{-1}$.[17,18] This yields,

$$E_{3,4}(C_2F_5I) = 13.5 \pm 0.8 \text{ kcal mole}^{-1}$$

$$E_{3,4}(n\text{-}C_3F_7I) = 14.2 \pm 1.2 \text{ kcal mole}^{-1}$$

The values of $k_{3,4}$ are

$$k_{3,4}(C_2F_5I) = 10^{10.0} \exp[-13500 \pm 800/RT] \text{ litre mole}^{-1} \text{ sec}^{-1}$$

$$k_{3,4}(n\text{-}C_3F_7I) = 10^{10.2} \exp[-14200 \pm 1200/RT] \text{ litre mole}^{-1} \text{ sec}^{-1}$$

5.2 PHOTOCHEMICAL EXCHANGE

If the photochemical exchange (5461 Å light) proceeds by a mechanism essentially identical to the thermal exchange, except that the initiation is now

$$I_2 + h\nu \rightarrow I + I \qquad (1a)$$

then, where for the thermal exchange under steady conditions, the iodine atom concentration is given by

$$k_{1d}[I_2] = k_7[I]^2[M]$$

now it will be given by

$$\phi I_{ABS} = k_7[I]^2[M] \ .$$

I_{ABS} is the rate of light absorption by the iodine, and ϕ is the quantum yield for iodine atom formation by (1d). In the banded region (which includes the 5461 Å light used in the exchange) of the molecular iodine spectrum the quantum yield for iodine atom formation has been measured by Rabinowitch and Wood[11] and found to be one, i.e. $\phi = 1.0$. The rate of exchange in the steady state is therefore

$$R_{ex} = (k_3 + k_4)(I_{ABS}/k_7)^{\frac{1}{2}}[RI]^{\frac{1}{2}} \qquad (13)$$

as (M) is equivalent to [RI] under the experimental conditions in which $[RI] \gg [I_2]$. Once again $k_2[RI]$ was neglected, as its contribution to the photochemical rate of exchange will be as small as for the thermal exchange, if not smaller.

The observed rate law is

$$R_{ex} = k_p[RI] \qquad (14)$$

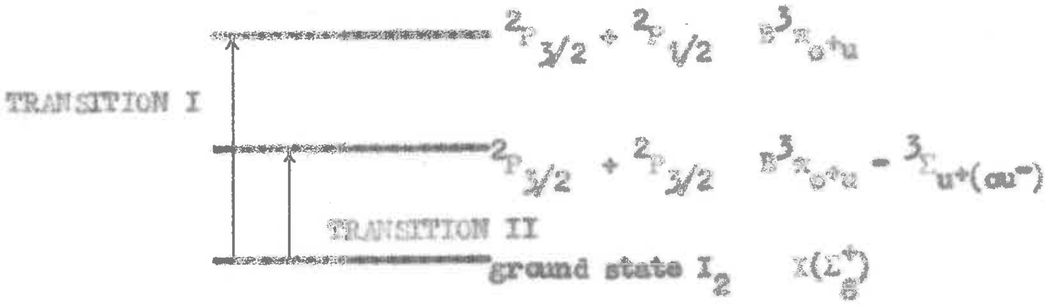
where k_x may perhaps be identified with $(k_3 + k_4)(I_{ABS}/k_7)^{\frac{1}{2}}$.

The unexpected difference between the observed rate law and that predicted on the basis of the reaction scheme is intimately linked with the mechanism of formation and recombination of iodine atoms and these two aspects will now be discussed in some detail.

5.2(a) Iodine Atom Formation

The potential energy diagram for molecular iodine is shown in figure 11. This figure is based on the data of Ogryzlo and Thomas[19] and Matheson and Rees.[20] Steinfeld[21] includes a number of other repulsive states which can lead to additional induced pre-dissociation quenching of fluorescence, but for the present discussion the effect of these additional states can be considered to be essentially the same as those given in figure 11.

The absorption by iodine vapour of light of wavelengths less than 4990 Å (in the region of the molecular iodine continium) corresponds to direct dissociation to a ground state ($^2P_{3/2}$) iodine atom and an excited ($^2P_{1/2}$) iodine atom (transition I)



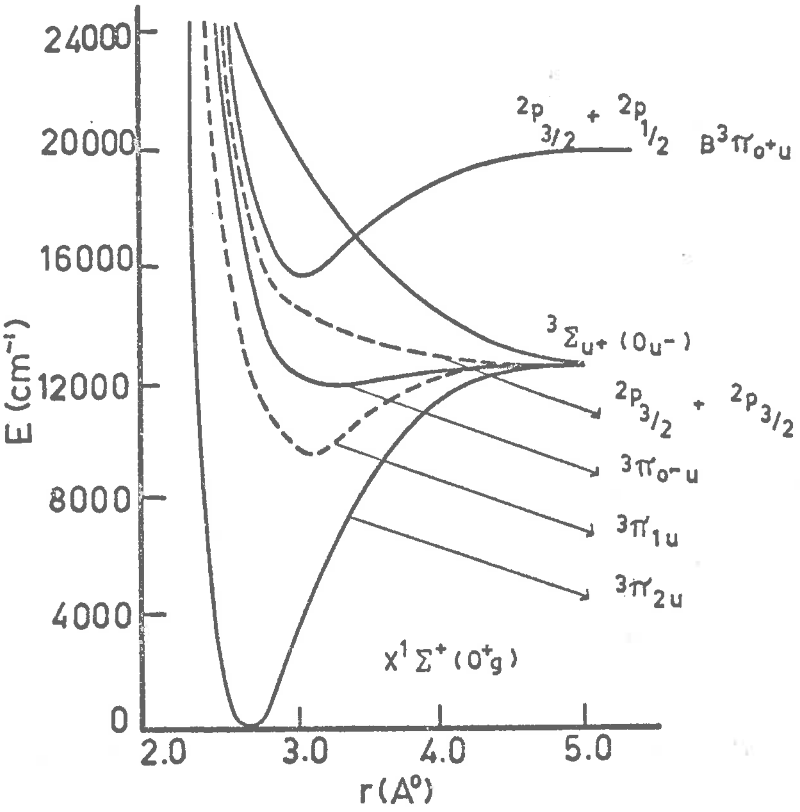


FIG.11

Potential energy levels of some low-lying states of I_2.

i.e. $$I_2 \quad X(\Sigma_g^+) \xrightarrow[\lambda < 4990 \text{ Å}]{h\nu} I({}^2P_{3/2}) + I({}^2P_{1/2})$$

The energy difference between the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states for iodine atoms is 21.7 kcal mole^{-1}.

When the I_2 molecule absorbs radiation (light of $\lambda > 4990$ Å) corresponding to transition II to the discrete bands of the $B({}^3\pi_{o^+u})$ state (the natural mean lifetime is of the order of 10^{-7} sec[11]) several secondary processes may occur. A return to the ground state $(X'\Sigma_g^+)$ may take place by fluorescent emission

$$I_2 \quad B({}^3\pi_{o^+u}) \rightarrow I_2 \; X(\Sigma_g^+) + h\nu'$$

or the excited molecule may undergo pre-dissociation[54] as the $B({}^3\pi_{o^+u})$ state is crossed by a dissociative state ${}^3\Sigma^+_{u(ou^-)}$. Pre-dissociation from the ${}^3\Sigma^+_{u(ou^-)}$ state leads to two ground state iodine atoms. An increase in the iodine pressure, the addition of a few millimetres of a foreign gas,[11,22] or the application of a magnetic field[23,24] increases the quenching of the iodine fluorescence by induced pre-dissociation. The mechanism of this dissociation results from the transition from the excited state $B({}^3\pi_{o^+u})$ to the unstable repulsive state ${}^3\pi_{o^-u}$. This transition is forbidden in a free iodine molecule but the selection rules which govern the transition break down in the presence of magnetic and inhomogeneous molecular fields.[11] The importance of the parts played by the various excited energy levels in the pre-dissociation is fully discussed by

Steinfeld.[21,25] The collision induced quenching efficiency has been correlated with the polarisability of the quenching gas[21,25-27] except that NO[28] and I_2 itself have abnormally high efficiencies. The high efficiency observed for I_2 may be due to the unique paths available to it by which the excited molecule in the $B(^3\pi_{o+u})$ state may be quenched.[29] First, is the one in which the ground state molecule acts as any other third body, and induces pre-dissociation of the excited molecule. The second, the excited molecule transfer its energy to the ground state molecule, which now becomes excited and dissociates. However the two reactions paths are kinetically indistinguishable.

The photochemical exchange was studied using the 5461 Å mercury line to produce the iodine atoms, and if the non-electronic contributions to the energy are neglected, then the processes taking place can be considered to be,

Excitation: $I_2 + h\nu \rightarrow I_2^{**}$ (1a)

Quenching and Dissociation: $I_2^{**} + M \rightarrow 2I(^2P_{3/2}) + M$ (1b)

Fluorescence: $I_2^{**} \rightarrow I_2 + h\nu'$ (1c)

where I_2^{**} represents the excited state $B(^3\pi_{o+u})$.

In the process (1b), M represents either a ground state iodine molecule or the perfluoroalkyl iodide; the steady-state concentration of I_2^{**} is sufficiently small for direct bimolecular interactions between the excited molecules to be negligible. The self-quenching reaction by the molecular iodine has been left out in the ensuing algebraic treatment of the above reactions, and M is the perfluoroalkyl iodide, as (RI) >> (I_2).

5.2(b) Iodine Atom Recombination

Rabinowitch and Wood[30] using steady-state methods measured the recombination rate constant of iodine atoms in the presence of various third bodies. In general, the efficiency of the third body increases with its complexity and the intensity of Van der Waal's forces between the colliding species.

The development of the flash photolysis technique brought about a renaissance in the study of the recombination of iodine atoms,[28,31-39,41] and led to the postulation of two different mechanisms for the recombination.

(i) Collisional Deactivation Mechanism.[46]

This involves the formation of an activated iodine molecule, which has to be deactivated by collision with a foreign molecule in order to be stabilised, i.e. the reaction scheme describing the process is

Association: $I + I \rightarrow I_2^{\ddagger}$ (7a)

Stabilisation: $I_2^{\ddagger} + M \rightarrow I_2 + M$ (7b)

Dissociation: $I_2^{\ddagger} \rightarrow I + I$ (7c)

(ii) Radical-Molecule Complex Mechanism.[36]

An addition complex is formed between an iodine atom and the third body. On collision with another iodine atom the complex dissociates into an iodine molecule and the third body:

Association: $$I + M \rightarrow IM^{**} \qquad (7_{1a})$$

$$IM^{**} + I \rightarrow I_2 + M^{*} \qquad (7_{1b})$$

Dissociation: $$IM^{**} \rightarrow I + M \qquad (7_{1c})$$

The merits and demerits of both theories have been fully discussed by Porter.[40] Reasonable agreement was obtained for the iodine recombination rate constant (k_r) calculated (semi-empirical) using the collisional deactivation approach and the experimentally measured value of the recombination activation energy for the inert gases as third bodies. However the values of k_r calculated for more complex molecules by this method are in poor agreement with the observed values.

Overall the radical-molecule complex theory provides better agreement between calculated (semi-empirical) and observed values of k_r. The main objection that can be raised to the complex theory concerns the nature of the complex. Earlier interpretations of the recombination rates in terms of molecular forces (e.g. Van der Waal's forces)[34,36] are not successful, as these forces are too small, and show too little variation between different third body molecules, to account for either temperature coefficients or relative rates. The charge-transfer complex theory advanced by Porter and Smith[38] accounts for the temperature coefficients and the relative rates in a more satisfactory manner. Recent flash photolysis work[28,39,42] has provided further evidence in support of the charge-transfer theory by direct observation of the absorption spectra of the charge-transfer complexes themselves.

A detailed algebraic analysis has been carried out assuming either the collisional deactivation or charge-transfer complex mechanism, in order to express the stationary state concentration of iodine atoms, and therefore exchange rate, under the present experimental conditions. It should be noted that for both reaction mechanisms, the reactions leading up to the iodine atom formation will be the same, i.e. both will include reactions 1a, 1b and 1c.

(i) The collisional deactivation mechanism.

$$\begin{array}{rcll}
I_2 + h\nu & \rightarrow & I_2^{**} & \qquad k_{1a} \\
I_2^{**} + M & \rightarrow & I + I + M & \qquad k_{1b} \\
I_2^{**} & \rightarrow & I_2 + h\nu' & \qquad k_{1c} \\
I + I & \rightarrow & I_2^{\pm} & \qquad k_{7a} \\
I_2^{\pm} + M & \rightarrow & I_2 + M & \qquad k_{7b} \\
I_2^{\pm} & \rightarrow & I + I & \qquad k_{7c}
\end{array}$$

Assuming a steady state for (I_2^{**}), $(I_2^{\pm})$ and (I), then

$$d[I_2^{**}]/dt = 0 = k_{1a}(I_2) - k_{1c}(I_2^{**}) - k_{1b}(I_2^{**})(M)$$

$$d[I_2^{\pm}]/dt = 0 = k_{7a}(I)^2 - k_{7b}(I_2^{\pm})(M) - k_{7c}(I_2^{\pm})$$

$$d[I]/dt = 0 = 2\,k_{1b}(I_2^{**})(M) - 2\,k_{7a}(I)^2 + 2\,k_{7c}(I_2^{\pm})$$

By substitution and rearrangement

$$[I]^2 = \frac{k_{1a}k_{1b}(I_2)}{k_{7a}k_{7b}} \cdot \frac{[k_{7c} + k_{7b}(M)]}{[k_{1c} + k_{1b}(M)]} \qquad (15)$$

Two limiting cases may be distinguished:

(a) $k_{7b}(M) \gg k_{7c}$ and $k_{1b}(M) \gg k_{1c}$

Then $[I]^2 = k_{1a}(I_2)/k_{7a}$

but $k_{1a}[I_2] = I_{abs}$

obtain $[I]^2 = I_{abs}/k_{7a}$ (16)

The requirement $k_{1b}(M) \gg k_{1c}$, i.e. $(M) \gg k_{1c}/k_{1b}$, means that there is sufficient third body to suppress fluorescence from (I_2^{**}) by pressure induced pre-dissociation; and requirement $k_{7b}(M) \gg k_{7c}$, i.e. $(M) \gg k_{7c}/k_{7b}$, means that (M) is great enough for the recombination to be in the pseudo second order region.

(b) $k_{7c} \gg k_{7b}(M)$ and $k_{1c} \gg k_{1b}(M)$

$$\text{Then } (I)^2 = \frac{k_{1a} \cdot k_{1b}}{k_{1c}} \cdot \frac{k_{7c}}{k_{7a} \cdot k_{7b}} \cdot [I_2]$$

now substituting $k_{1a}(I_2) = I_{abs}$ in the above equation

$$\text{obtain } (I)^2 = \frac{k_{1b}}{k_{1c}} \cdot \frac{k_{7c}^2}{k_{7a}k_{7b}}\; I_{abs} \qquad (16a)$$

This result means that fluorescence (1c) and dissociation on collision (7c) are the important processes. The iodine atom formation-recombination process is independent of the concentration of the third body.

(ii) The radical-molecule complex mechanism.

$$\begin{array}{rcll}
I_2 + h\nu & \rightarrow & I_2^{**} & k_{1a} \\
I_2^{**} + M & \rightarrow & I + I + M & k_{1b} \\
I_2^{**} & \rightarrow & I_2 + h\nu' & k_{1c} \\
I + M & \rightarrow & IM^{**} & k_{7\ 1a} \\
IM^{**} + I & \rightarrow & I_2 + M & k_{7\ 1b} \\
IM^{**} & \rightarrow & I + M & k_{7\ 1c}
\end{array}$$

Assuming steady state for (I_2^{**}), (IM^{**}) and (I)

$$d[I_2^{**}]/dt = 0 = k_{1a}(I_2) - k_{1c}(I_2^{**}) - k_{1b}(I_2^{**})(M) \quad (17a)$$

$$d[IM^{**}]/dt = 0 = k_{7\ 1a}(I)(M) - k_{7\ 1c}(IM^{**}) - k_{7\ 1b}(IM^{**})(I) \quad (17b)$$

$$d[I]/dt = 0 = 2\,k_{1b}(I_2^{**})(M) - k_{7\ 1a}(I)(M) - k_{7\ 1b}(IM^{**})(I) + k_{7\ 1c}(IM^{**}) \quad (17c)$$

From (17a) and (17b) obtaining (I_2^{**}) and (IM^{**}) respectively and substituting these in (17c), obtain

$$\frac{k_{1a}k_{1b}(I_2)(M)}{k_{1c} + k_{1b}(M)} = \frac{k_{7\ 1b}k_{7\ 1a}(M)(I)^2}{k_{7\ 1c} + k_{7\ 1b}(I)} \quad (18)$$

As before, two limiting cases may be distinguished:

(a) $k_{1b}(M) \gg k_{1c}$ and $k_{7\ 1b}(I) \gg k_{7\ 1c}$

Then equation (18) reduces to

$$\frac{k_{1a}(I_2)}{k_{7\ 1a}(M)} = (I)$$

and for $k_{1a}(I_2) = I_{abs}$

$$I = I_{abs}/k_{7\ 1a}(M) \qquad (19)$$

Once again the condition that $(M) \gg k_{1c}/k_{1b}$ implies (M) is large enough for pseudo second order recombination. The condition $k_{7\ 1b}(I) \gg k_{7\ 1c}$ implies that the radical-molecule complex is sufficiently stable to react with an iodine atom rather than dissociate; and that the reaction is in the second order region.

(b) $k_{7\ 1c} \gg k_{7\ 1b}(I)$ and $k_{1b}(M) \gg k_{1c}$

Equation (18) then becomes

$$(I)^2 = k_{1a}(I_2)\, k_{7\ 1c}/(k_{7\ 1b}\cdot k_{7\ 1a}(M))$$

and as $k_{1a}(I_2) = I_{abs}$

obtain $(I)^2 = I_{abs} \cdot k_{7\ 1c}/(k_{7\ 1b}k_{7\ 1a}(M))$ (20)

This result implies that the radical-molecule complex concentration is determined by $k_{7\ 1a}$ and $k_{7\ 1c}$, so that (7 1b) does not disturb the equilibrium.

Also (20) can be made identical to (16a) if the assumption made in obtaining (20), that is $k_{1b}(M) \gg k_{1c}$ is replaced by $k_{1c} \gg k_{1b}(M)$ as was the case for (16a),

obtain $$(I)^2 = I_{abs} \cdot \frac{k_{1b}}{k_{1c}} \cdot \frac{k_{7\,1c}}{k_{7\,1a}k_{7\,1b}} \qquad (20a)$$

The implication of $k_{1c} \gg k_{1b}(M)$ is that fluorescence of the excited iodine molecule is more important than its dissociation to two iodine atoms. The iodine atom formation-recombination process is independent of the concentration of the third body.

An expression identical to (20) can be derived for the collisional deactivation mechanism, provided $k_{1b}(M) \gg k_{1c}$ and $k_{7c} \gg k_{7b}(M)$.

3.2(c) <u>The implication of the formation-recombination iodine atom mechanisms as applied to the RI-I_2 photochemical exchange mechanism.</u>

The expression for the exchange rate is

$$R_{ex} = (k_3 + k_4)(RI)(I) \qquad (10a)$$

where (10a) is the modified expression of (10) after assuming that the probability factor P is unity and that there is no change in the concentration of reactants, and ignoring $k_2(RI)$ for the reasons already discussed.

The substitution of equation (20) in (10a) for the iodine atom concentration gives

$$R_{ex} = (k_3 + k_4)\left\{\frac{I_{abs}\cdot k_{7\,1c}}{k_{7\,1b}\cdot k_{7\,1a}}\right\}^{\frac{1}{2}}[RI]^{\frac{1}{2}}$$

for $[M] = [RI]$, as $[RI] \gg [I_2]$. This disagrees with the observed rate (equation (14))

$$R_{ex} = k_{\frac{1}{2}}[RI] \qquad (14)$$

and $k_{\frac{1}{2}} \propto (I_{abs})^{\frac{1}{2}}$. Similarly the substitution of (19) in equation (10a) gives a result which is incompatible with the observed rate law.

The substitution of either equation (20a) or (16a) for $[I]$ in (10a) leads to

$$R_{ex} = (k_3 + k_4)\left\{\frac{I_{abs}\cdot k_{7\,1c}k_{1b}}{k_{7\,1a}k_{7\,1b}k_{1c}}\right\}^{\frac{1}{2}}[RI] \qquad (21)$$

and the substitution of (16) similarly leads to

$$R_{ex} = (k_3 + k_4)\left\{\frac{I_{abs}}{k_{7a}}\right\}^{\frac{1}{2}}[RI] \qquad (22)$$

Both result in agreement between the proposed and the observed rate laws. Equation (21) was obtained by substituting (20a), and an identical expression is obtained by substituting (16a). The implication of the assumptions which lead to the derivation of (21) (via equations (16a) or (20a)) is that the iodine atom formation-recombination process is independent of the concentration of the third body, which is in disagreement with the currently held views on iodine recombination. On the other hand, equation (22) only involves the assumption that iodine atom formation-recombination is in the second order region over the RI concentration range used. This assumption is the one used in the remainder of the discussion: that is, the model is based on equation (16) as describing correctly the I atom concentration.

5.3 CALCULATION OF IODINE ATOM RECOMBINATION RATE CONSTANTS AND THE IODINE ATOM RECOMBINATION ACTIVATION ENERGY

If it is again assumed that the temperature dependence of $(k_3 + k_4)$ can be expressed by an activation energy $E_{3,4}$, then the observed activation energy

$$E_{obs} = E_{3,4} - 1/2\ E_7.$$

E_7 has not been measured for the perfluoroalkyl iodides. If the reaction proceeds through the same mechanism in the thermal and photochemical exchanges, then

$$E_{obs(photo)} = E_{3,4(thermal)} - 1/2\ E_7.$$

Then,

	kcal mole^{-1}		
	CF_3I [6]	C_2F_5I	n-C_3F_7I
$E_{obs(photo)}$	16.0 ± 0.3	14.5 ± 0.8	17.5 ± 0.8
$E_{3,4(thermal)}$	15.8 ± 0.7	13.5 ± 0.8	14.2 ± 1.2
E_7	−0.4 ± 1.0	−2.0 ± 1.6	−6.6 ± 2.0

Although the values for E_7 for CF_3I and C_2F_5I fall within the range of values obtained for CH_3I (−2.6 kcal mole^{-1})[41] and C_2H_5I (−2.4 kcal mole^{-1})[38], the value of E_7 obtained for n-C_3F_7I is highly suspect as it suggests that it is an highly efficient third body.

The third body efficiency has been related to the E_a for the iodine atom recombination; as a general rule, the more negative the E_a for the recombination the more efficient is the third body.[38]

The direct evaluation of $k_{3,4(photo)}$ is not possible as the iodine recombination rate constant in the presence of C_2F_5I and n-C_3F_7I has not been measured directly. If it is assumed that the thermal and photochemical exchange reactions proceed through the same mechanism, and $k_{3,4(photo)} = k_{3,4(thermal)}$, then the second order recombination rate constant may be calculated from

$$k_7 = k_{3,4(\text{thermal})} \cdot (I_{abs}/k_7^{\frac{1}{2}})^{\frac{1}{2}} \qquad (23)$$

The recombination rate constants, k_7, calculated in this way for CF_3I and C_2F_5I are compared with the value in the presence of other third bodies in Table III. The value of k_7 calculated from (23) is the second order rate constant. It was converted to the third order rate constant by dividing k_7 (2nd order) by the lowest concentration of RI used. The value of k_7 (3rd order) so obtained is the lower limit.

TABLE III

Iodine Atom Recombination Rate Constants at 100°C

Third Body	2nd order k_7 $\times 10^{-8}$ litre mole^{-1} sec^{-1}	3rd order k_7 $\times 10^{-10}$ litre^2 mole^{-2} sec^{-1}
CF_3I	2.6[a], 0.51[b]	3.2[a], 0.57[b]
CH_3I		7.0[c]
C_2F_5I	3.4[a]	30.0[a]
C_2H_5I		~11.6[c]
I_2		~39.0[c]

Ref. a. values obtained using equation (22).

Ref. b. value obtained using rotating sector method, Ref. 6.

Ref. c. values obtained from data in Ref. 41.

5.4 ARRHENIUS PARAMETERS FOR THE THERMAL EXCHANGE

Laurence[6] compared the Arrhenius parameters for the CF_3I-I_2 exchange with those of CH_3I abstraction studies[43,44] and interpreted the exchange as proceeding by an abstraction mechanism rather than by a direct substitution mechanism. In the exchange of iodine with alkyl iodides in the liquid phase, the rates of abstraction and substitution were found to be comparable.[5,45]

The frequency factors A (Table IV) although normal for halogen atom reactions of this type (abstraction)

$$RI + I \rightarrow R + I_2 \qquad (4)$$

are smaller for the perfluoroalkyl iodides than for alkyl iodides. The frequency factors for the alkyl iodides are greater than the collision frequencies, suggesting a relatively loose transition state,[48] but this would seem not to be characteristic of the reaction of iodine atoms with perfluorinated iodides.

On the basis of the results obtained for CF_3I-I_2 exchange[6] and those for $C_2F_5I-I_2$ and $n-C_3F_7I-I_2$ exchange, the abstraction mechanism is likely to be primarily responsible for the perfluoroalkyl iodide-iodine exchange reaction, that is the activation energy $E_{3,4}$ is the activation energy for the abstraction reaction (4),

$$E_{3,4} = E_4 = E_{3,4(\text{thermal})}$$

5.5 BOND DISSOCIATION ENERGY OF THE C-I BOND

Assuming that the exchange proceeds by abstraction (reaction (4)) the bond dissociation energy ($D(R_f - I)$) may be obtained from the relationship

$$D(R_f - I) = E_{3,4}(\text{thermal}) - E_5 + D(I-I)$$

where $D(I-I)$ is defined as the iodine dissociation energy and equal to 36.2 kcal mole^{-1}. For the reaction of CF_3 radicals with I_2, E_5 is zero[15] and is probably zero for C_2F_5 and n-C_3F_7 radicals also. The bond energies and the pre-expotential terms of the perfluoroalkyl iodides are compared with the corresponding alkyl iodides in Table IV.

TABLE IV

The Pre-expotential terms for Reaction $RI + I \rightarrow R + I_2$

Carbon-iodine Bond Dissociation Energies

Compound	log A l. mole^{-1} sec^{-1}	D(R - I) kcal mole^{-1}	Ref.
CH_3I	11.40	53.3 ± 1, 56.3	48, 51, 50
CF_3I	9.60	52.0 ± 0.8	6
	10.8	53.5	43, 50
		54.0	44
C_2H_5I	11.62	53.0 ± 1	47, 49, 50
C_2F_5I	10.00	49.5 ± 0.8	this work
n-C_3H_7I	11.04	54 ± 2	47, 50
n-C_3F_7I	10.20	50.4 ± 1.2	this work

The order of the perfluoroalkyl iodide bond strengths is in complete agreement with the observed order from the telomerisation reactions between the iodides and 1,1-difluoroethylene,[52] for which the efficiency of chain transfer depends on the C-I bond strength.

The value obtained by Lawrence[6] for the CF_3-I bond strength is 1.5-2.0 kcal lower than the currently accepted value of 54 kcal.[55] It is therefore probable that the value for D(C-I) for C_2F_5I and n-C_3F_7I is also 1-2 kcal low as the method of calculation and the assumptions made in this work are identical to those for CF_3I.

6.1 APPENDIX

Temperature Dependence of the Thermal Exchange Rate

[RI] moles cm^{-3}x10^{6}	[I$_2$] moles cm^{-3}x10^{9}	$t_{\frac{1}{2}}$ mins x10^{-2}	R_{ex} moles cm^{-3}min^{-1}x10^{13}	T °C	E_{obs} kcal mole^{-1}	Surface/Vol. cm^{-1}
C_2H_5I						
1.27	5.15	82.30	3.79	127.7	31.15 ± 0.81	0.98
		2.62	118.90	166.7		
		4.40	70.90	159.4		
		7.79	40.05	154.00		
		25.11	12.42	140.00		
		15.22	20.50	147.20		
1.28	3.95	10.91	21.92	147.10	30.04 ± 0.53	0.98
		22.82	10.48	140.0		
		70.47	3.39	126.0		
		2.48	96.32	166.3		
		7.22	33.12	154.0		
		39.70	6.03	134.0		
		4.64	51.58	159.5		

(contd.)

6.1 APPENDIX (contd.)

[RI] moles cm^{-3}x10^{6}	[I$_2$] moles cm^{-3}x10^{9}	$t_{\frac{1}{2}}$ mins x10^{-2}	R_{ex} moles cm^{-3}min^{-1}x10^{13}	T °C	E_{obs} kcal mole^{-1}	Surface/Vol. cm^{-1}
C_2F_5I 1.31	3.76	3.83	59.60	159.8	31.32 ± 0.62	0.98
		10.03	22.73	150.0		
		21.25	10.73	140.6		
		6.35	35.90	155.2		
		57.41	3.97	130.1		
		2.54	89.47	165.7		
		41.01	5.56	135.3		
		1.77	128.70	170.5		
1.32	13.03	181.4	4.35	126.6	30.20 ± 1.10	1.59
		5.71	138.3	166.8		
		36.51	21.63	147.0		
		105.2	7.50	134.0		
		10.74	73.48	159.2		
		17.53	45.03	153.9		
		62.60	12.61	140.0		

(contd.)

6.1 APPENDIX (contd.)

[RI] moles cm^{-3} x 10^6	$[I_2]$ moles cm^{-3} x 10^9	$t_{\frac{1}{2}}$ mins x 10^{-2}	R_{ex} moles cm^{-3} min^{-1} x 10^{13}	T °C	E_{obs} kcal $mole^{-1}$	Surface/Vol. cm^{-1}
C_2F_5I 1.34	4.78	14.57	19.88	147.0	29.31 ± 1.59	5.44
		4.08	71.00	158.9		
		29.39	9.85	140.0		
		40.24	7.20	133.8		
		8.20	35.34	153.5		
		4.02	72.11	158.9		
		8.55	33.88	153.5		
		3.25	89.21	165.4		
		65.99	4.39	126.7		
$n-C_3F_7I$ 0.96_4	3.55	2.97	72.42	156.0	32.20 ± 1.95	1.09
		26.98	7.96	131.0		
		0.90	238.6	165.1		
		1.25	171.5	165.10		
		12.52	17.16	136.5		
		7.34	29.30	146.0		
		5.85	36.76	146.5		
0.93_5	3.71	1.75	128.6	165.5	32.06 ± 1.80	1.09
		3.71	60.64	155.7		
		10.38	21.68	146.5		
		23.34	9.63	136.0		
		43.72	5.14	125.8		

(contd.)

6.1 APPENDIX (contd.)

[RI] moles cm^{-3}x10^{6}	[I$_2$] moles cm^{-3}x10^{9}	$t_{\frac{1}{2}}$ mins x10^{-2}	R_{ex} moles cm^{-3}min^{-1}x10^{13}	T $^{\circ}$C	E_{obs} kcal mole^{-1}	Surface/Vol. cm^{-1}
n-C_3F_7I						
1.00	4.18	64.01	3.96	125.2	32.90 ± 1.70	1.09
		21.57	11.74	136.0		
		6.50	38.95	146.0		
		2.73	92.69	156.0		
		1.49	169.8	166.0		
1.12	4.93	49.27	6.07	125.3	31.80 ± 1.60	5.44
		23.31	12.82	136.1		
		10.67	37.87	146.0		
		4.41	67.79	155.0		
		16.15	185.0	166.0		

6.2 APPENDIX

Temperature Dependence of the Photochemical Exchange Rate.

Effect of Light Intensity on Rate of Exchange.

[RI] moles cm^{-3}x10^{6}	[I$_2$] moles cm^{-3}x10^{9}	$t_{\frac{1}{2}}$ mins x10^{-2}	R_{ex} moles cm^{-3}min^{-1}x10^{12}	T °C	E_{obs} kcal mole^{-1}	Relative $I_{abs}^{\frac{1}{2}}$
C_2H_5I						
1.27	3.67	5.54	4.01	89.90	14.94 ± 1.17	1.0
		2.90	7.67	101.3		
		1.74	12.80	108.9		
		1.24	17.90	118.90		
1.25	3.05	6.91	2.68	84.6	17.05 ± 1.24	1.0
		4.71	3.93	94.4		
		2.02	9.14	104.9		
		1.36	13.62	113.5		
		0.87	21.31	118.9		
1.13	3.45	0.88	23.79	118.9	14.33 ± 1.04	1.0
		1.59	13.13	108.9		
		7.94	2.64	81.4		
		4.29	4.88	89.9		
		2.71	7.72	101.3		
		9.95	2.10	71.0		
		1.06	19.79	113.5		

(contd.)

6.2 APPENDIX (contd.)

	[RI] moles cm^{-3}x10^{6}	[I$_2$] moles cm^{-3}x10^{9}	$t_{\frac{1}{2}}$ mins x10^{-2}	R_{ex} moles cm^{-3}min^{-1}x10^{12}	T °C	E_{obs} kcal mole^{-1}	Relative $I_{abs}^{\frac{1}{2}}$
C_2F_5I	0.24_2	2.62	20.93	0.76	113.5		1.0
	1.22		2.82	5.63	113.5		
	1.43		2.27	6.99	113.5		
	0.46_3		9.46	1.68	113.5		
	0.93_4		4.03	3.94	113.5		
	0.66_6		5.57	2.85	113.5		
	0.16_6		27.37	0.58	113.5		
	1.19	3.61	0.95_0	23.00	113.5		1.00
			1.97	11.10			0.49_7
			1.27	17.26			0.70_3
			3.53	6.19			0.28_0
			1.51	14.49			0.64_4
			2.21	9.89			0.40_4
			4.14	5.27			0.21_2

(contd.)

6.2 <u>APPENDIX</u> (contd.)

[RI] moles cm^{-3}x10^{6}	[I$_2$] moles cm^{-3}x10^{9}	$t_{\frac{1}{2}}$ mins x10^{-2}	R_{ex} moles cm^{-3}min^{-1}x10^{12}	T °C	E_{obs} kcal mole^{-1}	Relative $I_{abs}^{\frac{1}{2}}$
$\underline{C_3F_7I}$						
0.94$_0$	2.86	0.35$_4$	48.89	99.5	14.30 ± 1.05	
		0.57$_7$	30.00	90.1		
		2.24	7.74	70.0		
		0.98$_9$	17.51	80.2		
		2.85	6.06	62.9		
		4.03	4.29	52.4		
0.95$_9$	3.96	2.34	10.22	69.9	17.84 ± 1.56	1.0
		0.45$_9$	52.26	90.1		
		2.64	9.06	62.9		
		0.83$_1$	28.86	80.2		
		0.21$_3$	112.5	99.5		
0.95$_6$	3.85	0.93	25.00	80.2	17.00 ± 1.20	1.0
		2.55	9.14	62.9		
		1.72	13.53	69.9		
		0.30	77.67	90.1		
		0.20	115.9	99.5		
		4.98	4.68	52.4		

(contd.)

6.2 APPENDIX (contd.)

[RI] moles $cm^{-3} x10^{6}$	$[I_2]$ moles $cm^{-3} x10^{9}$	$t_{\frac{1}{2}}$ mins $x10^{-2}$	R_{eq} moles $cm^{-3} min^{-1} x10^{12}$	T °C	E_{obs} kcal $mole^{-1}$	Relative $I_{abs}^{\frac{1}{2}}$
C_3F_7I						
0.97_4	3.85	5.90	3.95	52.4	17.92 ± 0.46	1.0
		0.78	29.85	80.2		
		0.17_1	136.5	99.5		
		0.35	67.17	90.1		
		2.56	9.08	62.9		
		1.45	16.04	69.9		
0.95_8	3.88	1.60	14.69	70.0	17.42 ± 0.35	1.0
		6.19	3.79	52.4		
		0.70_9	33.11	80.2		
		0.34_4	68.15	90.1		
		7.15	3.28	62.9		

(contd.)

6.2 APPENDIX (contd.)

$[RI]$ moles cm^{-3}x10^{6}	$[I_2]$ moles cm^{-3}x10^{9}	$t_{\frac{1}{2}}$ mins x10^{-2}	R_{ex} moles cm^{-3}min^{-1}x10^{12}	T °C	E_{obs} kcal mole	Relative $I_{abs}^{\frac{1}{2}}$
C_3H_7I 0.19_4	3.18	4.39	4.38	80.2		1.0
0.37_8	3.18	1.45	13.28			
0.58_0	3.18	0.91_6	21.00			
0.75_6	3.18	0.66_7	28.84			
0.95_5	3.18	0.60_6	31.48			
0.11_1	3.47	3.07	6.88			
0.38_3	3.47	1.22	12.90			
0.68_0	3.47	0.68_9	17.49			
0.84_3	3.47	2.69	30.62			
0.20_0	3.47	1.63	7.81			
0.96_4	3.55	5.72	3.76	80.2		0.28_5
		3.48	6.17			0.41_0
		3.25	6.62			0.49_7
		2.60	8.25			0.58_6
		2.04	10.53			0.70_2
		1.38	15.55			1.00

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PART 2

GAS-PHASE PHOTOLYSIS OF PERFLUOROETHYL IODIDE

1. SUMMARY

The products of 2537 Å photolysis of C_2F_5I are C_4F_{10} and I_2 and their quantum yields are pressure and time dependent. $\Phi(C_4F_{10})$ and $\Phi(I_2)$ increase with increasing pressure of C_2F_5I (from 0.0004 to 0.0014), and decrease with increasing irradiation time. When NO is added, $\Phi(C_2F_5NO) = 1.07 \pm 0.04$ at high (10.0 cm) C_2F_5I pressure; at low (1.0 cm) C_2F_5I pressure $\Phi(C_2F_5NO) = 0.82 \pm 0.03$.

The value for the ratio of rate constants for reactions

$$C_2F_5 + I_2 \xrightarrow{k_1} C_2F_5I + I$$

and

$$C_2F_5 + C_2F_5 \xrightarrow{k_2} C_4F_{10}$$

was calculated to be

$$\frac{k_1}{k_2^{\frac{1}{2}}} = (7.90 \pm 0.80) \times 10^4 \text{ litre}^{\frac{1}{2}} \text{ mole}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}.$$

The unfiltered light from a Hanovia low pressure mercury discharge lamp is a mixture of 2537 Å and 1849 Å light. If this unfiltered light is used for the photolysis of C_2F_5I a mixture of products is obtained as the result of interaction between the primary species produced by the photolysis of C_2F_5I at each wavelength. The products which were identified and analysed by UV spectrophotometry and vpc analysis are I_2, C_4F_{10}, C_3F_8, CF_3I and n-C_3F_7I. From mass-balances of products the formation of CF_2I_2 is assumed. The effect of pressure, time, temperature and the addition of argon, iodine

and NO was studied. The conclusion reached is that C_3F_8, CF_3I, n-C_3F_7I and CF_2I_2 are formed as a result of hot radical reactions involving the C-C bond fission of the energised C_2F_5 radical formed by the absorption of the 1849 Å radiation, i.e.

$$C_2F_5I \xrightarrow{h\nu\ (1849\ \text{Å})} (C_2F_5)_E + I(^2P_{1/2})$$

$$(C_2F_5)_E \rightarrow CF_2 + CF_3$$

To establish the mode of formation of CF_3I, abstraction studies using mixtures of hexafluoroacetone and C_2F_5I were carried out under conditions of variable C_2F_5I pressure and temperature. The rate constant for the reaction

$$C_2F_5I + CF_3 \xrightarrow{k_3} CF_3I + C_2F_5$$

was found to be

$$k_3 = [(1.18 \pm 0.03) \times 10^7]\ \exp[-2840 \pm 400/RT]\ \text{litre mole}^{-1}\text{sec}^{-1}$$

Evidence is also presented for a possible hexafluoroacetone sensitised reaction,

$$HFA^* + C_2F_5I \rightarrow C_2F_5 + I + HFA$$

The fate of the CF_2 species produced by 1849 Å light is discussed.

2. INTRODUCTION

The kinetics of photolysis of perfluoroalkyl iodides in a static system have not been previously investigated. However, there have been a number of short qualitative studies reported.

The first was by Banus, Emeleus and Haszeldine[1] in 1951 who found that when perfluoroalkyl iodides are heated above 100°C or irradiated with UV light perfluoroalkyl radicals are formed. The absorption spectra of perfluoroalkyl iodides resemble those of the corresponding alkyl iodides, showing continuous absorption with a maximum at about 2680 Å.[1] The irradiation with UV light of perfluoromethyl iodide for twenty six hours caused very little decomposition into iodine and perfluoroethane, with the quantum yield of the former being less than 0.002.[1]

Dacey[2] in 1953 photolysed perfluoromethyl iodide with 2537 Å light in a circulatory system, in which the iodine formed was removed by freezing out (at -78°C) and the remainder of the products and reactants recirculated for re-irradiation. The quantum yield of iodine for the overall process varied from 0.02 to 0.13 depending on the initial pressure, higher yields being found at lower pressure. The addition of NO increased the quantum yield of iodine, whereas the addition of Ag increased the quantum yield of perfluoroethane. He concluded that the primary process was the division of the perfluoromethyl iodide into a perfluoromethyl radical and an iodine atom with an efficiency of unity. The reverse reaction and the reaction of perfluoromethyl radicals with iodine molecules causes the low quantum yield. Therefore on this basis it would be expected that the quantum yields in a static photolytic system would be very low.

In 1966, Heicklen and co-workers photolysed perfluoromethyl iodide,[3] perfluoroethyl iodide and perfluoro-n-propyl iodide[4] using light of $\lambda > 2000$ Å. However, they did not give any yields as they were more interested in the effect of oxygen on the system.

Between the years 1953-1966 a considerable amount of work had been done on the perfluoroalkyl iodides as chain initiators in telomerization reactions and also as sources of perfluoroalkyl group for Grignard Reagents.

The lack of interest in perfluoroalkyl iodides as sources of perfluoroalkyl radicals for kinetic studies came about because of the preparation of perfluoroalkyl ketones and azines, which are not affected by the rapid back reaction of the recombination of primary radicals. In addition, both groups of compounds (ketones and azines) provide a direct internal monitor on the total decomposition by producing unreactive CO and N_2 respectively. A recent review by Tedder and Walton[5] summarises the various reactions with their associated kinetic parameters, of perfluoroalkyl radicals.

As the absorption spectra of the perfluoroalkyl iodides resemble those of the alkyl iodides,[1] it might be thought that the radicals generated in the primary process would behave in a similar manner in any subsequent reactions. The detailed studies of the photolysis of the alkyl iodides[6-17,33,54] show that 'hot' alkyl radicals are formed and these can undergo a hydrogen atom abstraction reaction before they are moderated by collision. As expected the probability of the 'hot' alkyl radical reaction was found to increase with an increase in photon energy.[7,9] However, the perfluoroalkyl radicals generated under similar conditions will not abstract fluorine from an fluoroalkyl group.[18,19]

Recent results of Kibby and Weston[20] have demonstrated the difference in the reactivities of perfluoromethyl and methyl radicals produced by the photo-dissociation of the corresponding iodides. It was found that for the abstraction reaction of the type

$$R_1 + R\text{-}H \rightarrow R_1\text{-}H + R$$

at 2537 Å, that the yield of R_1H for $R_1 = CH_3$ was about 10^3 times as great as for $R_1 = CF_3$, although a comparable yield was expected as both radicals had comparable amounts of excess energy (see Table I). By decreasing the wavelength of the photolysis to 1849 Å, that is increasing the photon energy, they found that the reaction of CF_3 with H_2 took place with a quantum yield of 0.1. They were, however, suspicious that there was contribution from a surface reaction. Photolysis at 1849 Å produced methyl radicals which were ten times more reactive and highly resistant to collisional deactivation as compared to methyl radicals by 2537 Å light.[9]

The analysis of the methyl iodide spectrum by Porret and Goodeve[21] indicated that excited iodine atoms, $I(^2P_{1/2})$, should be predominantly produced on the photolysis of this compound in the UV region ($\lambda < 3000$ Å). The spectroscopic state of the iodine atom produced in the primary step in the photolysis of alkyl iodides and perfluoromethyl iodide has been confirmed by flash photolysis.[22-29] Also laser emission from the $(^2P_{1/2}) \rightarrow (^2P_{3/2})$ iodine atom transition have been observed in the photodissociation of several alkyl and perfluoroalkyl iodides.[30] The absorption of a 2537 Å photon excites the iodides into a $^1(n,\sigma^*)$ state from which they dissociate, probably in the first vibration.[31] Light absorbed at 1849 Å however, excites a different transition, involving the non-bonding p electrons on the iodine and higher C-I anti-bonding orbitals, which have a high degree of s character. The transitions are allowed by Laporte's selection rules, and so the excited molecule is more stable than the one undergoing a (n,σ^*) transition, so that there is more time for energy redistribution.[32,33,52,88]

As the absorbed energy exceeds the dissociation energy of the C-I bond, the excess energy appears as electronic excitation of the iodine atom in the $^2P_{1/2}$ state and the vibration energy of the radical, with the remainder divided in translation between them. It is possible that the radical (alkyl or perfluoroalkyl) besides being vibrationally excited may also be electronically excited.

However as there is no evidence to substantiate this at present it will be assumed that there is no electronic excitation of the alkyl or perfluoroalkyl radical. The exact nature of the distribution between vibrational and translational energy will be governed by the geometry of the molecule.[20,31] The energies involved are summarised in Table I for the photolysis of alkyl and perfluoroalkyl iodides R-I.

TABLE I

Wavelength	kcal	R: CH_3	C_2H_5	CF_3	C_2F_5
	A	58	59	58	62
2537 Å	B	36	37	36	40
(112 kcal)	C	32	30	23	21
1849 Å	A	98	99	98	102
(152 kcal)	B	76	77	76	80
	C	68	63	49	41

(A = photon energy - bond dissociation energy

B = A - Iodine electronic excitation energy (22)

C obtained by assuming that if the excess energy (B) is entirely translational, then its distribution will be determined by the conservation of momentum and energy principle, i.e. inversely proportional to the mass of the particle.)

The quantities B and C are the possible upper and lower limits of the energy to be found in the excited alkyl or perfluoroalkyl radical.

At the present time the question which of the two forms of energy, i.e. vibrational or translational is more important in hot reactions has not been settled. Some workers[12,13] believe 'hot' reactions are due to excess translational energy. Simmons and co-worker[31,33-35] have shown that photodissociation of certain polyhalomethanes leads to radicals containing enough vibrational energy to undergo unimolecular decomposition as an alternative path to hydrogen abstraction. In these cases at least part of the vibrational energy probably results from extension of a carbon-halogen bond (other than the one being ruptured) in the excited state of the molecule.[33] Such an effect would be greatest when the two carbon-halogen bonds have similar dissociation energies and would be minimised in CF_3I.[33] In the case of perfluoroethyl iodide there are two bonds with comparable energy: C-I (50 kcal) and C-C (61 kcal). The former value is taken from Part 1 of this thesis and the latter is calculated from the standard heats of formation for the reaction

$$C_2F_5 \rightarrow CF_3 + CF_2$$

i.e. $D(CF_3 - CF_2) = \Delta H_f^o(CF_3) + \Delta H_f^o(CF_2) - \Delta H_f^o(C_2F_5)$, where

$\Delta H_f^o(CF_3)$ = -112.7 kcal mole,[36] $\Delta H_f^o(C_2F_5)$ = -212.0 kcal mole^{-1} [36] and $\Delta H_f^o(CF_2)$ = -39 kcal mole^{-1}.[37-39] Thus during the photolysis with 1849 Å light if the vibrational energy is given by B in Table I and the C-C bond is extended in the excited state, then C-C bond rupture may be observed. The present study describes such a process: a process involving a C-C bond fission rather than an abstraction of a fluorine atom (i.e. C-F bond fission). The latter process is energetically less favourable than the former by some 17 kcal.[40] The only other report of C-C bond fission is from Coomber and Whittle[41] studying the equilibrium

$$Br_2 + C_2F_5H \rightleftharpoons HBr + C_2H_5Br$$

reaction at temperatures greater than 516°C. However it was not as a consequence of a photolytic process, but rather due to thermal cracking.

The present investigation confirms that the primary process in the photolysis of C_2F_5I with 2537 Å light has an efficiency of unity, and the iodine recombination and C_4F_{10} formation show a pressure dependence.

The photolysis of C_2F_5I with unfiltered light from the low pressure mercury arc, containing both the 1849 Å and 2537 Å mercury resonance lines, yields C_3F_8, C_4F_{10}, CF_3I, n-C_3F_7I and CF_2I_2 as products. These products can only be explained by a C-C bond fission in the C_2F_5 radical formed in the primary step. The amount of the products formed is affected by the addition of foreign gases (argon, nitric oxide or I_2) suggesting it is the radical rather than an excited molecule which undergoes the C-C fission, i.e.

$$C_2F_5I \xrightarrow{h\nu\ (1849\ \text{Å})} (C_2F_5)_E + I(^2P_{1/2})$$

$$(C_2F_5)_E + M \rightarrow C_2F_5 + M$$

$$(C_2F_5)_E \rightarrow CF_3 + CF_2$$

The kinetics of the system are complicated by contribution of perfluoroethyl and iodine radicals formed as a result of photolysis of C_2F_5I by 2537 Å light.

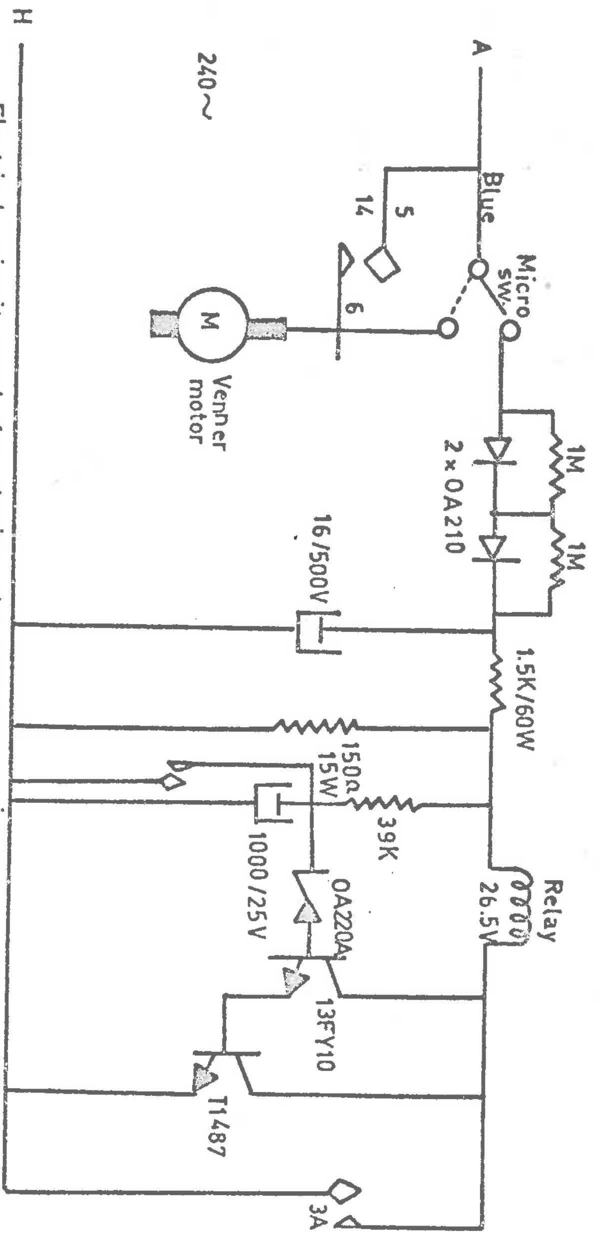
3. EXPERIMENTAL

3.1 MATERIALS

PERFLUOROETHYL IODIDE, C_2F_5I

Both the commercially obtainable C_2F_5I (Columbia Organic Chemicals) and that prepared by the decomposition of silver perfluoropropionate with iodine[42] were purified by fractional distillation. To remove higher boiling point impurities, the liquid C_2F_5I was passed through a silica gel column at 0°C.

The apparatus used for fractional distillation under conditions of controlled reflux is shown in figure 1. The C_2F_5I was condensed in D with liquid nitrogen, then heated to -22°C and kept at this temperature with a CCl_4 slush bath. E, a condenser,



Electrical circuit used for driving the motor. (Designed by A.D.THOMAS)

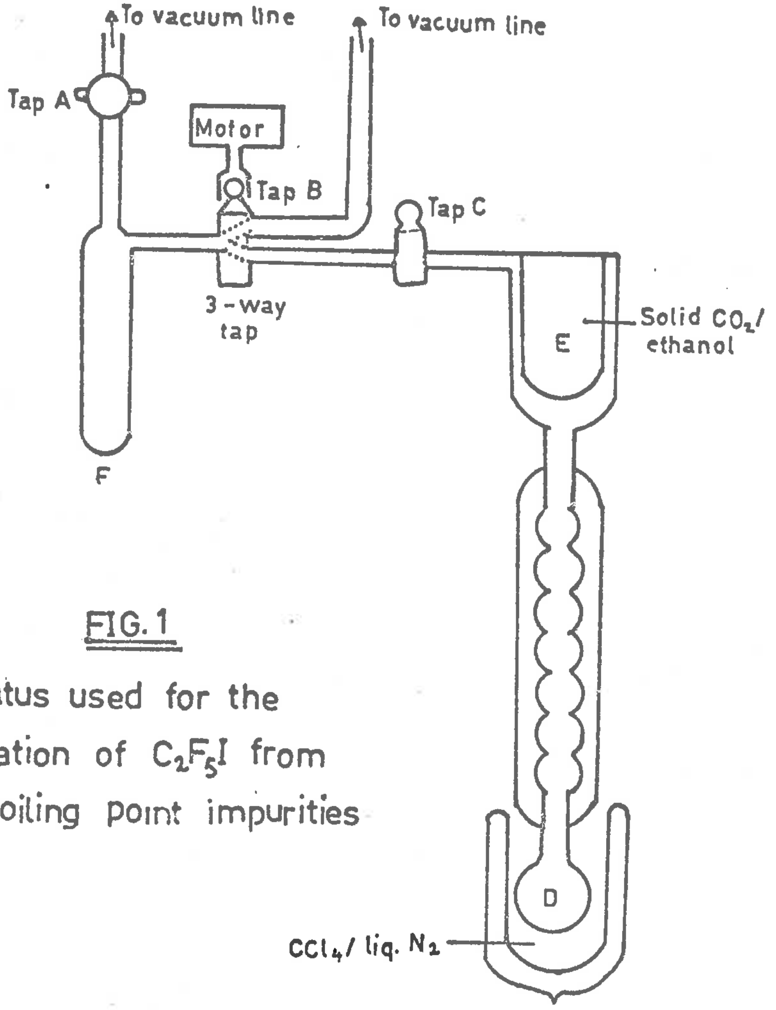


FIG. 1

Apparatus used for the purification of C_2F_5I from low boiling point impurities contained a solid CO_2/Ethanol slush bath. Tap A was closed and after the C_2F_5I started to reflux, the motor was turned on. The vapour was allowed to expand into bulb F for 40 seconds, then the motor turned the three-way tap (B) through 180° so that the bulb (F) was open to the vacuum line, and the vapour in F was pumped out. Forty seconds later the tap was rotated through another 180°, which allowed the vapour from the condenser to expand into F. The cycle, taking about 100 seconds, was repeated 100-200 times, until the C_2F_5I contained less than 0.01% impurity. The loss of C_2F_5I during its purification in this way was less than 5%, and even this could be recovered by inserting a trap further down the vacuum line.

Vapour phase chromatographic (vpc) analysis of the C_2F_5I samples used in the photochemical experiments contained less than 0.01% impurities. The C_2F_5I was stored in blackened bulbs to prevent decomposition.

PERFLUOROMETHYL IODIDE, CF_3I

CF_3I (Columbia Organic Chemicals) was purified in the same manner as C_2F_5I, except that different temperatures were used in the distillation column (solid CO_2/Ethanol, -78°C around D; methanol slush, -98°C in E).

PERFLUORO-n-PROPYL IODIDE, n-C_3F_7I

n-C_3F_7I was prepared by the method of Henne and Finnegan[43] by the decomposition of silver perfluorobutyrate with iodine.

PERFLUOROBUTANE, C_4F_{10}, and PERFLUOROPROPANE, C_3F_8

(Columbia Organic Chemicals). These were used as calibrants for the vpc, and were purified by trap to trap distillation at -78°C and -98°C, then thoroughly degassed at -196°C.

PERFLUOROMETHANE, CF_4, and PERFLUOROETHANE, C_2F_6 were donated by E.I. du Pont de Nemours Co., and were sufficiently pure to be used without any further purification.

TETRAFLUOROETHYLENE, C_2F_4

C_2F_4 was prepared by the thermal decomposition of polytetrafluoroethylene (Teflon). The gas was purified by distillation at -95°C, toluene slush bath, -161°C iso-pentane slush bath, collecting only the middle portion at -196°C.

NITRIC OXIDE, NO

Matheson Co. research grade NO was first purified by trap to trap distillation at -127°C (n-propanol slush bath) and at -152°C. The final distillation was at -185°C in a Buchann and Creutzberg[44] cryostat, using methane (Philips Petroleum Co.) as the thermometer gas.[50]

NITROUS OXIDE, N_2O

C.I.G. (B.P. grade) N_2O was purified by trap to trap distillation at -98°C and -127°C, then thoroughly degassed at -161°C and -196°C.

HEXAFLUOROACETONE, CF_3COCF_3

CF_3COCF_3 (Allied Chemicals) was purified by trap to trap distillation at -78°C, -127°C and pumped down at -161°C and -196°C. V.P.C. analysis showed a single impurity present at less than 0.01%. The amount of this impurity did not alter on the photolysis of CF_3COCF_3.

ARGON

C.I.G. (dry and oxygen-free grade) was used without any further purification except that the storage bulb was frozen down to -196°C. At this temperature the argon vapour pressure is approximately 22 cm; and was high enough to meter out into the reaction vessel.

PERFLUORONITROSO-ETHANE, C_2F_5NO

This was prepared by photolysing C_2F_5I and NO in the mole ratio of 1:3 in the presence of clean mercury at 2537 Å [45] for 8 hours, with continual shaking of the reaction vessel. The reaction products were separated by fractional distillation, collecting the middle fraction at -127°C. The final step in the purification was passing this middle fraction through a silica gel column kept at -78°C (solid CO_2/Ethanol). V.P.C. analysis showed C_2F_5NO to be the only product present.

All other reagents used were A.R. grade.

3.2 APPARATUS

CELL AND VACUUM LINE

A cylindrical 5 cm x 5 cm diameter quartz cell with a side arm was attached to the vacuum line and the gas chromatography injection apparatus as shown in figure 2. All taps through which the photolysed products pass or with which they are in contact were of the Springham greaseless type with Viton A diaphragms.

The v.p.c. line was made of capillary tubing to minimise the volume, so that the largest possible pressures (for low pressure runs) could be injected. In all runs the reaction products were "toeplered" into the v.p.c. line, as this gave much better agreement between duplicates than was obtained if the toepler pump was by-passed. The effect of mercury on the reaction products was investigated and it was found that at room temperature the mercury did not react with any of the fluorocarbons or fluorocarbon iodides. A possible exception was CF_2I_2, neither this, nor its possible decomposition product C_2F_4, could be detected by v.p.c.

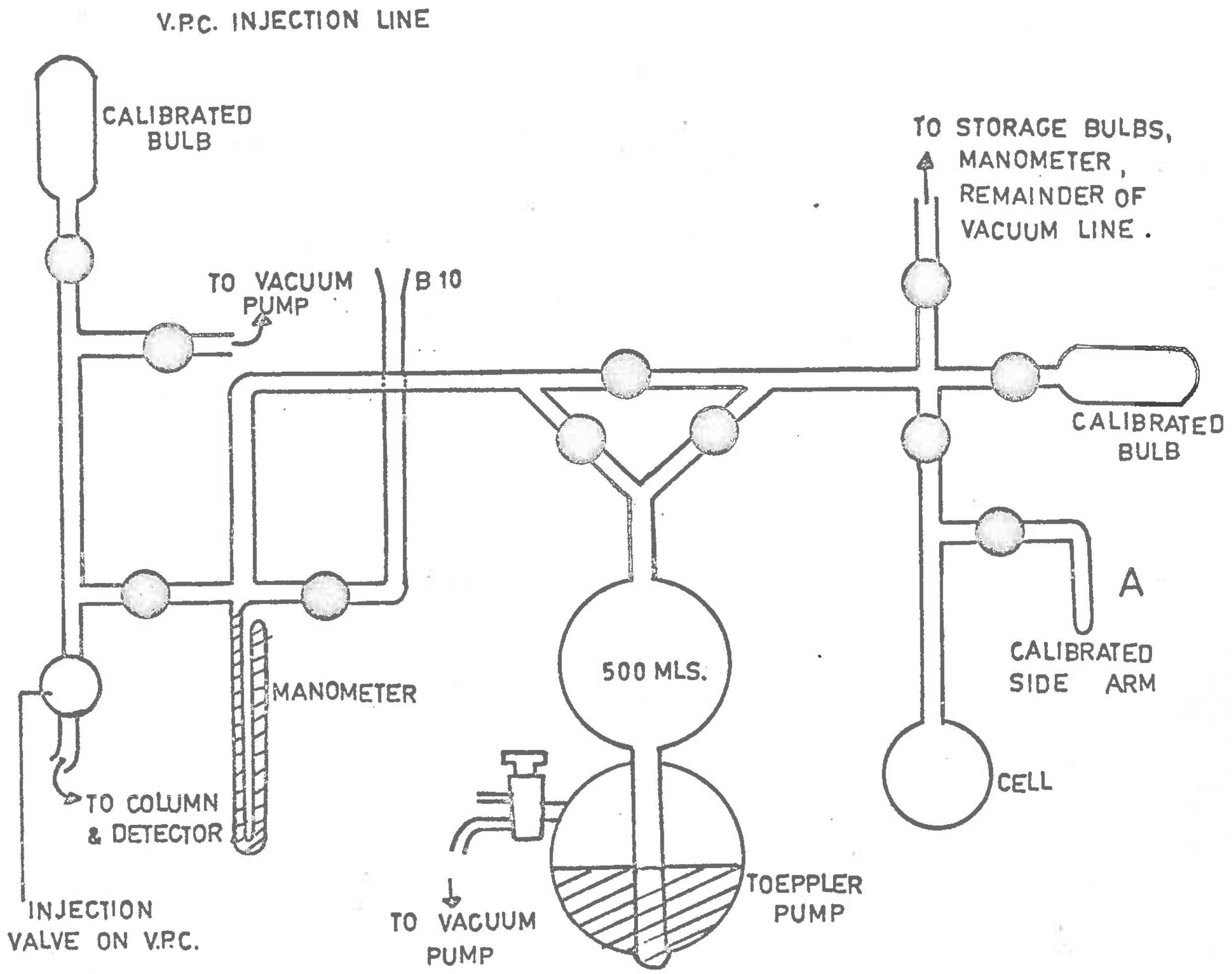


FIG 2

Schematic representation of cell and analytical vacuum line.

analysis. The mercury did react with iodine but this did not affect the v.p.c. results, as the detector is insensitive to iodine in any case.

The cell was flamed while being pumped out before each filling.

ULTRAVIOLET LIGHT SOURCE AND LIGHT FILTERS

A 5-watt Hanovia helical low pressure mercury discharge lamp was used. The lamp was operated from the laboratory A.C. line through a high voltage transformer.

The light intensity was not monitored, but the lamp current was. Frequent checks on the light intensity were performed using potassium ferrioxalate as an actinometer[46] for the 2537 Å radiation. The actinometer was prepared in situ by mixing solutions of ferric alum (0.01M) and potassium oxalate (0.03M).

The 1849 Å contribution to the light intensity was measured by using nitrous oxide[47] as an actinometer and analysing for nitric oxide on the v.p.c. The absorption coefficient of N_2O used in the calculation of the 1849 Å light absorbed was 3.82 cm^{-1}.[51] The output of the 1849 Å radiation was about 3% of the total.

The 1849 Å line was eliminated when required by inserting (between the light source and the reaction cell) a Corning 96% Silica glass (No. 7910) filter which begins transmission at 2200 Å.

A Mazda ME/D 250 watt mercury arc operating on a stabilized 3 amp D.C. current was used in the photolytic studies of the

$C_2F_5I-CF_3COCF_3$ system. The lamp circuit has already been described in the experimental section on the exchange work (Part 1 of this thesis).

Two filters were employed for the $C_2F_5I-CF_3COCF_3$ study:

(i) a 0.57 g/litre potassium hydrogen phthalate solution,[49] which transmits light of wavelength greater than 2800 Å (figure 3).

(ii) a Wladimiroff filter[48] consisting of 200 g/litre $CoCl_2.6H_2O$ and 100 g/litre $NiCl_2.6H_2O$ in a mixture of 35% ethanol, 25% acetone and 40% water, containing 1 mol/litre HCl, which transmits at 3100-3900 Å (figure 3).

As the filters get very warm during the irradiation, they were cooled by circulating water through an outer jacket; in this way temperature was kept down to 28-30°C as compared to 45-50°C if no cooling was used.

FURNACE AND TEMPERATURE CONTROL

The temperature studies were performed in a furnace made in two sections (or halves) each being constructed as a 53 mm diameter by 100 mm long and 2 mm thick brass cylinder. The two sections could be placed around the cell and joined in the middle to form one continuous cylinder. At one end of this cylinder was a transparent (to 1849 Å radiation) quartz window, and at the other an asbestos plug. The heating element was nichrome wire (30.5 Ω/yd, 7 yards on

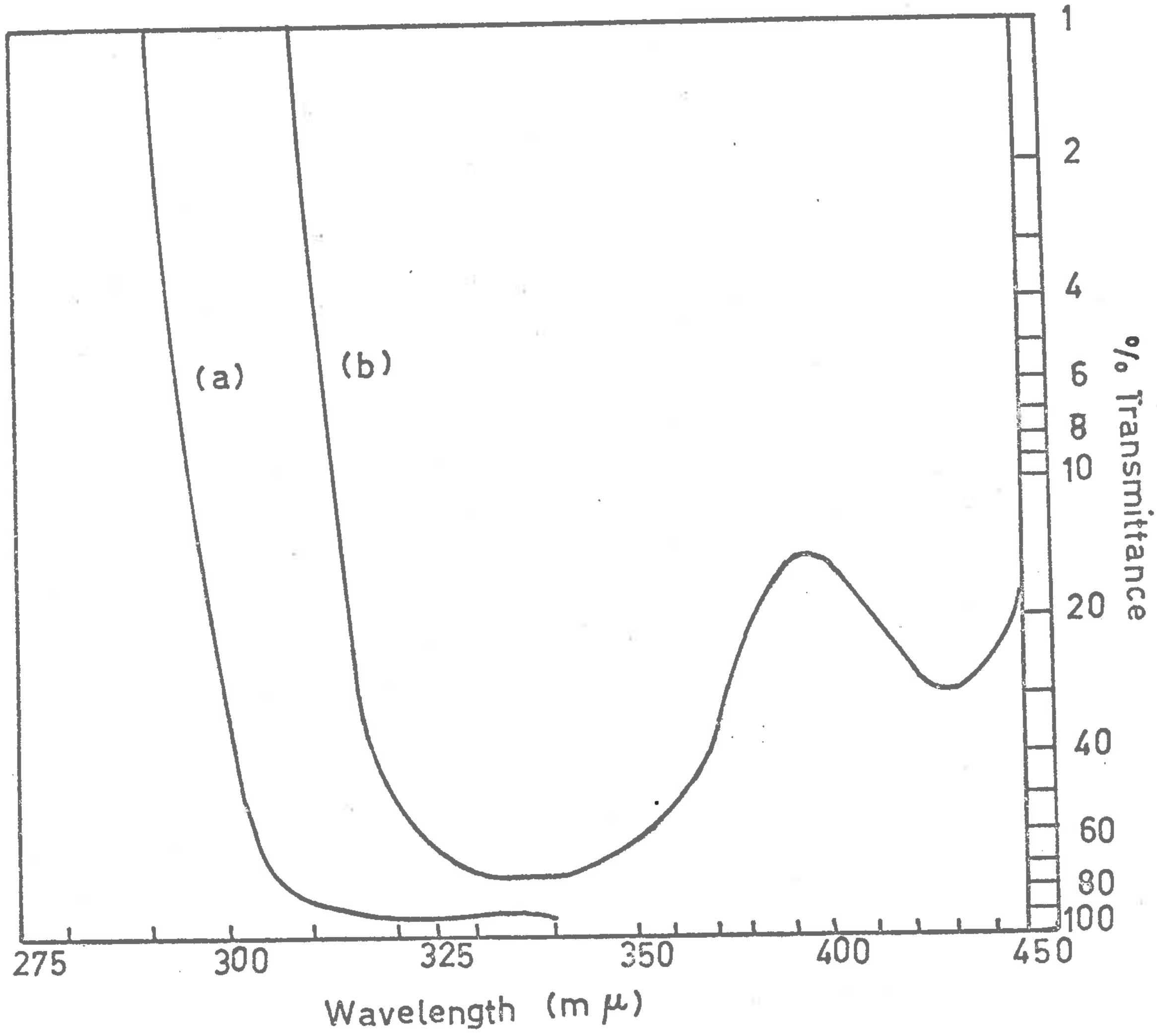


FIG 3

Transmission properties of light filters used in CF_3COCF_3/ C_2F_5I abstraction studies.

(a) 0.55 / litre - potassium hydrogen phthalate ($\lambda >$ 280mμ)

(b) Wladimiroff filter ($\lambda >$ 310 mμ) .

each section) which was wound over a thin layer of asbestos paper covering the brass cylinder. The winding was more congested at the ends of each section to achieve a more uniform heat distribution down the length of the furnace. The two heating elements were connected in parallel and the total resistance was 110 Ω. The heat losses were reduced by enclosing each of the two sections in an asbestos cylinder and filling the space between the casing and the heating elements with vermiculite.

A thermistor probe was inserted at the junction of the two sections and touching the cell.

The heating elements were run from a Variac which was connected to a thermistor control box. The temperature at a fixed point within the furnace was controlled to within ± 0.02°C by the thermistor and thyraton control.

The temperature gradient down the length of the cell was measured using a copper-constantan thermocouple[50] and the temperature variation was ± 0.3°C. The temperature where the thermistor made contact with the cell, agreed with the average temperature of the cell to within ± 0.1°C.

GAS CHROMATOGRAPH - FLAME IONIZATION DETECTOR

The detector used was made in the departmental workshop to specifications supplied by Dr. G.S. Laurence.

Briefly, the carrier gas (C.I.G. oxygen-free nitrogen, 0.03 l/min) was mixed with hydrogen (C.I.G.) and burnt at a jet (21 gauge syringe needle, 45 mm long) above which was placed a platinum wire loop (1 mm thick, 12.5 mm diameter) which acted as the collector electrode. The loop was 35 mm above the jet. The jet and the loop were housed in a 230 mm high and 70 mm diameter brass cylinder. The detector was purged with clean air, admitted through a number of holes in the base of the detector.

A potential difference of 90V was applied between the jet and the collector electrode. The measuring circuit is given in figure 4. As the jet was earthed and the power supply was floating, the batteries were in polythene bags to prevent electrical leakage, and the complete measuring circuit was mounted in an earthed aluminium box. In addition, the jet and the collector electrode were insulated from the body of the detector by being mounted in Teflon. The output of the measuring circuit was fed through a vibrating reed electrometer converter and an electrometer (E.I.L.) and then to a Sunvic pen recorder.

Aluminium columns, 12 ft long, 1/4 inch diameter packed with Chromosorb P (68/80) coated with 20% silicone (John Morris Co.), were operated at 0°C.

3.3 PROCEDURE

The desired pressure of C_2F_5I or other gases used was measured using a mercury manometer, either directly in the cell or via a calibrated volume. The sample was irradiated for a given time and then analysed on the vapour phase chromatograph (v.p.c.). The sample was "toepplered" into the v.p.c. injection line for the reasons already given. Each cell filling gave one point under a particular set of variable conditions (time, pressure etc.).

C_4F_{10} was chosen as a standard for the v.p.c. because it is stable, obtainable in high purity, had a short retention time on the column used, and its peak was very sharp.

The chromatogram peaks were identified by comparing their retention times with those of pure samples.

The amount of iodine formed during the photolysis was determined by freezing down the products at -196°C in the side arm (A) of the cell, then cutting it off and dissolving the contents in carbon tetrachloride. The optical density of the solution was measured at 5150 Å in a Unicam SP500 spectrophotometer (ε = 940 litre moles^{-1} cm^{-1}, see exchange experimental section, Part 1 of this thesis).

In the runs in which the effect of added iodine was studied the iodine was generated by photolysing a C_2F_5I-NO mixture with 2537 Å light for given periods of time, then distilling off all other products (C_2F_5I, HI, C_2F_5NO, NOI (?)) at -63°C ($CHCl_3$ slush). The iodine vapour pressure at this temperature is less than 10^{-5} mm. It was thoroughly degassed by pumping at -63°C and -196°C.

This procedure was developed for a number of reasons: first, the method provided a clean way of preparing iodine in situ without

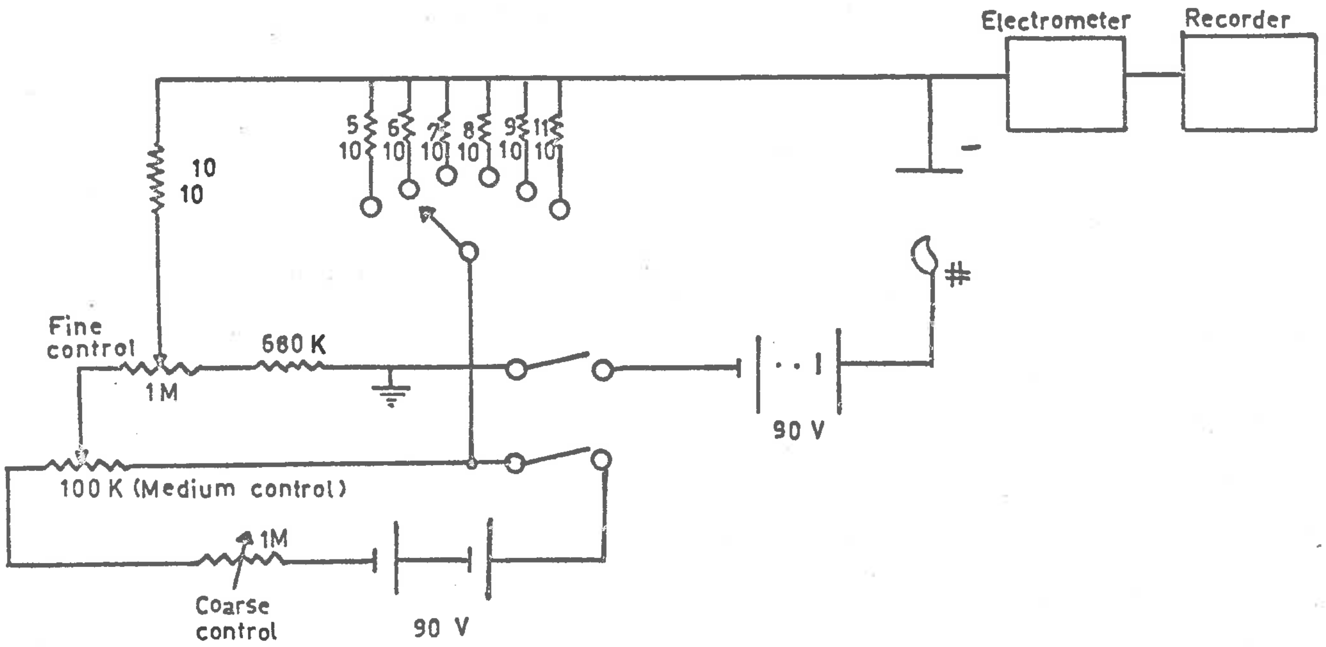


FIG. 4

Measuring circuit for flame ionization detector.

involving trap to trap transfer, which could result in the loss of iodine. Second, the method also avoids contamination due to moisture which could be introduced if molecular iodine was used. Third reason, as the iodine quantum yield should be half of the C_2F_5NO yield, the amount of iodine formed may be calculated from the light absorption and irradiation time. However this procedure was in fact complicated by the formation of NOI, so that the iodine yield was not half the C_2F_5NO yield, consequently the amount of iodine formed could not be calculated in a simple manner. The alternative method of preparing dry iodine has been used for preparing iodine-131 in the exchange studies (see Part 1 of this thesis). This latter method suffers from the disadvantage that the iodine concentration is not initially known, although this could be eventually overcome by using spectrophotometric techniques to measure the concentration.

The extinction coefficient of C_2F_5I at the two wavelengths 2537 Å and 1849 Å was measured. The value at 2537 Å (ϵ = 119 litre mole^{-1} cm^{-1}) was measured on a Unicam SP500 spectrophotometer. The value at 1849 Å (ϵ = 27 litre mole^{-1} cm^{-1}) was measured using a Unicam SP700 recording spectrophotometer. The error in the latter value is expected to be large, as the measurement was performed at the extreme end of the range of the instrument.

3.4 SOURCES OF ERROR

1. LIGHT INTENSITY

As the Hanovia low pressure mercury discharge lamp was not stabilised fluctuation in the light intensity could be expected. From actinometry experiments the fluctuations could be responsible for an error of about 2% in light intensities.

2. V.P.C. ANALYSIS

The concentrations and the response (sensitivity) of the v.p.c. detector were calculated from peak heights except for n-C_3F_7I, for which peak areas were used, as the peak was broader (approximately twice as broad as for C_2F_5I, but very much smaller particularly for low pressure and short time experiments) than any other obtained. The retention times of various compounds at 0°C are given below:

Compound	C_3F_8	C_4F_{10}	CF_3I	C_2F_5I	n-C_3F_7I
retention time (mins)	1 3/4	2	4	8	16

The injection pressure was used in the calculation of concentration of a photolysis product and for low (1.0 cm in cell) pressure C_2F_5I photolysis injection pressures of 1.0 to 2.0 cm were used. The mercury manometer could be read to the nearest ± 0.02 cm, i.e. the error was 2-4%.

The response was calculated from least squares slope of peak height versus injection pressure, and the error in the slope varied from 2-6% depending on the compound.

Each sample was analysed in triplicate and the results given in the tables are the average values.

3. DEAD VOLUME - (SIDE ARMS OF THE CELL)

The volume of the cell which is subject to irradiation is 83 ccs. The side arm occupies a volume of approximately 15 ccs. Thus the concentration of the products formed during the photolysis is reduced by 15%, as the concentrations are calculated for the total volume of the cell which includes the side arm.

The total possible error in the experimental results could be as high as 12% under some experimental conditions. There may be a systematic error of as much as 15% due to the dead volume effect.

4. RESULTS AND DISCUSSION

Mercury sensitization can be dismissed on the grounds that all the mercury vapour (v.p. at 20°C is 0.0012 mm[55]) trapped in the cell during the filling would be removed within about 5×10^{-3} seconds after commencement of the photolysis, as HgI_2. If mercury is deliberately added to C_2F_5I and the mixture photolysed, a whitish-yellow film of HgI_2 forms on the walls of the irradiation vessel. No such film was observed, even after many runs, for the photolysis of pure C_2F_5I.

4.1 2537 Å PHOTOLYSIS OF PERFLUOROETHYL IODIDE

The photolysis was performed with a Corning filter inserted between the lamp and the cell to cut out the 1849 Å radiation. The filter transmits light of wavelength greater than 2200 Å.

The photolysis products are C_4F_{10} and I_2 only.

(a) Effect of time of irradiation on the quantum yield of products.

The variation of the iodine and perfluorobutane (C_4F_{10}) quantum yields with time of irradiation is shown in figure 5. The basic data are given in Appendix 5.1. The photolyses were performed at constant C_2F_5I pressure: for I_2 measurement, p = 10.39 ± 0.08 cm, and for C_4F_{10} measurement, p = 10.30 ± 0.05 cm. The method of analysis did not allow both I_2 and C_4F_{10} to be measured on the same cell filling without distillation, which could introduce errors, consequently each point on the graph represents a separate cell filling.

As may be expected the quantum yields are low[1] suggesting a rapid back reaction between the primary fragments.

(b) Effect of pressure on the quantum yield of products.

Figure 6 and Appendix 5.2 show the pressure dependence on C_2F_5I pressure of the C_4F_{10} and I_2 quantum yields. Again each point on the graph represents a separate cell filling.

The error in the values of $\Phi(I_2)$ in the C_2F_5I concentration range less than 0.5×10^{-3} moles litre^{-1} increases from 15 to 50% with decreasing concentration. The optical density measurement of the iodine produced was of the same order as the precision with

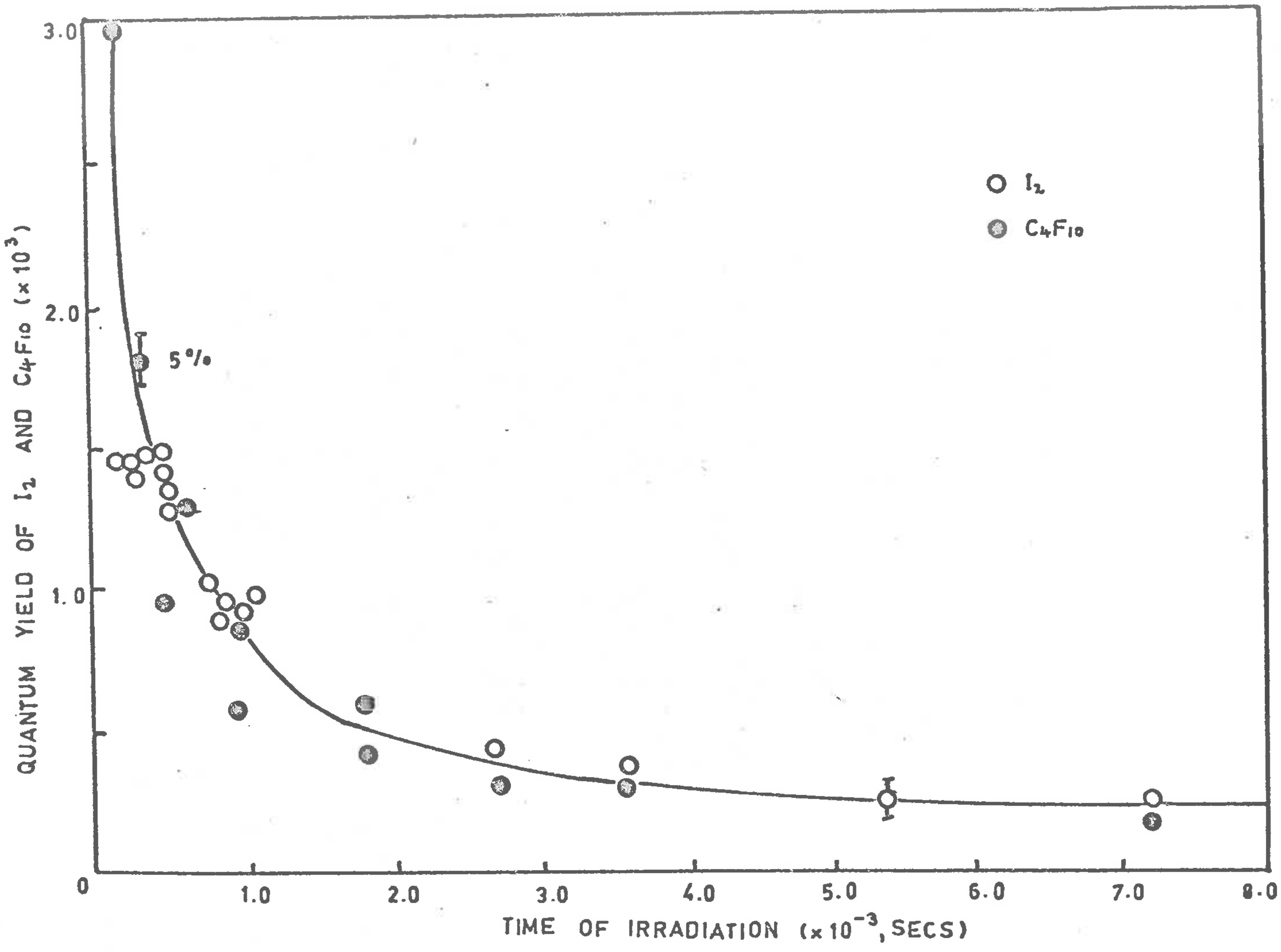


FIG. 5

Time dependence of Φ (I_2) and Φ (C_4F_{10}) for the photolysis of C_2F_5I with 2537°A light.

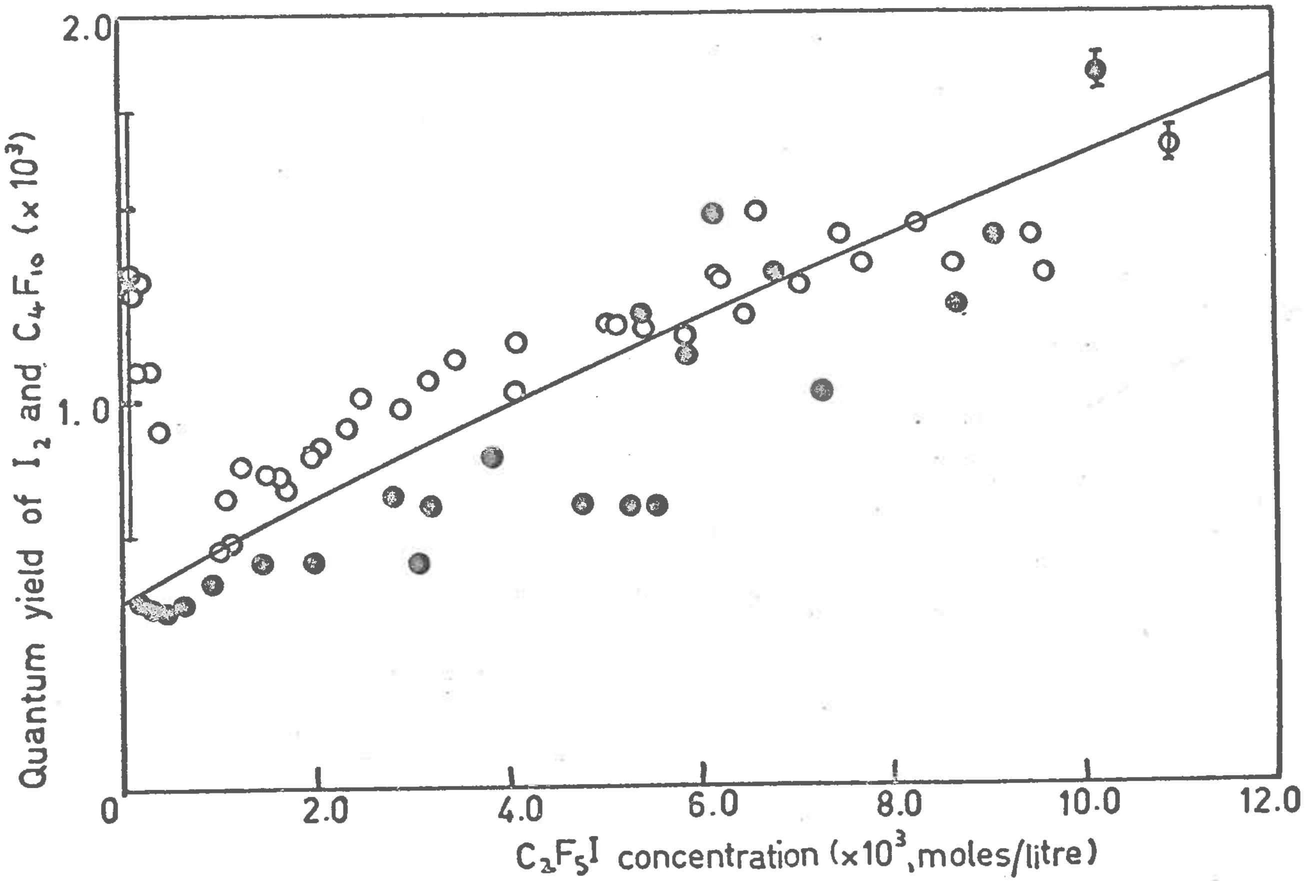


FIG. 6

Pressure dependence of $\Phi(I_2)$ and $\Phi(C_4F_{10})$ for the photolysis of C_2F_5I with 2537A° light.

○ I_2

● C_4F_{10}

which the Unicam SP600 spectrophotometer could be read, i.e. the readings ranged from 0.006 to 0.002 optical density units, and the precision to which the instrument could be read is ± 0.001.

(c) Effect of NO.

The results of the photolysis of C_2F_5I with NO as scavenger, under various conditions of NO concentration and irradiation time are summarised in Tables II and III respectively. The formation of C_2F_5NO during the photolysis of C_2F_5I-NO mixture was confirmed by infrared spectrophotometry, where the growth of the C-NO band at 6.24 μ[45] was followed. The values of C_2F_5NO concentration used for calculating $\Phi(C_2F_5NO)$ were obtained from the v.p.c. analysis.

At high C_2F_5I concentration $\Phi(C_2F_5NO) = 1.07 \pm 0.04$ which agrees with the value obtained by Emeey for CF_3I[2] and indicates that at 2537 Å C-I bond rupture is a consequence of the light absorption. The lower value of $\Phi(C_2F_5NO)$, 0.82 ± 0.03, at low C_2F_5I pressure may be due to the reactions[3]

$$C_2F_5NO + 2NO \rightarrow C_2F_5 + N_2 + NO_3 \tag{11}$$

$$NO_3 + NO \rightarrow 2NO_2 \tag{12}$$

$$C_2F_5 + NO_2 \rightarrow C_2F_5NO_2 \tag{13}$$

$$C_2F_5 + I_2 \rightarrow C_2F_5I + I \tag{6}$$

TABLE II

The Pressure Dependence of the Photolysis of C_2F_5I in the Presence of NO as Scavenger at 2537 Å

Irradiation time: 30.1 ± .1 seconds

Concn. C_2F_5I x 10^4 moles litre^{-1}	Concn. NO x 10^4 moles litre	Concn. C_2F_5NO x10^5 moles litre	$\Phi_{C_2F_5NO}$
6.27	4.55	2.89	0.83
6.22	10.49	2.86	0.83
6.33	18.8	2.99	0.85
6.24	19.98	2.98	0.85
6.17	43.18	2.39	0.72
6.30	80.90	1.50	0.43
59.6	1.79	6.78	1.11
59.2	17.6	6.30	1.03
58.9	10.58	7.08	1.15
58.8	17.61	6.51	1.07
59.1	49.78	6.52	1.05
59.3	83.34	6.21	1.02

TABLE III

The Irradiation Time Dependence of the Photolysis of C_2F_5I in the Presence of NO as Scavenger at 2537 Å

Time of irradiation $\times 10^{-1}$ secs.	Concn. C_2F_5I $\times 10^{3}$ moles litre^{-1}	Concn. NO $\times 10^{3}$ moles litre^{-1}	Concn. C_2F_5NO $\times 10^{5}$ moles litre^{-1}	$\Phi_{C_2F_5NO}$
1.01	5.88	6.14	2.24	1.10
2.03	5.76	6.06	4.30	1.05
3.02	5.99	6.16	7.03	1.10
4.53	5.79	6.13	10.27	1.10
6.01	5.99	6.11	15.83	1.30

which would lower the C_2F_5NO yield.

Reaction (11) depends on the $[NO]/[C_2F_5NO]$ ratio which must be at least of the order of 2. The amount of C_2F_5NO formed will depend on the light absorbed by C_2F_5I, and consequently there is more C_2F_5NO formed at high pressure of C_2F_5I ($\sim 10^{-3}$ moles litre^{-1}). The conditions under which reaction (11) may occur are more easily attained in the runs in which low C_2F_5I pressure ($\sim \times 10^{-4}$ moles litre^{-1}) was used.

Another odd feature of the low pressure C_2F_5I-NO mixture photolysis is that $\phi(I_2) \neq 0.5\ \phi(C_2F_5NO)$. A mixture of C_2F_5I (8.35×10^{-4} moles litre^{-1}) and NO (20.0×10^{-4} moles litre^{-1}) was photolysed for 30.2 seconds. All the volatile products were distilled off at -63°C and the iodine dissolved in CCl_4. The iodine concentration was measured spectrophotometrically; this gave $\phi(I_2) = 0.31$. Under essentially identical conditions, $\phi(C_2F_5NO) = 0.82$. The difference may be due to the formation of NOI,[56] which may distil off at -63°C; or to a fault in the separation and analytical techniques.

(d) Mechanism.

On the basis of the experimental evidence and the evidence already discussed in the introduction, the following mechanism is proposed for the photolysis of C_2F_5I with 2537 Å light:

$$C_2F_5I \xrightarrow{h\nu\ (2537\ \text{Å})\ I_{abs}} (C_2F_5)_E + I(^2P_{1/2}) \quad (1)$$

$$(C_2F_5)_E + M_1 \xrightarrow{k_2} C_2F_5 + M_1 \quad (2)$$

$$M_1 + C_2F_5 + C_2F_5 \xrightarrow{k_3} C_4F_{10} + M_1 \quad (3)$$

$$I(^2P_{1/2}) + M_2 \xrightarrow{k_4} I(^2P_{3/2}) + M_2 \quad (4)$$

$$2I(^2P_{3/2}) + M_2 \xrightarrow{k_5} I_2 + M_2 \quad (5)$$

$$C_2F_5 + I_2 \xrightarrow{k_6} C_2F_5I + I \quad (6)$$

In the presence of NO as scavenger, the following reactions, besides those already proposed in the presentation of results, have to be added:

$$C_2F_5 + NO \rightarrow C_2F_5NO \quad (7)$$

$$I + NO = NOI \quad (8)$$

$$NOI + I \rightarrow NO + I_2 \quad (9)$$

$$2NOI \rightarrow 2NO + I_2 \quad (10)$$

Reactions (8) to (10) are those proposed by Porter et al.[56] to account for the rapid recombination of iodine atoms in the presence of nitric oxide. Also, NO rapidly deactivates $I(^2P_{1/2})$ to $I(^2P_{3/2})$.[25]

Meyer[54] has suggested that the molecular iodine formation during the flash photolysis of methyl iodide is due to the abstraction reaction involving $I(^2P_{1/2})$ i.e.,

$$I(^2P_{1/2}) + CH_3I \rightarrow CH_3 + I_2 + 3 \text{ kcal.}$$

However the contribution of this type of reaction to the deactivation of the $I(^2P_{1/2})$ by CF_3I has been suggested by Donovan and Husian[24] to be negligibly small and may be assumed to be small in C_2F_5I photolysis also.

The need of a third body for CF_3 radical recombination has been suggested,[57] consequently M_1 is included in (3) but the increased vibrational modes of C_2F_5 over CF_3 make it less necessary and probably the recombination is in the second order region at C_2F_5I pressures greater than 1 cm (6×10^{-4} moles litre^{-1}).

Returning to the reaction scheme if a steady state is assumed then

$$d[C_2F_5]/dt = 0 = k_2(C_2F_5)_E(M_1) - k_3(C_2F_5)^2(M_1) - k_6(C_2F_5)(I_2) \qquad (i)$$

$$d[C_2F_5]_E/dt = 0 = I_{abs} - k_2(C_2F_5)_E(M_1) \qquad (ii)$$

$$d(I(^2P_{1/2}))/dt = 0 = I_{abs} - k_4(I(^2P_{1/2}))(M_2) \qquad (iii)$$

$$d[I]/dt = 0 = k_4(I(^2P_{1/2}))(M_2) - k_5(I)^2(M_2) + k_6(C_2F_5)(I_2) \qquad (iv)$$

where $I = I(^2P_{3/2})$

Combining (i) and (ii), obtain

$$(C_2F_5) = -\frac{k_6(I_2) + (k_6^{\,2}(I_2)^2 + 4k_3(M_1)I_{abs})^{\frac{1}{2}}}{2k_3M_1}$$

$$R_{C_4F_{10}} = k_3(C_2F_5)^2(M_1)$$

$$= \frac{1}{4k_3(M_1)} \cdot (-k_6(I_2) + (k_6^{\,2}(I_2)^2 + 4k_3(M_1)I_{abs})^{\frac{1}{2}})^2 \qquad (v)$$

Rearranging (v) and ignoring (M_1), one obtains

$$\frac{k_6}{k_3^{\frac{1}{2}}} = \frac{1}{R^{\frac{1}{2}}_{C_4F_{10}}} \cdot \frac{I_{abs} - R_{C_4F_{10}}}{(I_2)}$$

But as $I_{abs} \gg R_{C_4F_{10}}$

then,

$$\frac{k_6}{k_3^{\frac{1}{2}}} = \frac{I_{abs}}{R^{\frac{1}{2}}_{C_4F_{10}}(I_2)}$$

The values of the ratio $k_6/k_3^{\frac{1}{2}}$ are given in table IV.

The value of $R_{C_4F_{10}}$ used is the overall rate of formation during the time of photolysis, whereas $[I_2]$ is the final concentration as measured at the end of the run. Probably a better approximation to the $[I_2]$ would be 0.5 x $[I_2]$, that is, the average value. This would, however, make $k_6/k_3^{\frac{1}{2}}$ twice as great and probably be the upper limit of the ratio. In the initial stages ($t < 300$ seconds) reaction

$$C_2F_5 + I \rightarrow C_2F_5I$$

TABLE IV

Calculation of the $k_6/k_3^{\frac{1}{2}}$ for the 2537 Å Light Photolysis of C_2F_5I

Time $\times 10^{-2}$ secs	$[I_2] \times 10^7$ moles litre^{-1}	$R_{C_4F_{10}} \times 10^9$ moles litre^{-1} sec^{-1}	$k_6/k_3^{\frac{1}{2}} \times 10^4$ mole$^{-\frac{1}{2}}$ litre$^{\frac{1}{2}}$ sec$^{-\frac{1}{2}}$
0.30	0.83	13.38	26.02
0.60	1.65	9.37	15.55
1.20	3.23	6.20	9.78
3.00	8.27	3.72	4.94
6.00	13.91	2.66	3.47
9.00	14.44	1.80	4.06
18.00	20.15	1.23	3.52
27.00	23.91	0.67	4.02
36.00	26.55	0.65	3.67

may be more important than reaction (6), resulting in the increase in the values of $k_6/k_3^{\frac{1}{2}}$. The average value of the ratio $k_6/k_3^{\frac{1}{2}}$ at longer irradiation times is $3.95 \pm 0.40 \times 10^4$ litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec$^{\frac{1}{2}}$.

The recombination rate constant k_{31} for reaction

$$CF_3 + CF_3 \xrightarrow{k_{31}} C_2F_6$$

is 2.3×10^{10} litre mole^{-1} sec^{-1} 60 and for the reaction

$$CF_3 + I_2 \xrightarrow{k_{61}} CF_3I + I$$

k_{61} is 2.6×10^9 litre mole^{-1} sec^{-1},[58] and the ratio $k_{61}/k_{31}^{\frac{1}{2}}$ is 1.72×10^4 litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec$^{-\frac{1}{2}}$. The ratio of $k_6/k_3^{\frac{1}{2}}$ and $k_{61}/k_{31}^{\frac{1}{2}}$ are of the same order, with the ratio involving C_2F_5 radicals being slightly larger as may be expected on the basis of collision diameters.[59]

4.2 PHOTOLYSIS OF PERFLUOROETHYL IODIDE WITH UNFILTERED LIGHT

The unfiltered light from a Hanovia low pressure mercury discharge lamp is a mixture of 2537 Å light (~97%) and 1849 Å light (~3%). The products of the photolysis with unfiltered light therefore include those formed by the cross combination of the primary products resulting from the photolytic decomposition of C_2F_5I with light of the two wavelengths as well as the products themselves. The principle products are I_2, C_4F_{10}, C_3F_8, CF_3I, n-C_3F_7I and CF_2I_2. Only I_2 and C_4F_{10} are formed when 2537 Å light alone is used. The remaining products are the result of 1849 Å photolysis of C_2F_5I. There may be C_4F_{10} and I_2 formed from 1849 Å photolysis, but the actual contribution is difficult to measure under the experimental conditions used.

The products formed as a result of 1849 Å photolytic decomposition of C_2F_5I have CF_3 and CF_2 species as their precursors;

the production of CF_2 can only be explained by the C-C bond fission of a C_2F_5 radical. Both the CF_2 and CF_3 combine with the primary radicals C_2F_5 and I formed as the result of the simultaneous 2537 Å photolysis of C_2F_5I.

An attempt was made to isolate the 1849 Å light by using a γ-irradiated LiF crystal as a filter.[63] However in contrast to the reported transmission of such crystals, the transmission of 1849 Å light by the crystal was only 2%, and consequently the irradiation periods needed to produce sufficient decomposition were too long to be practical. Even after six hours irradiation no decomposition of C_2F_5I was observed.

In photochemical experiments the standard procedure is to express the yields of products as quantum yields. In this case the products are formed as the result of cross combination of primary species formed by the absorption of two different wavelengths by the C_2F_5I. Hence two quantum yields for each product may be calculated.

(a) Effect of pressure on the yield of products.

Figure 7 (1849 Å) and figures 8A (2537 Å) and 8B (2537 Å), Appendix 5.3, show the dependence of the quantum yields of products on C_2F_5I pressure (concentration). Probably the most striking feature of the diagrams, is that the n-C_3F_7I shows two distinctly different patterns of behaviour: Φ (1849 Å) decreases with increasing pressure, whereas Φ (2537 Å) remains constant or

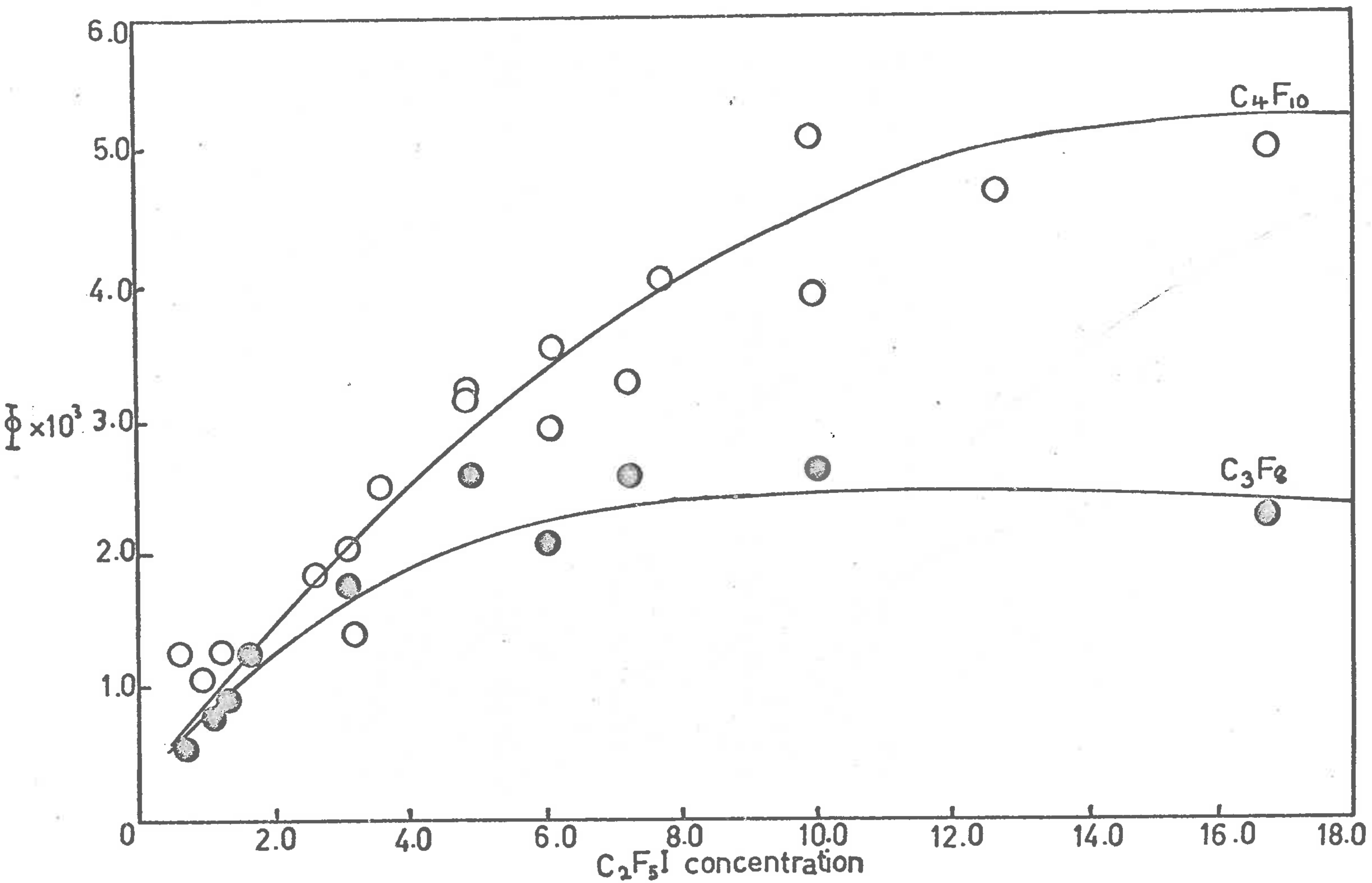


FIG 8A

Pressure dependence of $\Phi(C_4F_{10})$ and $\Phi(C_3F_8)$ for the photolysis of C_2F_5I with unfiltered light. Φ's calculated with respect to the 2537 A° light absorbed.

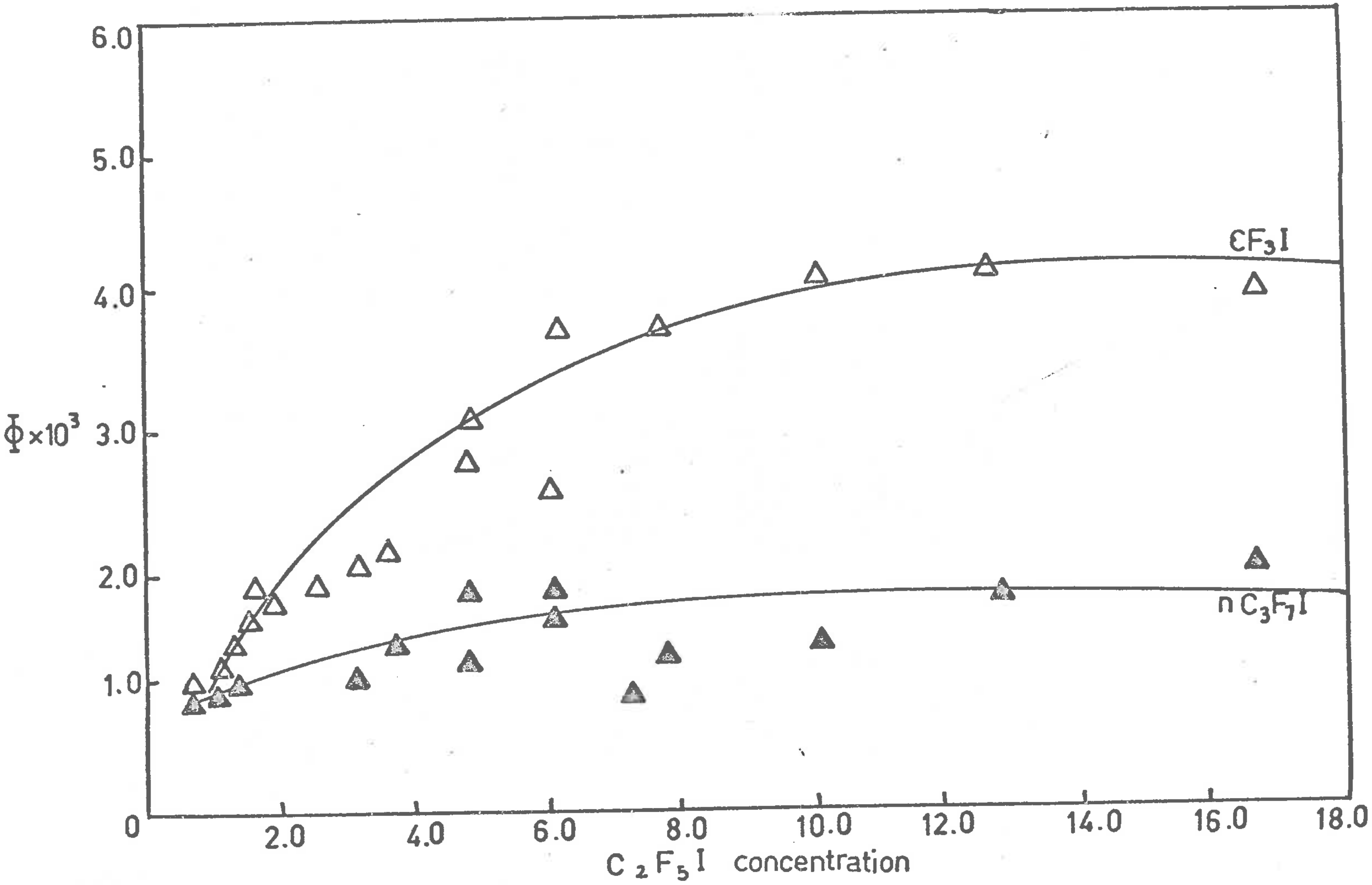


FIG. 8B

Pressure dependence of $\Phi(CF_3I)$ and $\Phi(n\,C_3F_7I)$ for the photolysis of C_2F_5I with unfiltered light. Φ's calculated with respect to the 2537 Å light absorbed.

possibly slightly increases with increasing pressure. The same significance cannot be attached to ϕ's in this case as could be if monochromatic light was used. Hence the yields of products will be given in concentration units: moles litre^{-1}.

(b) Time dependence.

The time dependence study of the photolysis at low pressure of C_2F_5I, figure 9, and high pressure of C_2F_5I, figure 10, show that the formation of n-C_3F_7I is favoured at lower pressures, and the rate of formation of CF_3I as compared to C_3F_8 is reduced by going to higher pressures of C_2F_5I.

As CF_2 and CF_3 are probably formed in the same step by the carbon-carbon bond fission of the C_2F_5 radical formed by the absorption of 1849 Å light, a mass balance in the resultant products of CF_2 and CF_3 may be expected. A mass balance was attempted on the basis of the products obtained in the v.p.c. analysis but no balance was obtained, that is $[CF_3I] + [C_3F_8] \neq$ [n-C_3F_7I]. The CF_2 must therefore disappear by a process other than n-C_3F_7I formation. There was also a lack of iodine atom mass balance. The ratio of (unaccounted) iodine atoms to CF_2 is given in table V, the figures for which were obtained from the time dependence studies of the photolysis of C_2F_5I at high pressure given in Appendix 5.4. The values of $[I_2]$ at intermediate times were obtained by interpolation.

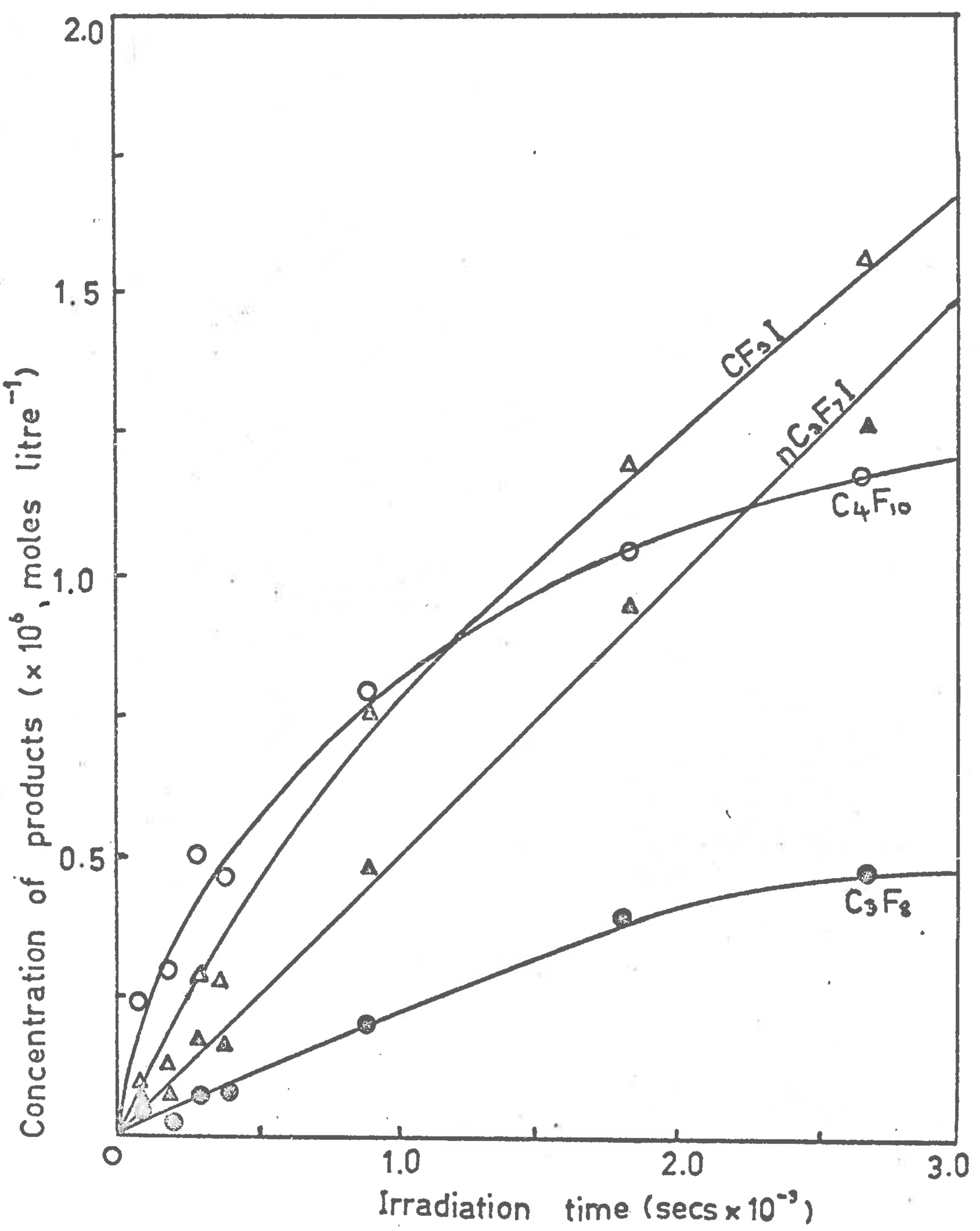


FIG 9

Low pressure (1.05 cms.) C_2F_5I photolysis with unfiltered U.V. Time dependence of product formation.

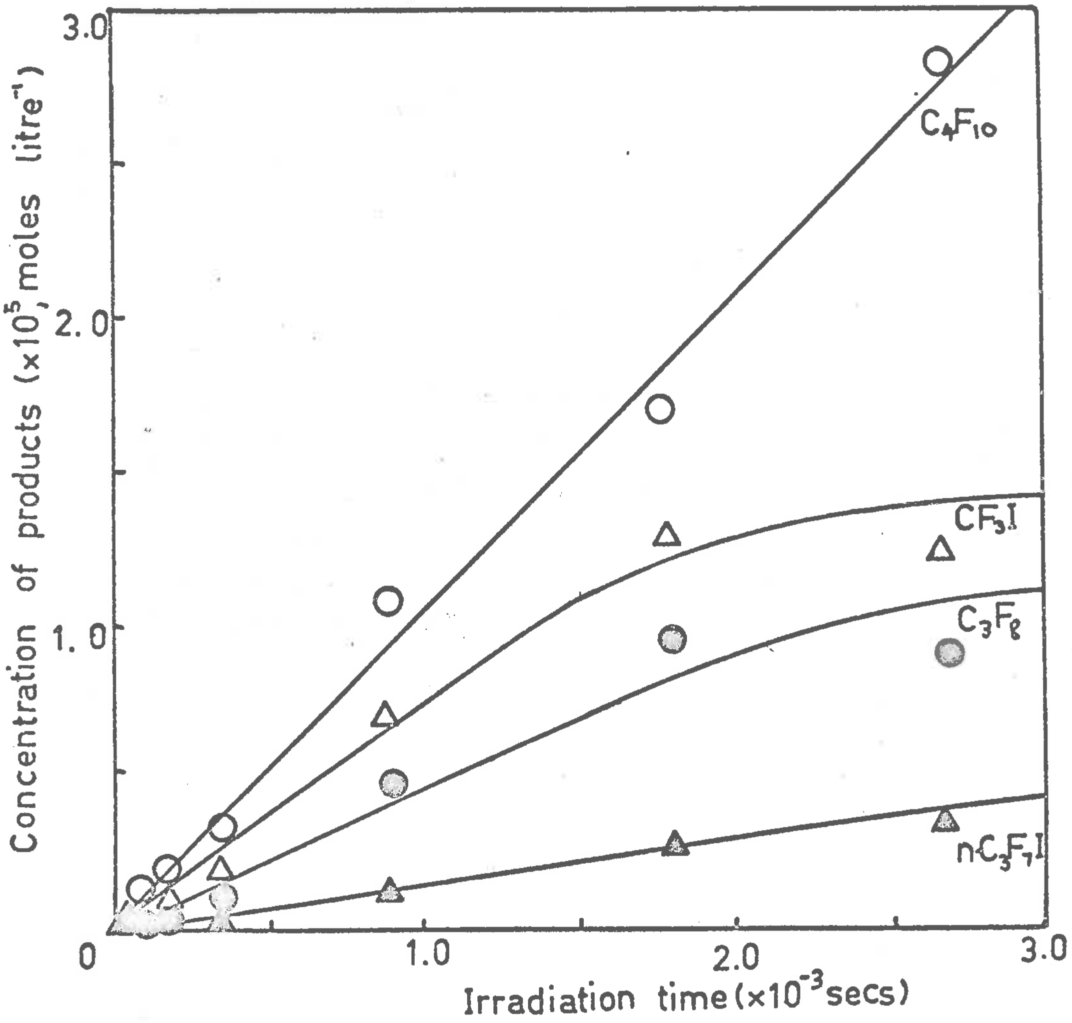


FIG. 10

High pressure (10.3 cms.) C_2F_5I photolysis with unfiltered U.V. light. Time dependence of product formation.

TABLE V

Mass Balance of Products Produced by the Photolysis of 6.05 x 10^{-3} moles litre. C_2F_5I with Unfiltered U.V. Values Taken from the Time Dependence Studies

Time x 10^{-3} secs	Unaccounted CF_2 (A) x 10^6 moles litre^{-1}	Unaccounted I (B) x 10^6 moles litre	$[I]/[CF_2]$	
0.045	0.11	1.0	9.1	
0.09	0.42	1.82	4.3	
0.18	0.98	2.57	2.6	2.2 ± 0.4
0.36	2.65	4.68	1.8	
0.90	10.75	21.55	2.0	
1.80	19.47	35.55	1.8	
2.70	17.30	54.15	3.1	

$A = C_3F_8 + CF_3I - C_3F_7I$

$B = 2(C_4F_{10} + C_3F_8) - (CF_3I + n\text{-}C_3F_7I + 2I_2)$

$2(C_4F_{10} + C_3F_8)$ was used for the calculation of total iodine atoms formed because C_3F_8 is formed by a process such as

$$CF_3 + C_2F_5 \rightarrow C_3F_8$$

and therefore for every CF_3 and C_2F_5 radical there is a corresponding iodine atom. It can be seen that with the exception of the first two values (at 0.045, 0.09 x 10^3 secs) the approximate ratio of unaccounted species, $[I]/[CF_2]$ is 2:1, suggesting the formation of a compound of the type CF_2I_2. The two high values obtained at low irradiation times for $[I]/[CF_2]$ ratio are inexplicable.

(c) Temperature dependence.

The Arrhenius plots of the log rate of formation of products versus 1/T (°K) for various initial pressures of C_2F_5I are shown in figures 11 (1.05 cm), 12 (10.25 cm), 13 (20.20 cm) and 14 (C_4F_{10} at various C_2F_5I pressures). The Arrhenius plot of log $R_{CF_2I_2}$ is not shown, as it is very similar to CF_3I and C_3F_8, showing similar type of scatter etc. ($R_{CF_2I_2}$ is obtained as the difference $R_{C_3F_8} + R_{CF_3I} - R_{C_3F_7I}$.) The values of E_a for CF_2I_2 given in table VI were calculated by least squares method.

The basic experimental data for the temperature dependence is given in Appendix 5.5, and the results are summarised in table VI.

The striking feature of the table is that both the CF_3I and C_3F_8 formation require an activation energy in excess of 3 kcal. The E_a reported in the literature for the formation of C_3F_8 and CF_3I by the following reactions

$$CF_3 + I \text{ (or } I_2) \rightarrow CF_3I \text{ (+ I)} \qquad (14)$$

$$CF_3 + C_2F_5 \rightarrow C_3F_8 \qquad (15)$$

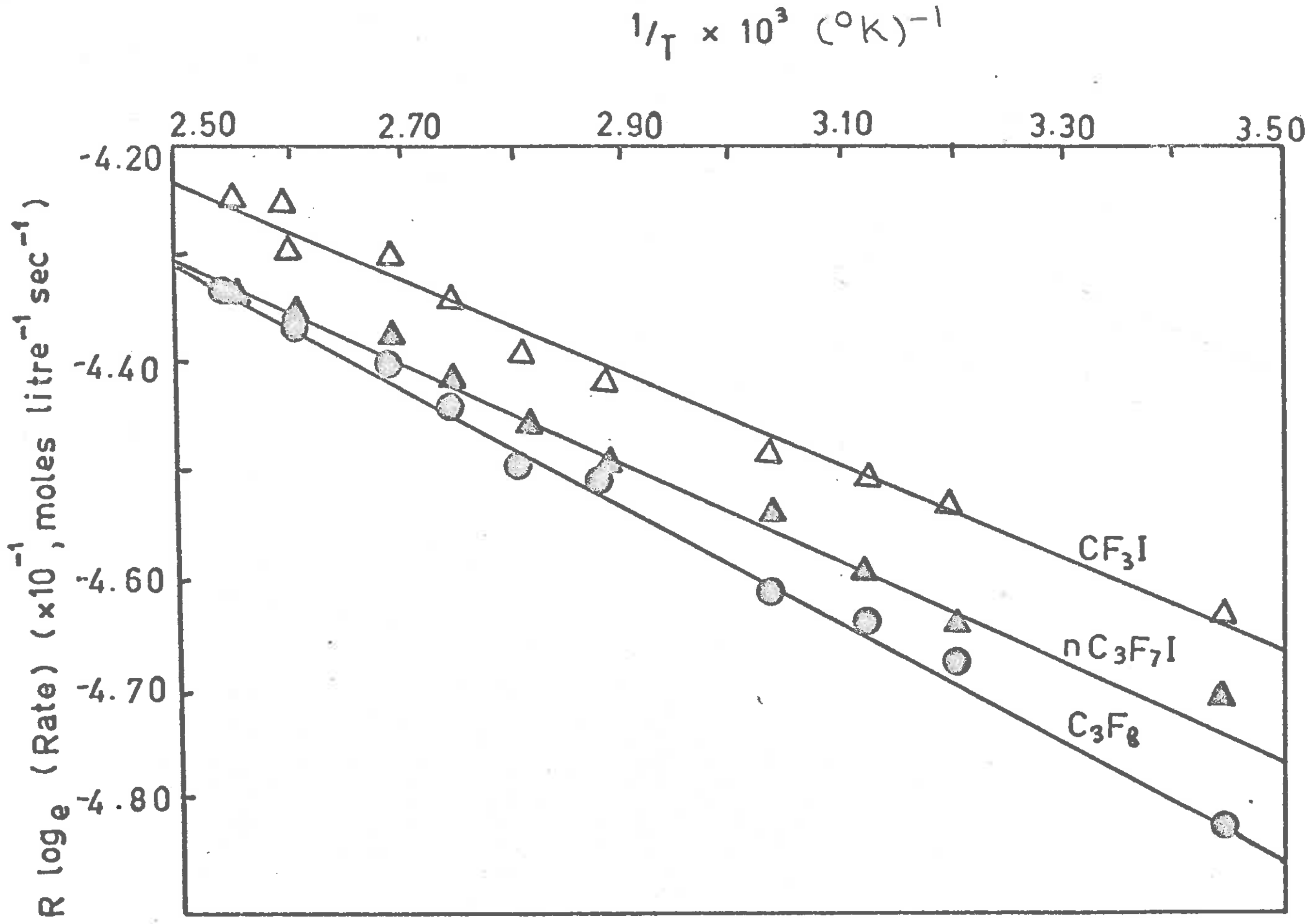


FIG. 11

Temperature dependence of product formation for low pressure (1.05 cms) photolysis of C_2F_5I with unfiltered light.

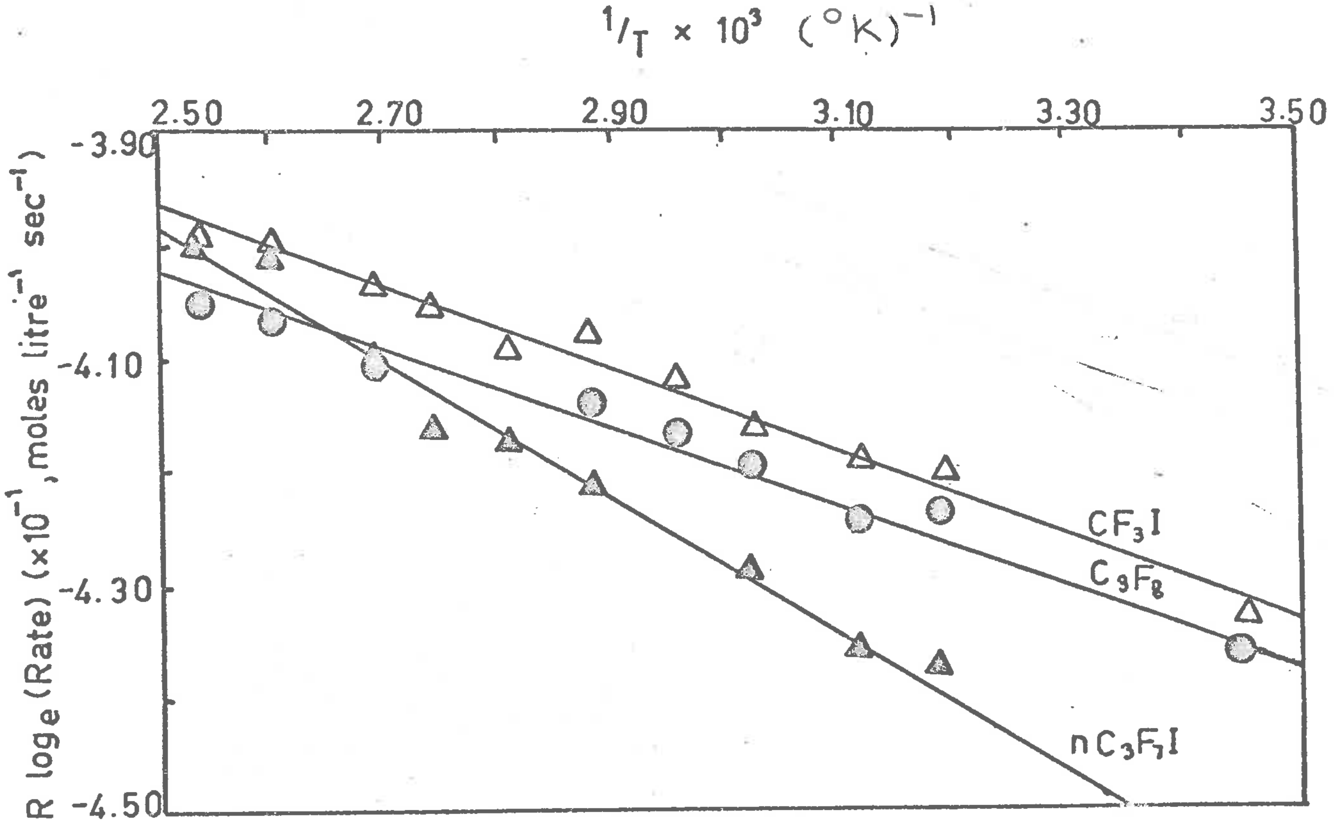


FIG. 12

Temperature dependence of product formation for medium (10.25 cms) pressure photolysis of C_2F_5I with unfiltered U.V.

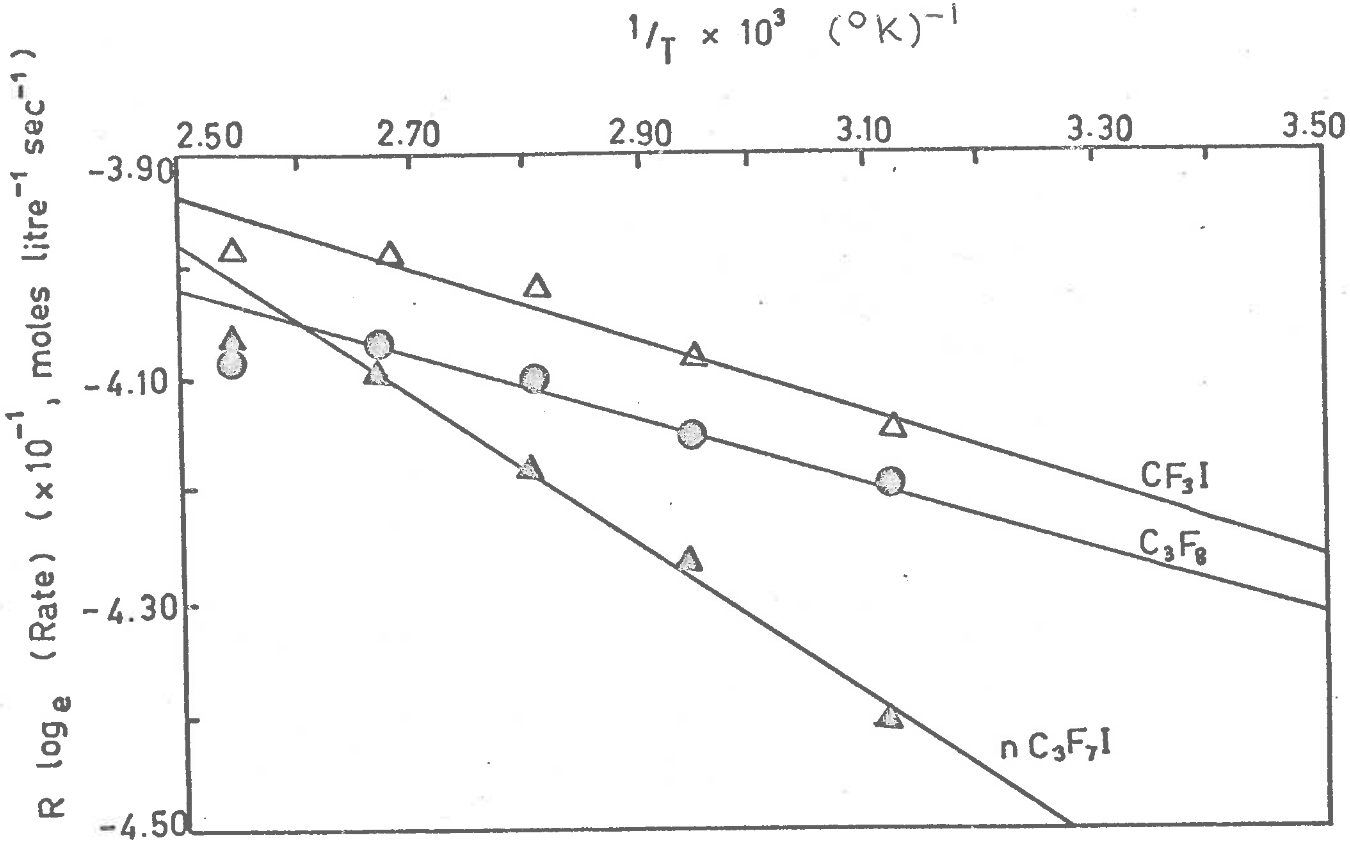


FIG. 13

Temperature dependence of product formation for high pressure photolysis of C_2F_5I with unfiltered U.V.. (pressure 20 cms.)

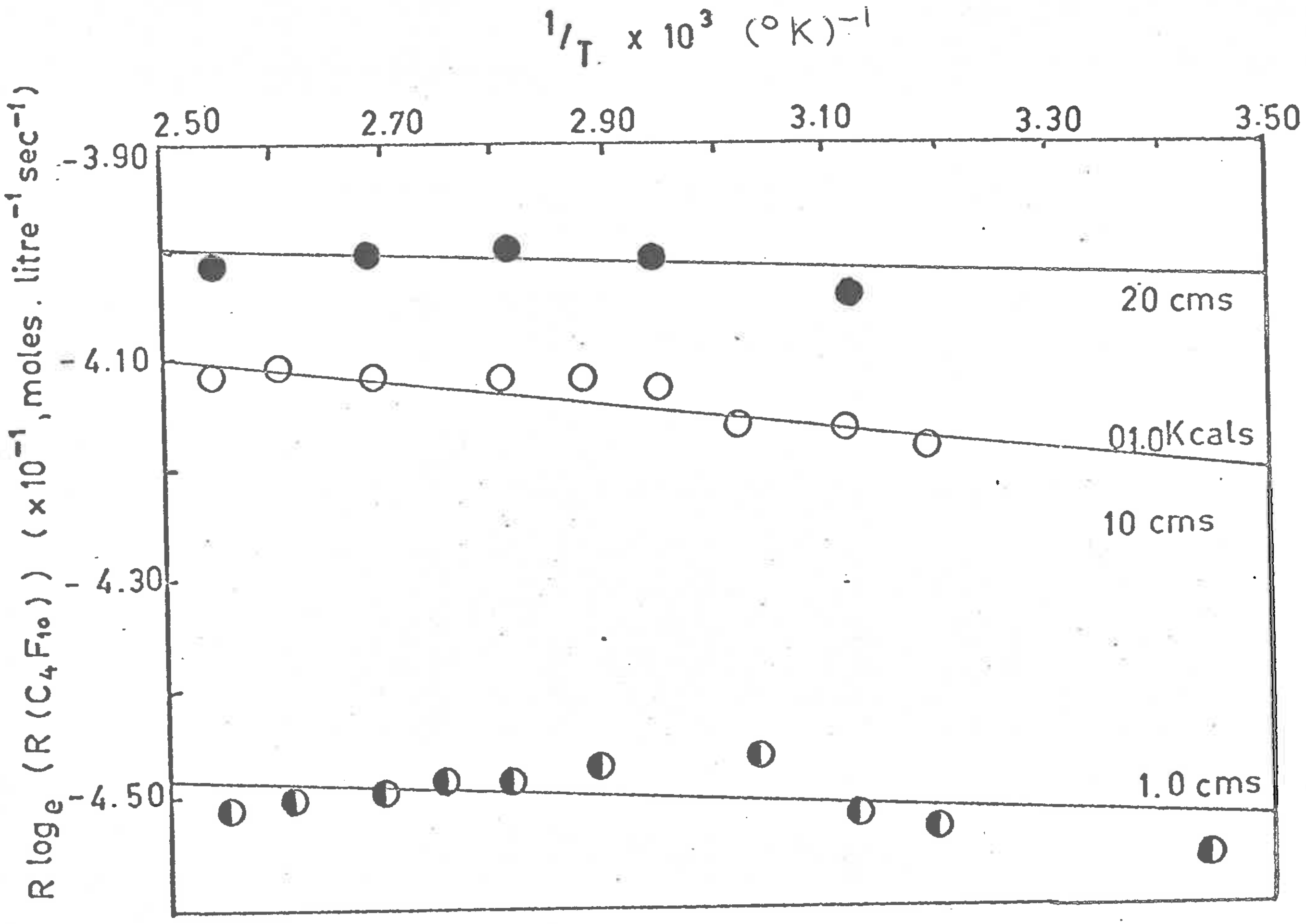


FIG 14

Temperature dependence of C_4F_{10} formation at various pressures of C_2F_5I photolysed with unfiltered light.

TABLE VI

Observed Activation Energies for the Formation of Products Produced by the Photolysis of C_2F_5I with Unfiltered U.V. Light

C_2F_5I pressure (cm)	C_3F_8	C_4F_{10}	CF_3I kcal mole^{-1}	n-C_3F_7I	CF_2I_2
1.05	3.47 ± 0.10	0.46 ± 0.16	4.12 ± 0.14	4.56 ± 0.13	4.70 ± 0.20
10.25	3.23 ± 0.17	0.50 ± 0.17	3.42 ± 0.13	6.57 ± 0.45	2.80 ± 0.30
20.20	3.00 ± 0.30	0.60 ± 0.38	3.10 ± 0.22	6.50 ± 0.41	2.30 ± 0.20

are zero.[58,59] Therefore at least some of the C_3F_8 and CF_3I is formed by processes other than those above and which require an activation energy of 3 kcal. There is an alternative mechanism of CF_3I formation

$$CF_3 + C_2F_5I \rightarrow CF_3I + C_2F_5.$$

Although in terms of bond energies the reaction is exothermic, the E_a as measured in $CF_3COCF_3 - C_2F_5I$ abstraction studies was 2.8 kcal. The abstraction studies will be discussed later. Although the E_a of 3 kcal for CF_3I formation can be identified with the abstraction process, the value is still difficult to accept for C_3F_8 formation, unless in both cases it was "inherited", that is the process <u>leading</u> to the formation of the CF_3 radical required an activation energy of 3 kcal. The activation energy of any subsequent reaction would require 3 kcal plus whatever energy was needed for that particular step.

Another odd feature of table VI is the increase in activation energy for CF_3I and C_3F_8 with decreasing pressure.

The E_a for CF_2I_2 was calculated from slope of the Arrhenius plot of $\log_{10} (R_{C_3F_8} + R_{CF_3I} - R_{n\text{-}C_3F_7I})$ versus 1/T.

(d) <u>Effect of argon</u>.

The addition of argon to a low pressure of C_2F_5I results in a decrease in the yields of CF_3I, C_3F_8 and $n\text{-}C_3F_7I$ (figure 15), Appendix 5.6, thus providing further evidence that the primary step

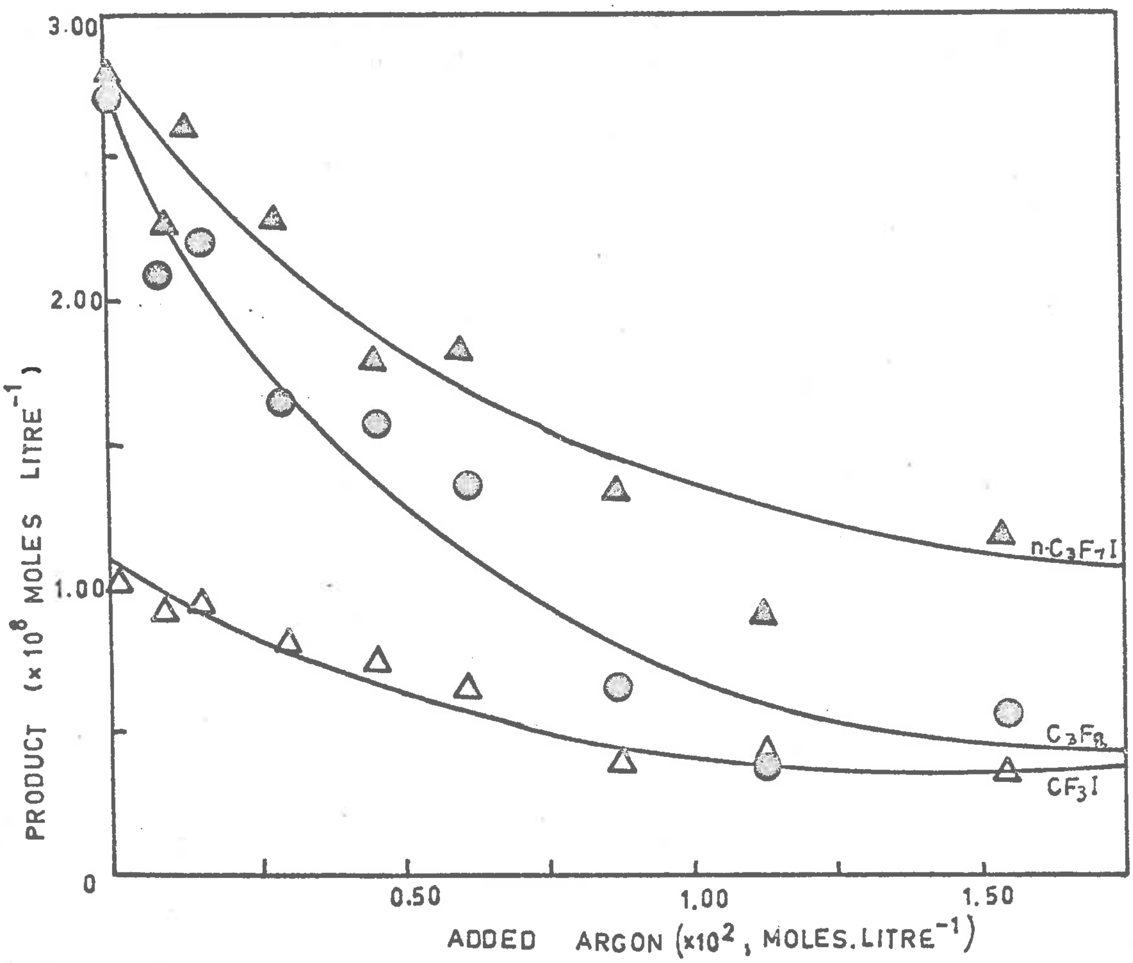


FIG 15

The effect of Argon on C_3F_8, CF_3I and n-C_3F_7I production during the photolysis of C_2F_5I with unfiltered U.V. . C_2F_5I $(6.30 \pm 0.05) \times 10^{-4}$ moles.litre^{-1}.

in the formation of CF_3 and CF_2 involves hot radicals which can be moderated by argon.

(e) Effect of iodine.

Iodine was also added to low pressures of C_2F_5I before photolysing with unfiltered light. The method of preparing the iodine was by photolysing a mixture of C_2F_5I-NO with 2537 Å light then distilling all other products off at -63°C. Unfortunately, the exact amount of iodine is not known as an independent measurement of $\phi(I_2)$ generated under these conditions disagreed with the value calculated from the known $\phi(C_2F_5NO)$ by about 15%. However the values in Appendix 5.7 and those used in the graphical representation (figure 16) serve the purpose of demonstrating that products (C_4F_{10} and to some extent C_3F_8) which depend on the radicals generated by 2537 Å light are inhibited to a greater extent than those (e.g. CF_3I) which depend on the radicals generated by 1849 Å light.

(f) Effect of NO.

An alternative method of establishing the primary process in the photolysis is to add nitric oxide which will scavenge the fluorocarbon radicals, C_2F_5, n-C_3F_7 or CF_3. At very low pressures of NO (~ 10^{-6} moles litre^{-1}), (Table VII), the reaction due to hot radicals (formation of CF_3I) does not appear to be inhibited. The 30 second photolysis of C_2F_5I-NO mixtures suggests that any C_4F_{10} is formed only after a considerable amount of NO has been consumed

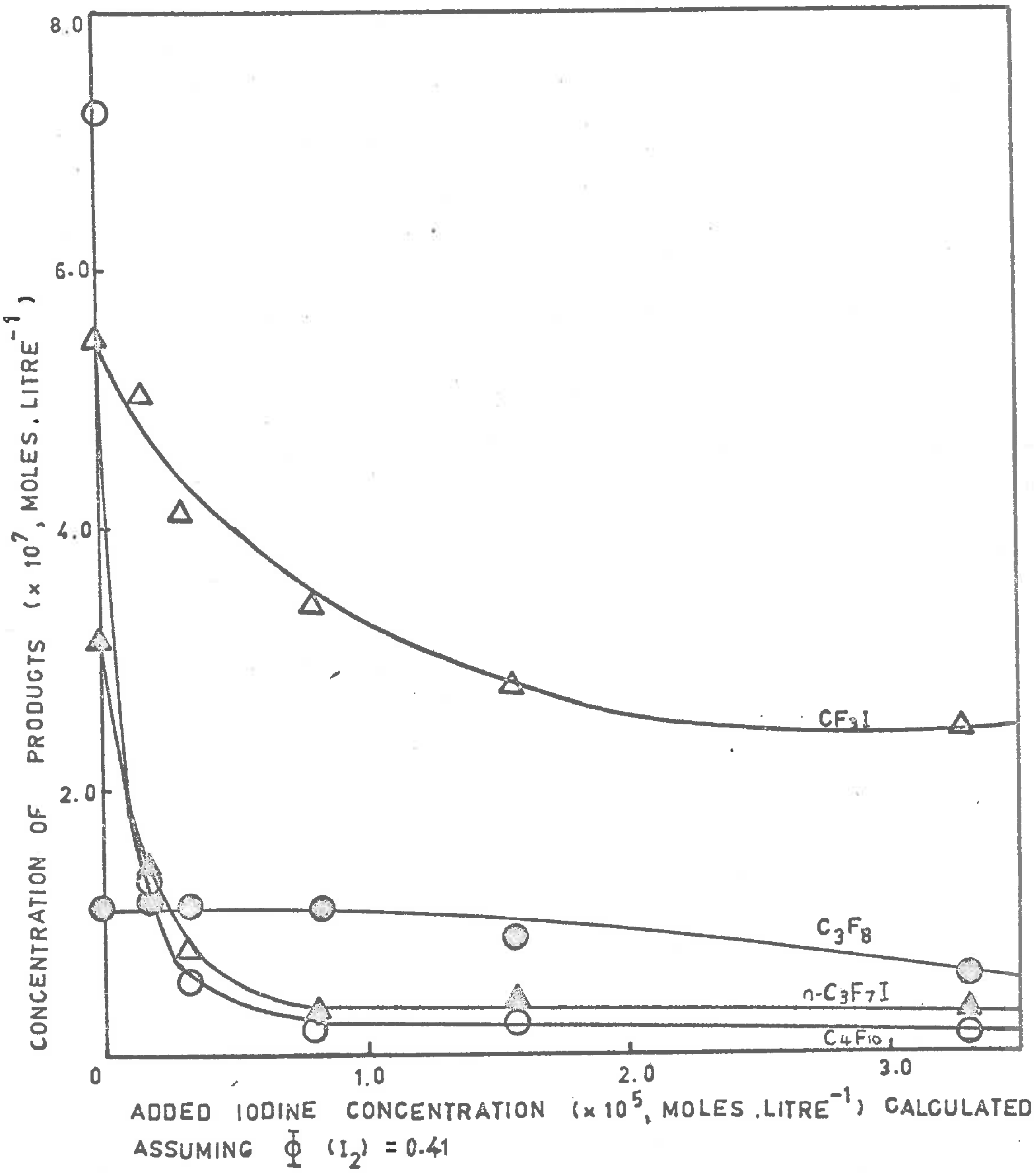


FIG 16

The effect of added Iodine on C_3F_8 , C_4F_{10} , CF_3I and n-C_3F_7I formation during the photolysis of C_2F_5I with unfiltered U.V.

C_2F_5I conc. = $(6.28 \pm 0.05) \times 10^{-4}$ moles litre^{-1}

TABLE VII

Photolysis of C_2F_5I with Very Low Added Concentration of NO with Unfiltered U.V. Light

Time x 10^2 secs	NO x 10^6	C_2F_5NO x 10^7	C_3F_8 x 10^8	C_4F_{10} x 10^8	CF_3I x 10^7
1.20	0.0	0.0	1.80	20.82	0.69
1.20	0.89	0.97	0.0	8.00	2.96
1.20	1.53	2.56	0.0	1.44	4.26
1.20	3.89	7.78	0.0	0.0	6.70
1.20	5.99	30.46	0.0	0.0	7.28
0.30	1.46	3.82	0.0	0.0	1.47

Units: moles litre^{-1}

I (1849 Å) 5.00 x 10^{15} hv/sec

I (2537 Å) 1.49 x 10^{17} hv/sec

Concentration of C_2F_5I (5.52 ± 0.06) x 10^{-4} moles litre^{-1}

TABLE VIII

Photolysis of C_2F_5I with High Concentration of Added NO with Unfiltered U.V. Light. Φ Calculated W.R. to 2537 Å Light Absorbed.

Time $\times 10^{-1}$	C_2F_5I $\times 10^4$	NO $\times 10^3$	C_2F_5NO $\times 10^5$	$\Phi(C_2F_5NO)$
1.01	6.25	6.01	1.18	0.81
2.02	6.35	6.00	1.78	0.61
4.52	6.37	6.08	3.77	0.59
6.01	6.25	5.93	8.22	0.94
6.00	5.87	5.91	9.15	1.07
12.02	6.31	6.13	12.50	.72
				Av. 0.80 ± 0.15

to form C_2F_5NO. Only then is the radical recombination reaction

$$2C_2F_5 \rightarrow C_4F_{10}$$

competitive with C_2F_5NO formation

$$C_2F_5 + NO \rightarrow C_2F_5NO.$$

At high NO pressures ($NO: C_2F_5I \simeq 10:1$) in Table VIII, there is no evidence of hot radical processes. No products such as CF_3I which have their origins from hot radical reaction were detected. This suggests that C_2F_5 radicals formed as a result of 1849 Å light absorption by the C_2F_5I, are thermalised before they can undergo C-C bond fission.

The value of $\phi(C_2F_5NO) \simeq 0.80 \pm 0.15$ calculated on the basis of the 2537 Å absorbed light is in good agreement with the value $\phi(C_2F_5NO) = 0.82 \pm 0.03$ obtained for the low pressure C_2F_5I-NO mixture photolysis with 2537 Å light.

The low value for both wavelength photolyses (i.e. $\phi(C_2F_5NO) < 1.0$) may be due to reactions[3]

$$C_2F_5NO + 2NO \rightarrow C_2F_5 + N_2 + NO_3$$

$$NO_3 + NO \rightarrow 2NO_2$$

$$C_2F_5 + NO_2 \rightarrow C_2F_5NO_2$$

which have already been discussed in section 4.1(c). The $C_2F_5NO_2$

may undergo further breakdown of the perfluoroalkyl chain depending on the nature of the bond between the radical and NO_2.[45] If the bonding is nitrito, i.e. $C_2F_5O.NO$, then this will undergo chain degradation via the alkoxy radical to yield COF_2 and CF_3I. The latter was not detected under experimental conditions, however, this does not eliminate the above sequence of reactions as the degradation may have not stopped at the CF_3I stage.

Before proposing a mechanism to describe the reactions which occur when C_2F_5I is photolysed with unfiltered light some further evidence must be considered.

(g) Photolysis of CF_3COCF_3 – C_2F_5I mixtures.

If CF_3 radicals are the precursors of CF_3I then the CF_3I may be formed in the photolysis of pure C_2F_5I by the following two reactions:

$$CF_3 + I \text{ (or } I_2) \rightarrow CF_3I \text{ (or } + I) \qquad (a)$$

$$CF_3 + C_2F_5I \rightarrow C_2F_5 + CF_3I \qquad (b)$$

Reaction (a) has been studied by Amphlett and Whittle[58] who report the rate constant as 2.6×10^9 litre $mole^{-1}$ sec^{-1} and the activation energy as 0 ± 0.5 kcal.

Reaction (b) on the basis of C–I bond strengths would be exothermic by 2–4 kcal and as $(C_2F_5I) \gg (I)$ or (I_2) during the photolysis, (b) could be very important.

A convenient source of CF_3 radicals is hexafluoroacetone, which has a maximum absorption at 3030 Å.

Two different wavelength bands were used in the photolysis of $CF_3COCF_3 - C_2F_5I$ mixtures. At first the potassium hydrogen phthalate solution filter[49] which transmits a $\lambda > 2900$ Å was used; but when blanks were carried out on C_2F_5I alone, the C_2F_5I was found to decompose. Consequently most of the work was carried out using the Wladimiroff filter[48] which starts to transmit at $\lambda > 3100$ Å. The long wavelength limit of absorption by C_2F_5I is 3270 Å [64] and under the experimental conditions the absorption by C_2F_5I can be ignored. This was confirmed by blank tests.

The products obtained in the photolysis of $CF_3COCF_3 - C_2F_5I$ mixtures are C_2F_6, C_3F_8, C_4F_{10} and CF_3I, and on the basis of product analysis, the following mechanism is proposed:

$$CF_3COCF_3 + h\nu \rightarrow 2CF_3 + CO \qquad I_{abs}$$

$$CF_3 + CF_3 \rightarrow C_2F_6 \qquad k_{1B} \; (1B)$$

$$CF_3 + C_2F_5I \rightarrow CF_3I + C_2F_5 \qquad k_{2B} \; (2B)$$

$$CF_3 + C_2F_5 \rightarrow C_3F_8 \qquad k_{3B} \; (3B)$$

$$C_2F_5 + C_2F_5 \rightarrow C_4F_{10} \qquad k_{4B} \; (4B)$$

A number of workers[65] carrying out abstraction studies involving methyl or perfluoromethyl radicals would have ignored reactions (3B) and (4B) on the basis that these are minor products and under steady state conditions derive a relationship

$$\frac{R_{CF_3I}}{R^{\frac{1}{2}}_{C_2F_6}} = \frac{k_{2B}}{k_{1B}^{\frac{1}{2}}} [C_2F_5I]. \qquad (5B)$$

The plot of rate ratios in (5B) versus $[C_2F_5I]$ should be linear. As figure 17 shows, linearity is obtained in the initial concentration range (up to 3×10^{-5} moles litre^{-1}) (Appendix 5.8). The curvature at higher pressures is difficult to explain unless there are some energy transfer reactions occurring or the importance of reactions (3B) and (4B).

Quick and Whittle[62] studied the abstraction by CF_3 of H and Br from CH_3CF_2Br. They obtained CH_2CF_2 as a product which could only be explained adequately by hexafluoroacetone (HFA) sensitization

$$HFA^* + CH_3CF_2Br \rightarrow HFA + CH_3CF_2Br^*$$

$$CH_3CF_2Br^* \rightarrow CH_2{=}CF_2 + HBr.$$

McIntosh and Porter[67] have confirmed that hexafluoroacetone can be chemically quenched in this way. There is also a quenching of hexafluoroacetone fluorescence which can occur without chemical reaction and is in competition with intersystem crossing to the triplet state so that the yield of products decreases with increasing pressure of the quencher.[67]

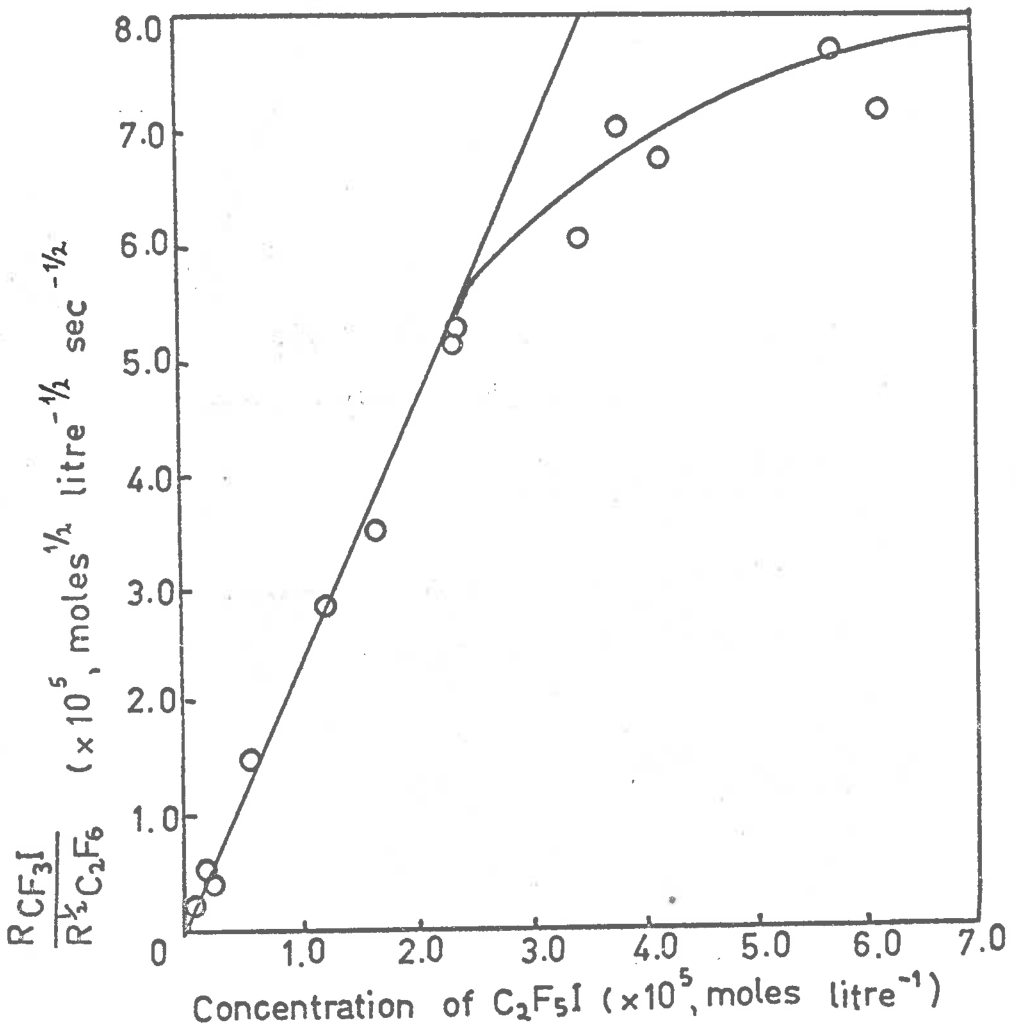


FIG. 17

CF_3COCF_3 - C_2F_5I abstraction studies at $\lambda > 3100$ A°. Dependence of $R(CF_3I)/(R(C_2F_6))^{1/2}$ on C_2F_5I concentration.

If, however, all the reactions are taken into account then the following steady state relationship is deduced:

$$\frac{R_{CF_3I} \cdot R^{\frac{1}{2}}_{C_4F_{10}}}{R_{C_3F_8}} = \frac{k_{2B}\ k^{\frac{1}{2}}_{4B}}{k_{3B}} \cdot [C_2F_5I] \qquad (6B)$$

and when this rate ratio is plotted against $[C_2F_5I]$, a linear relationship is observed over the whole C_2F_5I concentration range used (figure 18, Appendix 5.8). There is considerable scatter of points about the line calculated by least squares, but this is probably due to the method of calculating $R_{C_4F_{10}}$ from the difference, $R_{CF_3I} - R_{C_3F_8}$.

A plot of the above ratio (6B) versus $[C_2F_5I]$ for experiments carried out with light $\lambda > 2900$ Å is only linear in the $[C_2F_5I]$ concentration range below 10^{-5} moles litre^{-1} (figure 19) (see Appendix 5.9). The curvature may be due to the photolysis of C_2F_5I.

The cross combination ratio $R_{C_3F_8}/(R_{C_2F_6}\ R_{C_4F_{10}})^{\frac{1}{2}}$ determined by Gordon[59] in the study of the $CF_3COCF_3 - C_2F_5COC_2F_5$ system was 2.08 ± 0.04. In the present system $(CF_3COCF_3 - C_2F_5I)$ with $\lambda > 3100$ Å the ratio is 2.60 ± 0.70; [for photolysis with $\lambda > 2900$ Å the ratio ranges from 3.5 at low C_2F_5I (5.3×10^{-7} mole litre^{-1}) to 0.26 at high C_2F_5I (6.7×10^{-4} mole litre^{-1})]. In the temperature dependence studies for $\lambda > 3100$ Å, where the cross combination ratio

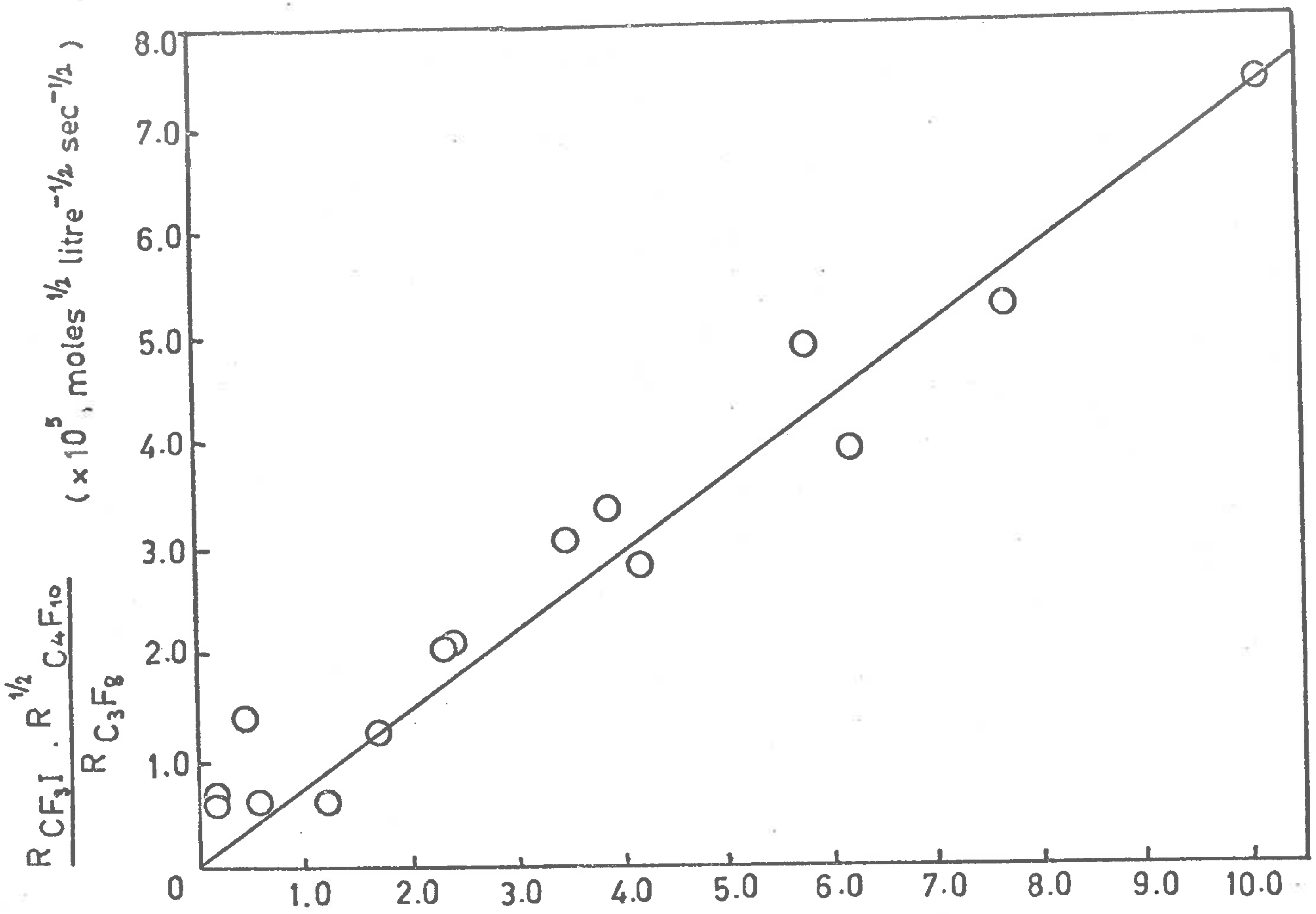


FIG. 18

Dependence of $R^{1/2}_{C_4F_{10}}$ R_{CF_3I} / $R_{C_3F_8}$ on C_2F_5I concentration in CF_3COCF_3 abstraction studies with light > 3100 A°

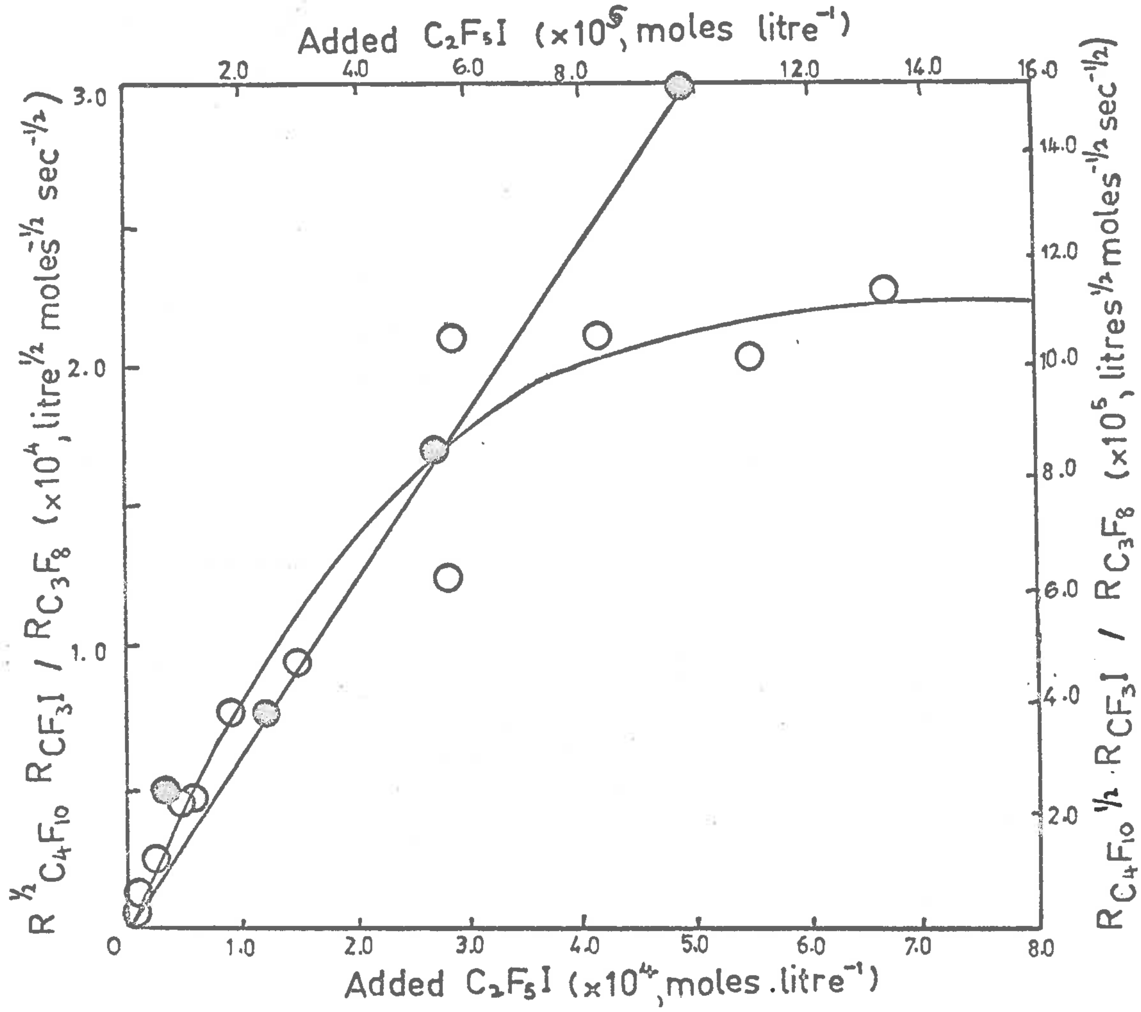


FIG. 19

Dependence of $R^{1/2}_{C_4F_{10}} - R_{CF_3I} / R_{C_3F_8}$ on C_2F_5I concentration in $CF_3COCF_3 - C_2F_5I$ abstraction studies with light $\lambda > 2800$ A°.

● Scales x 10^5, 10^5

○ Scales x 10^4, 10^4

can be calculated for two different CF_3COCF_3 - C_2F_5I composition mixtures the cross combination ratios are found to be 1.85 ± 0.08 and 2.20 ± 0.26.

Figure 20 shows the temperature dependence of function (6B) for two different CF_3COCF_3 - C_2F_5I mixture compositions (see Appendix 5.10). There is curvature in the Arrhenius plot which suggests that energy transfer reactions may be involved.[61,66]

If the activation energy for the abstraction process is that given by the straight lines in figure 20, then the rate constant k_{28} and its activation energy, calculated from both relationships, (5B) and (6B), are given in table IX.

TABLE IX

Activation Energy and Rate Constants for the System CF_3COCF_3 - C_2F_5I, and Reaction $CF_3 + C_2F_5I \rightarrow C_2F_5 + CF_3I$

λ of irrad. Å	k_{28} from (5B) $\times 10^5$	k_{28} from (6B)	E_{obs} from (6B) kcal mole^{-1}
	litre mole^{-1} sec^{-1} (at room temp. $\simeq 20^\circ C$)		
2800		4.52 ± 0.37	
3100	3.26 ± 0.16	2.20 ± 0.16	2.84 ± 0.30

As there is some doubt that the value of k_{28} measured at room temperature is the true rate for the abstraction process due to

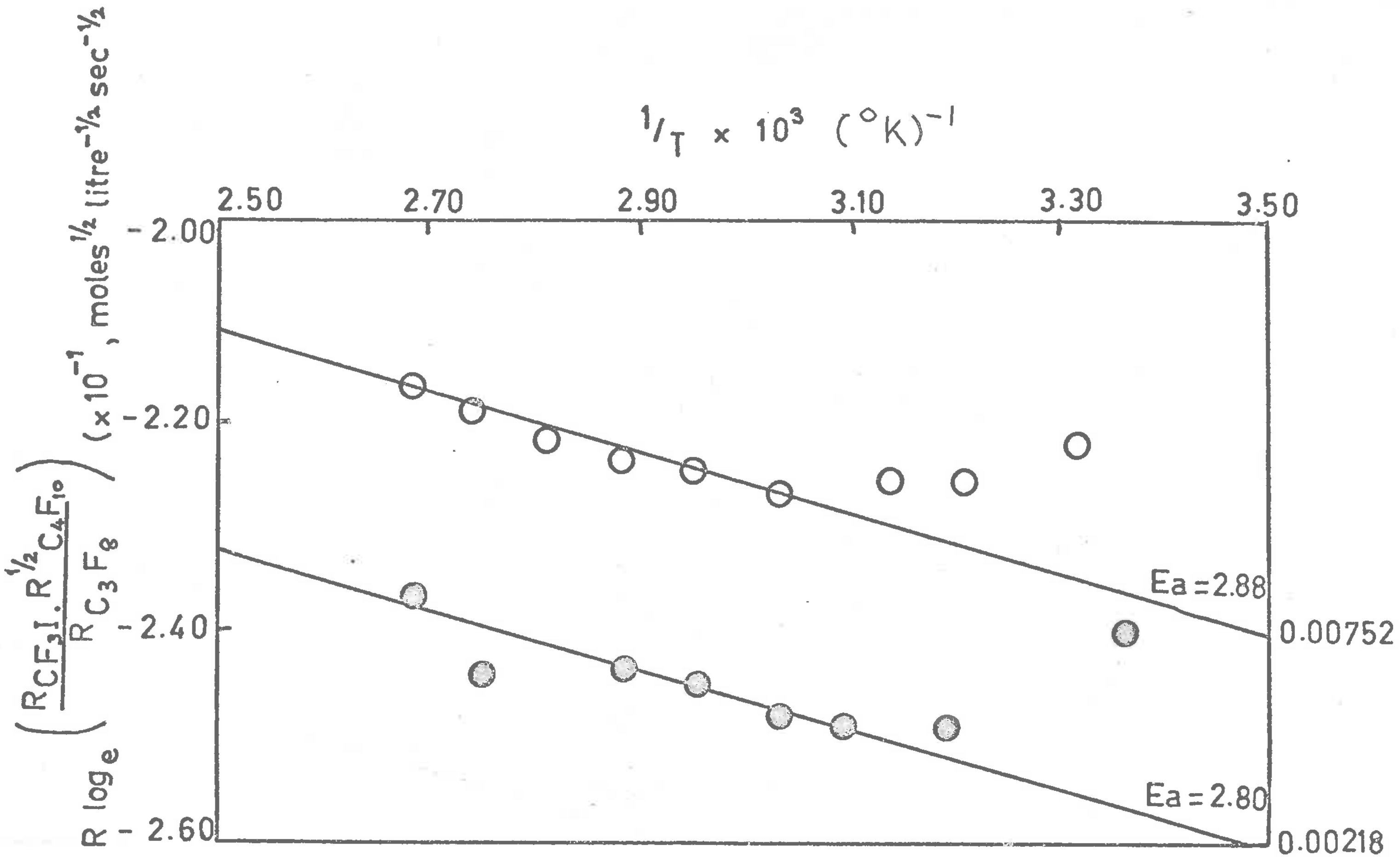


FIG. 20

Temperature dependence of ratio $\left(\frac{R_{CF_3I} . R^{1/2}_{C_4F_{10}}}{R_{C_3F_8}}\right)$ for a CF_3COCF_3 + C_2F_5I mixture photolysed with light > > 3100 A°

possible energy transfer reactions, values of k_{2B} were calculated from the points which lay on the straight line in the Arrhenius plot used for figure 20. The value of k_{2B} calculated in this way is given by

$$k_{2B} = (1.18 \pm 0.03 \times 10^{7}) \exp[-2840 \pm 300/RT] \text{ litre mole}^{-1}\text{sec}^{-1} \qquad (7B)$$

The assumption made is that $E_{obs} = E_{2B}$, assuming the radical recombination processes have zero activation energy.[59,60] A considerably larger activation energy, 11.5 ± 0.3 kcal, was obtained[68] for the abstraction of H-atoms by CF_3 radicals from C_2F_5H even though $D(CF_3-H) - D(C_2F_5H) \simeq 3.5$ kcal.[69]

The value of k_{2B} from (7B) at 20°C is 0.92×10^{5} litre mole^{-1} sec^{-1} which 30-40% of the value obtained at room temperature (table IX) from the $C_2F_5I-CF_3COCF_3$ pressure dependence studies, that is, the sensitization (the energy transfer) reaction is responsible for 60-70% of the CF_3I formed.

(h) <u>Fate of the CF_2 radical.</u>

The only thing that can be said with any certainty about the CF_2 formed in the photolysis of C_2F_5I with unfiltered light is that some of it disappears to form n-C_3F_7I; the remainder can only be accounted for by postulating, from the mass balances, the formation of CF_2I_2.

The species CF_2 may be generated by the thermal or photolytic decomposition of C_2F_4 or CF_2X_2 where X_2 may be hydrogen or a halogen (except F) or a combination of both.[33,70] Its ultraviolet[71,72,73] and infrared[74,75] spectra have been reported. From the flash photolysis[76] studies of C_2F_4 the second order rate constant for the recombination of CF_2 was determined to be

$$k = [(1.3 \times 10^{8})][T/300^{\circ}K]^{\frac{1}{2}} \exp[-1200/RT] \text{ litre mole}^{-1}\text{sec}^{-1}$$

and its reactivity towards olefins and oxygen was found to be surprisingly low.

The reactivity of the CF_2 species is governed by its multiplicity[77-79] that is, whether the electrons are paired (singlet) or unpaired (triplet), and this has been shown to depend on the mode of formation.

The heat of formation, ΔH_f^{o} (CF_2), -39.3 ± 3 kcal mole^{-1} has now been established by pyrolytic,[37] shock tube[38] and mass spectrometric[39] measurements.

Probably the most convenient source of CF_2 is difluorodiazirine, CF_2N_2.[80] The photolysis[81] and pyrolysis[81-83] of CF_2N_2 alone and in the presence of iodine[84] has been studied. In the presence of iodine, CF_2N_2 decomposed to form CF_2I_2 as the major product with a trace amount of $C_2F_4I_2$.[82]

The products of photolysis of a mixture of C_2F_5I and I_2 for six hours (with 2537 Å + 1849 Å light) were dissolved in petroleum ether and the U.V. spectrum of the solution recorded on a Unicam SP700 recording spectrophotometer. The spectrum showed the presence of a peak at 296 ± 2 mμ, which was attributed at the time to CF_2I_2.[85]

Even though the experiment was subsequently repeated several times no 296 mμ peak could be detected again. CF_2I_2 reacts with mercury at room temperature to give C_2F_4,[65] however no peaks due to C_2F_4 were detected on v.p.c. analysis.

Some $C_2F_4I_2$ was prepared by the reaction

$$C_2F_4 + I_2 \rightarrow C_2F_4I_2$$

and identified using ultraviolet spectroscopy, λ_{max} being 282.5 mμ.[89] The $C_2F_4I_2$ was found to be very unstable, and it decomposed within the v.p.c. injection line. Its retention time was considerably higher (~ 36 minutes) than any other product identified from the photolyses, and the peak was very broad (x 5 that for C_2F_5I). This suggested that the compound, if formed, would be very difficult to detect in small quantities under the experimental conditions used.

As CF_2N_2 absorbs light in the region 2900-3600 Å,[81] a number of photochemical experiments could be set up to determine the behaviour of CF_2 in the presence of C_2F_5 and C_2F_5I. The formation of CF_2I_2 is by a straightforward reaction of the type

$$CF_2 + I_2 \rightarrow CF_2I_2$$

or a two-stage one

$$CF_2 + I \rightarrow CF_2I$$

$$CF_2I + I \rightarrow CF_2I_2$$

The latter path may lead in addition to the formation of $C_2F_4I_2$. The formation of n-C_3F_7I may occur by a number of reactions:

$$\text{(i)} \quad \begin{cases} C_2F_5I + CF_2 \rightarrow C_2F_5 + CF_2I \\ CF_2I + C_2F_5 \rightarrow n\text{-}C_3F_7I \end{cases}$$

$$\text{(ii)} \quad \begin{cases} C_2F_5 + CF_2 \rightarrow n\text{-}C_3F_7 \\ n\text{-}C_3F_7 + I \text{ (or } I_2) \rightarrow n\text{-}C_3F_7I \end{cases}$$

Reaction (i) would require an activation energy at least comparable to the CF_3 - C_2F_5I abstraction energy if not larger and the mechanism allows for the formation of CF_2I_2. Reactions of type (i) have been postulated for Cl abstraction from CH_3Cl by CH_2.[86] but CH_2 is much more reactive than CF_2.[70]

The alternative scheme, reaction (ii), would have a zero or a slightly negative activation energy if the addition of CF_3 to C_2F_4 is any indication.[87]

Therefore it is probable that n-C_3F_7I is formed by reaction mechanism (i) in the present system.

(i) Mechanism.

On the basis of the evidence presented so far, the following mechanism is proposed to account for the reactions which occur when C_2F_5I is photolysed with unfiltered light (a mixture of 1849 Å and 2537 Å light).

$$C_2F_5I + \xrightarrow{h\nu\ (1849\ \text{Å})} (C_2F_5)_{E2} + I(^2P_{1/2})$$

$$C_2F_5I + \xrightarrow{h\nu\ (2537\ \text{Å})} (C_2F_5)_{E1} + I(^2P_{1/2})$$

$$(C_2F_5)_{E2} + \left\{\begin{matrix} C_2F_5I \\ \text{or } M \end{matrix}\right\} \rightarrow C_2F_5 + \left\{\begin{matrix} C_2F_5 \\ \text{or } M \end{matrix}\right. + I$$

$$(C_2F_5)_{E2} \rightarrow CF_3 + CF_2$$

$$(C_2F_5)_{E1} + \left\{\begin{matrix} C_2F_5I \\ \text{or } M \end{matrix}\right. \rightarrow C_2F_5 + \left\{\begin{matrix} C_2F_5I \\ \text{or } M \end{matrix}\right.$$

$$I(^2P_{1/2}) + M_1 \rightarrow I(^2P_{3/2}) + M_1$$

$$2I + M_1 \rightarrow I_2 + M_1$$

$$CF_3 + I\ (\text{or } I_2) \rightarrow CF_3I + (\text{or } I)$$

$$CF_3 + C_2F_5I \rightarrow CF_3I + C_2F_5$$

$$CF_3 + C_2F_5 + M \rightarrow C_3F_8 + M$$

$$C_2F_5 + C_2F_5 + M \rightarrow C_4F_{10} + M$$

$$CF_2 + C_2F_5I \rightarrow CF_2I + C_2F_5$$

$$CF_2I + C_2F_5 \rightarrow n\text{-}C_3F_7I$$

$$CF_2I + I\ (\text{or } I_2) \rightarrow CF_2I_2$$

$$CF_2 + I_2 \rightarrow CF_2I_2$$

$$C_2F_5 + I_2\ (\text{or } I) \rightarrow C_2F_5I + I$$

Probably much more information about the CF_2 radicals would have been gained if only 1849 Å light was used. The increase in E_{obs} for CF_3I and C_3F_8 at low pressure is rather puzzling as it is contrary to the present ideas on hot radical-molecule reactions.

5.1 APPENDIX

Time Dependence of I_2 and C_4F_{10} Formation During the Photolysis of C_2F_5I with 2537 Å Light

$^{*}I_o$ (2537 Å) = 1.45×10^{17} hr sec^{-1}

$^{**}I_o$ (2537 Å) = 1.19×10^{17} hr sec^{-1}

Time $\times 10^{2}$	I_2 $\times 10^{7}$	$\Phi(I_2)^{*}$ $\times 10^{3}$	Time $\times 10^{-2}$	C_4F_{10} $\times 10^{6}$	$\Phi(C_4F_{10})^{**}$ $\times 10^{3}$
1.50	5.65	1.48	0.30	0.40	6.52
1.80	6.64	1.48	0.60	0.56	4.96
2.40	8.45	1.39	1.20	0.75	3.02
3.00	11.40	1.52	3.00	1.13	1.81
3.60	13.69	1.51	9.00	1.62	0.87
4.20	14.82	1.40	6.00	1.59	1.25
4.50	14.69	1.28	18.00	2.21	0.60
4.80	16.93	1.39	9.00	1.12	0.59
7.20	18.90	1.03	27.00	1.79	0.32
8.40	20.32	0.95	36.00	2.33	0.31
9.00	18.88	0.83	4.50	0.83	0.96
9.60	21.45	0.88	18.00	1.67	0.43
10.80	27.35	0.99	72.00	2.78	0.18
36.00	35.30	0.38			
27.00	31.79	0.46			
54.00	38.80	0.28			
72.00	46.00	0.25			

5.2 APPENDIX

Pressure Dependence of I_2 and C_4F_{10} Formation During the Photolysis of C_2F_5I with 2537 Å Light

$^*I_0$ (2537 Å) = 1.45 x 10^{17} hr/sec; $^{**}I_0$ (2537 Å) = 1.19 x 10^{17} hr/sec.

C_2F_5I x 10^3	I_2 x 10^7	$\Phi(I_2)^*$ x 10^3	C_2F_5I x 10^3	C_4F_{10} x 10^7	$\Phi(C_4F_{10})^{**}$ x 10^3
0.03	0.56	1.34	6.18	13.70	1.46
0.05	0.71	1.25	11.90	13.02	1.41
0.12	2.42	1.36	8.71	11.68	1.26
0.13	1.83	1.10	3.89	7.68	0.84
0.31	3.67	1.01	3.04	5.22	0.57
0.41	4.08	0.92	1.53	5.04	0.62
1.06	5.92	0.73	2.70	6.63	0.74
1.10	5.07	0.61	1.95	4.87	0.56
1.32	7.33	0.82	0.91	3.62	0.56
1.67	7.90	0.82	1.12	4.77	0.66
1.70	7.90	0.82	0.64	2.45	0.45
1.77	7.60	0.78	0.49	2.00	0.45
1.99	8.74	0.87	0.36	1.59	0.45
2.11	9.02	0.89	0.27	1.38	0.48
2.35	9.58	0.94	10.18	16.87	1.86
2.55	10.46	1.01	5.48	11.19	1.21
2.55	10.59	1.01	6.81	12.37	1.33
2.98	10.46	0.99	7.70	12.41	1.34
3.26	11.30	1.07	9.20	13.31	1.44

(contd.)

5.2 APPENDIX (contd.)

C_2F_5I x 10^3	I_2 x 10^7	$\phi(I_2)^*$ x 10^3	C_2F_5I x 10^3	C_4F_{10} x 10^7	$\phi(C_4F_{10})^{**}$ x 10^3
3.52	11.72	1.12	5.98	10.46	1.12
4.12	12.16	1.14	7.28	9.50	1.00
4.12	11.02	1.03	5.33	6.72	0.72
5.11	13.00	1.22			
5.11	13.00	1.22			
5.48	12.72	1.19			
5.93	12.72	1.19			
5.96	14.13	1.19			
6.18	14.13	1.32			
6.22	12.85	1.32			
6.46	15.11	1.22			
6.63	13.84	1.48			
7.05	15.28	1.29			
7.51	15.55	1.43			
8.52	14.40	1.45			
8.68	14.40	1.35			
9.43	15.27	1.43			
9.52	14.28	1.35			
11.09	14.83	1.40			

[*] The iodine concentration measured independently of other products by spectrophotometric technique. Irradiation time of 30 mins used, also I_o (2537 Å) = 1.63 x 10^{17} hv/sec, I_o (1849 Å) = 5.48 x 10^{17} hv/sec.

[**] Units of concentration are moles litre^{-1}. Also I_o (2537 Å) = 1.49 x 10^{17} hv/sec, I_o (1849 Å) = 5.00 x 10^{15} hv/sec.

5.3 APPENDIX

Pressure Dependence of Product Formation During the Photolysis of C_2F_5I with Unfiltered Light

Irradiation Time 420.0 seconds

$C_2F_5I^{*}$ x 10^3	I_2^{*} x 10^7	$C_3F_8^{**}$ x 10^3	$C_3F_8^{**}$ x 10^6	$C_4F_{10}^{**}$ x 10^6	CF_3I^{**} x 10^6	$n\text{-}C_3F_7I^{**}$ x 10^6
0.35	8.46	0.66	0.27	0.70	0.53	0.35
0.44	8.46	1.12	0.54	0.76	0.82	0.36
0.87	7.90	0.32	0.09_2	0.44	0.31	0.14
1.06	5.65	1.29	0.67	0.96	0.97	0.38
1.47	6.48	4.88	2.35	2.90	2.50	0.66
1.82	6.77	10.17	2.35	3.53	2.73	0.49
3.00	6.48	6.10	1.84	2.63	2.20	0.57
4.29	7.60	7.27	2.28	3.00	2.34	0.37
7.22	8.20	3.06	1.55	1.91	1.69	0.36
8.80	8.20	16.82	1.76	4.55	3.55	0.68
9.16	7.60	1.59	0.95	1.16	1.23	0.56
11.89	8.75	7.81	0.11	3.65	3.40	0.32
13.92	8.18	12.66	1.04	4.20	4.00	0.94
		2.61	0.05_1	1.63	1.58	0.35
		6.02	0.12	3.25	3.39	0.72
		10.18	0.14	4.66	4.18	0.82
		3.72	0.07_5	2.25	1.90	0.50
		1.86	0.07_5	1.63	1.35	0.23
		4.84	0.10_9	2.90	2.82	0.37

* Low pressure 1.06 cm ($6.30 \pm 0.08 \times 10^{-4}$) I_o(2537 Å) 1.49×10^{17} hν/sec

** High pressure 10.3 cm ($6.05 \pm 0.06 \times 10^{-3}$) I_o(1849 Å) 5.00×10^{17} hν/sec

*** I_2 conc. measured by spectrophotometric method.

Other photolysis products not analysed for

I_o (2537 Å) 1.63×10^{17} hν/sec

I_o (1849 Å) 5.48×10^{17} hν/sec

All concentrations given in moles litre^{-1}.

5.4 APPENDIX

Effect of Irradiation Time on Products During the Photolysis of C_2F_5I with Unfiltered U.V.

Time $\times 10^3$ secs.	I_2*** $\times 10^7$	Time $\times 10^{-3}$ secs.	C_3F_8 $\times 10^7$	C_4F_{10} $\times 10^7$	CF_3I $\times 10^7$	n-C_3F_7I $\times 10^7$
HIGH PRESSURE		LOW PRESSURE*				
0.09	1.27	0.09	0.45	2.38	0.95	0.86
0.21	2.12	0.18	0.25	2.95	1.35	0.75
0.45	2.84	0.27	0.74	5.00	2.91	1.85
0.66	3.81	0.36	0.76	4.59	2.70	1.60
0.90	5.21	0.90	1.90	7.93	7.64	4.80
0.90	4.38	1.80	3.80	10.32	12.03	9.50
1.32	5.79	2.70	4.70	11.90	15.77	12.70
1.80	6.91	5.40	22.50	39.50	51.00	29.80
2.70	8.45	HIGH PRESSURE**	$\times 10^6$	$\times 10^6$	$\times 10^6$	$\times 10^6$
3.60	9.85					
4.50	11.85	0.045	0.12	0.69	0.20	0.21
7.20	14.69	0.09	0.22	1.17	0.46	0.26
10.80	16.80	0.18	0.48	1.84	1.11	0.60
		0.36	0.99	3.02	2.27	0.59
		0.90	4.70	10.70	7.25	1.20
		1.80	9.40	17.00	13.00	2.93
		2.70	8.37	28.50	12.48	3.55
		5.40	14.00	40.00	20.77	7.35

3.5 APPENDIX

Temperature Dependence of C_2F_5I Photolysis with Unfiltered Light at Various C_2F_5I Pressures

Irradiation Time 3.600 seconds

$I_o(1849) = 6.8 \times 10^{14}$ hv/sec $I_o(2537) = 2.03 \times 10^{16}$ hv/sec

	C_2F_5I $\times 10^4$	Temp. °C	C_3F_8 $\times 10^7$	C_4F_{10} $\times 10^7$	CF_3I $\times 10^7$	$n\text{-}C_3F_7I$ $\times 10^7$
	6.18	17.3	1.04	4.05	2.60	1.92
	"	39.4	2.21	4.57	4.52	2.69
	"	46.7	2.66	4.63	5.20	3.15
	"	56.3	2.81	6.30	5.90	4.30
1.0 cm	"	73.8	5.00	5.50	7.95	5.39
	"	82.4	5.33	5.30	9.48	6.43
	"	90.6	7.35	5.70	11.68	8.30
	"	98.2	8.75	5.24	13.76	9.95
	"	109.9	10.10	5.00	14.75	11.00
	"	119.0	12.70	4.67	18.70	12.22
	$\times 10^3$		$\times 10^6$	$\times 10^6$	$\times 10^6$	$\times 10^6$
	6.03	16.2	1.10	1.80	1.31	0.34
	"	39.6	2.00	2.69	2.43	0.58
	"	47.1	1.90	3.00	2.73	0.60
	"	57.7	2.46	2.92	2.96	0.93
	"	65.3	2.86	3.55	3.78	1.20
10.0 cm	"	73.7	3.25	3.68	4.85	1.69
	"	82.9	2.45	3.55	4.00	1.79
	"	90.9	3.39	3.89	5.03	2.51
	"	98.7	3.93	3.68	5.64	3.52
	"	110.9	4.60	3.82	6.70	3.69
	"	119.8	5.21	3.62	7.14	4.05

(contd.)

5.5 APPENDIX (contd.)

	C_2F_5I x 10^3	Temp. °C	C_3F_8 x 10^6	C_4F_{10} x 10^6	CF_3I x 10^6	n-C_3F_7I x 10^6
	11.76	46.8	2.56	5.26	3.12	0.79
	"	65.5	3.02	6.50	4.50	1.78
20.0 cm	"	82.3	3.78	8.26	5.89	2.70
	"	98.7	4.69	6.73	7.16	4.11
	"	119.1	4.49	6.06	7.36	4.50

5.6 APPENDIX

Effect of Added Argon During the Photolysis of Low Pressure C_2F_5I with Unfiltered U.V.

Argon x 10^3	C_3F_8 x 10^8	C_4F_{10} x 10^8	CF_3I x 10^9	n-C_3F_7I x 10^8
0	1.65	6.32	10.13	2.80
0.81	2.10	6.60	9.40	2.27
1.47	2.33	7.68	9.40	2.63
2.99	1.64	7.41	8.13	2.27
4.61	1.57	6.80	7.60	1.80
6.10	1.35	7.65	6.64	2.12
8.75	0.64	3.70	3.88	1.05
11.23	0.40	4.00	4.27	0.93
15.41	0.61	3.78	3.78	1.21

Units: moles $litre^{-1}$

Irradiation time 450 seconds

C_2F_5I concentration (6.30 ± 0.06) moles $litre^{-1}$

I_o (2537 Å) 1.49×10^{17} hν/sec

I_o (1849 Å) 5.0×10^{15} hν/sec

5.7 APPENDIX

The Effect of Added Iodine on the Photolysis of Low Pressure C_2F_5I with Unfiltered U.V.

Added I_2 x 10^5	C_3F_8 x 10^8	C_4F_{10} x 10^8	CF_3I x 10^7	n-C_3F_7I x 10^8
0	11.10	72.33	5.53	31.35
0.18	11.80	12.90	5.03	14.00
0.31	11.00	5.09	4.15	8.00
0.84	10.90	2.36	3.44	2.79
1.59	8.72	1.96	2.79	4.50
3.33	5.87	1.32	2.48	3.18

Units: moles $litre^{-1}$

I_o (2537 Å) 1.47×10^{17} hv/sec
I_o (1849 Å) 5.0×10^{15} hv/sec
Irradiation time 450 seconds

Note: The added iodine calculated on the basis of the quantum yield of I_2 during C_2F_5I-NO photolysis being 0.41.

5.8 APPENDIX

Photolysis of $C_2F_5I-CF_3COCF_3$ Mixture with Light $\lambda > 3100$ Å for 2700 Seconds

C_2F_5I x 10^6	C_2F_6 x 10^7	C_3F_8 x 10^7	C_4F_{10}* x 10^7	CF_3I x 10^7	A x 10^5	B x 10^5	C
0.53	18.22	2.98	-	1.80	0.26	-	-
1.53	21.24	5.17	0.48	4.60	0.56	0.74	-
1.70	18.80	4.67	0.41	3.12	0.45	0.77	3.61
4.93	12.73	9.00	1.67	12.80	2.40	1.53	1.95
5.93	11.00	8.90	0.50	8.43	1.55	0.67	2.40
9.80	8.32	12.70	8.23	33.10	6.13	5.65	1.50
12.56	6.32	11.90	0.50	11.82	2.89	0.66	-
23.25	3.24	10.80	2.52	15.20	5.23	2.10	3.60
24.54	3.12	10.51	2.63	15.71	5.34	2.11	3.40
35.34	2.15	7.76	3.59	14.96	6.16	3.11	2.70
42.91	1.82	8.45	3.28	14.37	6.79	2.86	3.35
58.41	0.81	4.32	3.87	12.15	7.77	4.91	2.35
62.28	0.93	4.27	3.28	10.68	7.19	3.97	2.43
77.60	0.78	2.90	3.33	9.62	6.62	5.38	1.75
101.8	0.27	1.90	3.67	9.34	10.63	7.50	1.97
38.62	1.27	6.05	3.78	14.18	7.14	3.45	2.75

$A = R_{CF_3I}/R_{C_2F_6}^{\frac{1}{2}}$ litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$sec$^{-\frac{1}{2}}$

$B = R_{CF_3I}\,R_{C_4F_{10}}^{\frac{1}{2}}/R_{C_3F_8}$ litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$sec$^{-\frac{1}{2}}$

$C = R_{C_3F_8}/R_{C_2F_6}^{\frac{1}{2}}\,R_{C_4F_{10}}^{\frac{1}{2}}$

* $C_4F_{10} = CF_3I - C_3F_8$

Units: moles litre^{-1}

5.9 APPENDIX

Variation of C_2F_5I Pressure During Photolysis of C_2F_5I-CF_3COCF_3 Mixture at λ > 2900 Å for 1800 Seconds

C_2F_5I x 10^5	C_2F_6 x 10^7	C_3F_8 x 10^7	C_4F_{10} x 10^7	CF_3I x 10^7	A x 10^5	B x 10^5	C
0.053	10.20	2.42	0.22	1.35	0.32	0.25	1.39
0.24	12.28	10.63	0.71	6.53	1.39	0.39	3.30
0.55	8.40	17.27	2.41	12.38	3.17	0.85	3.71
0.97	4.70	17.24	5.03	14.45	5.29	1.45	3.65
1.73	3.82	27.09	13.35	25.69	9.81	2.59	3.79
4.56	1.60	15.16	18.00	24.27	14.24	4.72	2.78
5.88	0.74	5.52	7.48	13.20	10.75	4.71	2.46
8.99	0.69	5.31	11.98	15.24	12.20	7.67	1.52
14.52	1.01	3.08	10.36	12.67	10.82	9.43	1.05
28.49	0.96	1.24	7.61	9.25	10.30	16.92	0.54
41.21	0.75	0.78	7.24	8.36	7.17	21.38	0.33
55.32	0.97	0.62	5.98	6.02	5.58	20.40	0.25
67.42	0.90	0.73	6.61	9.18	7.82	23.00	0.35

Refer to Appendix 5.8 for identification of A, B, and C.

Concentration units: moles litre^{-1}

5.10 APPENDIX

Temperature Dependence of CF_3COCF_3-C_2F_5I Mixture Photolysed at $\lambda > 3400$ Å for 7200.0 seconds

Temp. °C	C_2F_6 $\times 10^7$	C_3F_8 $\times 10^7$	C_4F_{10} $\times 10^7$	CF_3I $\times 10^7$	A $\times 10^5$	B $\times 10^5$	C
SERIES A							
26.3	2.40	5.77	5.42	8.09	2.30	0.87	1.84
38.6	5.65	11.70	6.62	14.61	2.23	0.73	1.91
46.4	10.90	17.80	7.54	20.58	2.37	0.73	2.00
56.3	13.60	19.63	7.50	23.03	2.25	0.77	2.02
65.10	25.90	26.54	8.45	30.50	2.23	0.97	1.82
73.5	23.61	25.25	8.34	30.00	2.34	1.06	1.81
82.4	26.90	27.80	9.41	35.56	2.57	1.34	1.74
91.2	37.70	44.26	13.50	50.06	3.13	1.22	1.86
99.4	33.89	43.23	16.61	52.48	3.55	1.38	1.82
28.5	2.00	5.58	5.50	8.96	2.37	1.13	1.65

(contd.)

5.10 APPENDIX (contd.)

Temp. °C	C_2F_6 x 10^7	C_3F_8 x 10^7	C_4F_{10} x 10^7	CF_3I x 10^7	A x 10^5	B x 10^5	C
SERIES B							
24.0	8.31	6.57	1.88	6.30	0.93	0.57	1.64
40.1	4.17	7.79	1.26	5.86	1.27	0.34	3.20
49.8	17.43	10.62	1.26	8.64	0.91	0.37	2.20
56.3	36.10	14.19	1.54	11.55	0.86	0.39	2.00
65.1	46.08	17.55	2.48	14.63	0.89	0.49	1.85
73.5	41.88	18.02	2.12	12.96	0.86	0.45	1.90
82.0	42.53	16.10	1.14	12.79	0.87	0.35	2.20
91.2	37.08	15.53	1.46	12.97	0.92	0.44	2.10
99.4	43.57	22.30	2.15	21.45	1.38	0.66	2.20
25.0	5.00	6.87	2.16	6.55	1.25	0.61	2.12

SERIES A $\frac{C_2F_5I}{CF_3COCF_3}$ $\frac{1.75 \times 10^{-5}\ \text{moles litre}^{-1}}{2.35 \times 10^{-3}\ \text{moles litre}^{-1}}$ 0.00752

SERIES B $\frac{C_2F_5I}{CF_3COCF_3}$ $\frac{0.51 \times 10^{-5}\ \text{moles litre}^{-1}}{2.35 \times 10^{-3}\ \text{moles litre}^{-1}}$ 0.00218

All concentrations in moles litre^{-1}

Rates moles litre^{-1} sec^{-1}

Refer to Appendix 5.8 for identification of A, B, and C

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