KINETICS AND MECHANISM OF SOME GAS PHASE REACTIONS

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Summary

This thesis is divided into three sections. The first section describes the irradiation by ultraviolet light of hydrogen sulphide in the presence of C_2-olefins, the second is concerned with the kinetics of the thermal decomposition of trifluoroacetaldehyde, and the third, with the rate of abstraction of hydrogen from hydrogen sulphide by trifluoromethyl radicals.

(1) The Photochemical Addition of Hydrogen Sulphide to C_2 Olefins.

Irradiation by ultraviolet light of mixtures of hydrogen sulphide and ethylene, 1,1-difluoroethylene, or tetrafluoroethylene, yields mainly addition products RSH and R_2S. The secondary products from the reaction of ethylene with hydrogen sulphide are hydrogen, ethane, diethyl disulphide, and sulphur. In order to account for their formation, a free radical chain mechanism is postulated in which the hydrosulphide radical and hydrogen atom, formed by the photolysis of hydrogen sulphide, add to the C=C of the olefin. The main chain propagator is the hydrosulphide radical.

(2) The Kinetics of the Thermal Decomposition of Trifluoroacetaldehyde.

The thermal decomposition of trifluoroacetaldehyde at pressures up to 180 mm. and temperatures between 471 and 519°, yields carbon monoxide and trifluoromethane in accordance with the stoicheiometry:

$$CF_3CHO = CF_3H + CO$$

Small quantities of hexafluoroethane and hydrogen are also formed. The experimental rate equation is of the form,

$$R = k[CF_3CHO]^{\frac{3}{2}}$$

where

$$k = 10^{12.2} \exp(-49{,}000/RT) \ l.^{\frac{1}{2}}mole^{-\frac{1}{2}}sec.^{-1}$$

Inert gases, namely carbon monoxide and carbon dioxide, increase the rate of decomposition, and the rate equation is of the form:

$$R = \left\{k'[CF_3CHO]^3 + k''[CF_3CHO]^{2.2}[X]\right\}^{\frac{1}{2}}$$

A radical chain mechanism is proposed which predicts the form of the experimental rate equations. The rate of formation of hexafluoroethane is found to be dependent on $[CF_3CHO]^2$, and therefore initiation is postulated to occur by a second order energy transfer process, and termination is considered to involve the third order recombination of trifluoromethyl radicals.

(3) The Kinetics of the Abstraction of Hydrogen Atoms from Hydrogen Sulphide by Trifluoromethyl Radicals.

Trifluoromethyl radicals, produced by the photolysis of hexafluoroacetone, abstract hydrogen from hydrogen sulphide.

$$CF_3 + H_2S \rightarrow CF_3H + SH$$

The rate constant of the abstraction, measured by comparing its rate with that of the recombination of trifluoromethyl radicals, is given by:

$$k = 10^{11.65 \pm 0.16} \exp[-(3880 \pm 260)/RT] \ cc.mole^{-1}sec.^{-1}$$

A value of 10^{-3} is calculated for the steric factor.

To the best of the author's knowledge, this thesis contains no material submitted for a degree or diploma in any University, or any material previously published or written by any other person, except where due reference is made in the text.

Department of Physical and Inorganic Chemistry
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N.L. Arthur

SECTION I

THE PHOTOADDITION OF HYDROGEN SULPHIDE TO SOME C_2-OLEFINS.

Chapter 1

Introduction

In order to discuss the photoaddition of hydrogen sulphide to olefins it is necessary to consider the mechanism of photochemical decomposition of hydrogen sulphide. A survey of the literature on this subject is therefore presented, and this is followed by a review of free radical addition of hydrogen sulphide to olefins.

The Photolysis of Hydrogen Sulphide

The photochemical decomposition of gaseous hydrogen sulphide has been the subject of several investigations. In each case the products of photolysis were found to be hydrogen and sulphur. Goodeve and Stein[1] (1931) obtained the absorption spectrum of hydrogen sulphide, and found a continuum beginning at 2800 Å. Because the convergence limit was in agreement with the value of the heat of dissociation into normal hydrogen and ^1D sulphur atoms, Goodeve and Stein concluded that the primary process was

$$H_2S \rightarrow H_2 + S(^1D) \qquad \Delta H = 105 \text{ kcal./mole.}$$

Herzberg[2], however, contended that both hydrogen atoms should not be split off in a single process because they are not bound together in the original molecule. He proposed that dissociation of hydrogen sulphide occurred by

$$H_2S \xrightarrow{h\nu} H + SH$$

$$H + H_2S \rightarrow H_2 + SH$$

$$SH + SH \rightarrow H_2S + S$$

Stein[3] (1933) photolysed hydrogen sulphide with approximately monochromatic light of wavelength 2050 Å, and measured the small quantities of hydrogen formed. The quantum yield was found to increase from 2.0 at 75 mm. of hydrogen sulphide to 3.5 at 1380 mm. These high values Stein attributed to short chains initiated by excited sulphur atoms or molecules.

The photolysis of hydrogen sulphide was compared with that of hydrogen bromide at 2080 Å by Forbes, Cline and Bradshaw[4] (1938). On the assumption that the quantum yield for hydrogen formation from hydrogen bromide was unity, that for hydrogen sulphide was calculated to be 1.02 ± 0.05. The quantum yield was independent of pressure between 8 and 1400 mm., and of light intensity over a fourteen fold range. Forbes, Cline and Bradshaw considered that Herzberg's mechanism explained their results more satisfactorily than that of Goodeve and Stein.

Using the technique of flash photolysis, Porter[5] (1950) and Ramsay[6] (1952) detected hydrosulphide radicals in the photolysis of hydrogen sulphide. These studies also revealed the presence of strong S_2 bands, and this was regarded as evidence that S_2 was produced in one step and not by the combination of sulphur atoms.

In order to decide between the results of Stein and Forbes et al., Darwent and Roberts[7] (1953) re-examined the photolysis of hydrogen sulphide at pressures between 8 and 550 mm. and at temperatures between 27 and 650°, using the narrow cadmium line (wavelength 2288 Å) and the broad mercury band (about 2550 Å). As in the investigation of Forbes et al., the quantum yield was calculated from a comparison of the rates of hydrogen production in the photolyses of hydrogen bromide and hydrogen sulphide. At room temperature the quantum yield was found to increase with pressure from 1.09 at 30 mm. to 1.26 at 200 mm., above which pressure there was no further increase. Temperature had little effect on the quantum yield at 2550 Å but there was a marked increase in the rate of hydrogen production between 500 and 650° at 2288 Å. Darwent and Roberts argued that all available evidence suggested that hydrogen sulphide decomposes initially into hydrogen atoms and hydrosulphide radicals,

$$H_2S \xrightarrow{h\nu} H + SH \qquad [1]$$

and that the most probable fate of the hydrogen atoms was to react with hydrogen sulphide, which was present in great excess.

$$H + H_2S \rightarrow H_2 + SH \qquad [2]$$

If reactions [1] and [2] were rapid and no other fate was possible for hydrogen atoms, then provided that radicals were removed by the process

$$SH + SH \rightarrow H_2S + S \qquad [12]$$

the quantum yield of hydrogen would be unity and independent of pressure. To account for the rise of the quantum yield above unity they postulated the reaction

$$SH + SH \rightarrow H_2 + S_2 \qquad [13]$$

which was shown to be feasible energetically while agreeing qualitatively with the spectroscopic studies of Porter and Ramsay.

The quantum yield of hydrogen, Φ, predicted by these reactions is given by

$$\Phi = 1 + \frac{k_{13}}{k_{12} + k_{13}}$$

This relation indicates that Φ should be greater than unity and independent of pressure. Experimentally it was found that at pressures above 200 mm. Φ remained constant at 1.26. The small effect of temperature on Φ at 2550 Å suggested that reactions [12] and [13] required little activation energy, in agreement with the proposed mechanism since both [12] and [13] are radical combination reactions. The rise in quantum yield at high temperatures with the higher energy radiation (2288 Å) was ascribed to the formation of vibrationally excited SH radicals. Darwent and Roberts considered that these radicals decomposed yielding hydrogen atoms which formed more hydrogen via reaction [2].

The Addition of Hydrogen Sulphide to Olefins

The first successful additions of hydrogen sulphide to olefins, achieved at temperatures between 200 and 300°, in the presence of catalysts, and at pressures greater than one atmosphere, yielded mixtures of thiols and sulphides.[8,9] The thiols were "normal" addition products, the hydrosulphide group adding to the carbon atom bonded to the lesser number of hydrogen atoms, in accordance with the arbitrary extension of Markownikoff's rule for the addition of halogen acids to double bonds.

Vaughan and Rust[10] (1942) showed that the photoaddition of hydrogen sulphide to olefinic bonds could easily be effected by ultraviolet radiation. Reactions were carried out in the liquid phase in quartz tubes at 0° and at -78° with the full radiation of a quartz mercury arc lamp. Propene, 1-butene, 2-chlorobut-2-ene, and several allyl derivatives, all yielded mixtures of thiols and sulphides, the hydrosulphide group adding exclusively to the carbon atom bonded to the greater number of hydrogen atoms. The gas phase addition of hydrogen sulphide to 1-butene in a Pyrex vessel was very slow, but addition of acetone as a photosensitiser increased the rate, as did a change to a silica vessel.

Vaughan and Rust considered the hydrosulphide radical to be the initiator in the addition of hydrogen sulphide to π-bond systems, and proposed the following radical chain mechanism to account for the formation of the thiol:

$$H_2S \xrightarrow{h\nu} \cdot H + \cdot SH \qquad [1]$$

$$\cdot SH + RCH{=}CH_2 \rightarrow R\dot{C}HCH_2SH \qquad [5]$$

$$R\dot{C}HCH_2SH + H_2S \rightarrow RCH_2CH_2SH + \cdot SH \qquad [6]$$

It was thought that the di-normal sulphide resulted from combination of the thiol and olefin,

$$RCH_2CH_2SH + RCH{=}CH_2 \rightarrow RCH_2CH_2SCH_2CH_2R$$

and that the chain length under the prevailing conditions precluded detection of products from secondary reactions.

The work reported in this thesis was undertaken in an attempt to elucidate the complete reaction mechanism of the gas phase photoaddition of hydrogen sulphide to ethylene, 1,1-difluoroethylene, and tetrafluoroethylene. It was found that the SH radical from photolysis of hydrogen sulphide added to each olefin forming a thiol and a sulphide. Examination of the secondary products enabled a free radical mechanism to be postulated. The results of this investigation were published in 1962.[11]

Harris and Stacey[12] (1963) surveyed the X-ray initiated, liquid phase addition of hydrogen sulphide to the fluoroolefins: tetrafluoroethylene, chlorotrifluoroethylene, trifluoroethylene, 1,1-difluoroethylene, bromotrifluoroethylene, vinyl fluoride, and trifluorovinyl methyl ether. The reactions were carried out at room temperature with radiation dose rates of 4,000 to 15,000 rads./min. The products were characterised by chemical analysis and proton nuclear magnetic resonance spectroscopy. It was found that the orientation of the product thiols was consistent with the radical addition of thiols[13] to these olefins; in each case the adding radical (SH or RS) attacked the carbon indicated by the arrow.

$$\mathrm{CF{=}\underset{\uparrow}{C}F_2} \quad \mathrm{CF_2{=}\underset{\uparrow}{C}FH} \quad \mathrm{CF_2{=}\underset{\uparrow}{C}H_2} \quad \mathrm{CHF{=}\underset{\uparrow}{C}H_2} \quad \mathrm{CH_3COCF{=}\underset{\uparrow}{C}F_2}$$

Harris and Stacey considered that their reactions proceeded by a free radical chain mechanism of the kind proposed by Vaughan and Rust and ourselves.

The γ-radiation induced addition of hydrogen sulphide to propylene, iso-, cis-, and trans-butylene, in the liquid phase, was studied by Sugimoto and Ando[14,15] (1963). Their experiments were conducted at room temperature with radiation dose rates of 95, 183 and 467 rads./min. Propylene yielded propanethiol and di-n-propyl sulphide, and the butylenes yielded, in each case, a butanethiol and a dibutyl sulphide. The formation of propanethiol was shown to be favoured by a large concentration of hydrogen sulphide and short irradiation times, while smaller concentrations of hydrogen sulphide and long irradiation times favoured the formation of the sulphide.

Again Sugimoto and Ando explained their findings in terms of the established free radical chain mechanism, in which the thiol was formed by addition to the olefin of the SH radical resulting from radiolysis of hydrogen sulphide. The large chain length, indicated by high G-values, prevented ready detection of the expected products, propane and hydrogen.

The free radical addition of hydrogen sulphide to allene has been reported by Griesbaum et al.[16] (1964). Liquid phase mixtures of allene and hydrogen sulphide were irradiated with ultraviolet light at temperatures around -80°, and in the presence and absence of initiators. The main products were 3-propenethiol and 1,3-propanedithiol formed by attack of the SH radical from hydrogen sulphide on the terminal allene carbon atoms.

Chapter 2

Experimental and Results

Materials

Hydrogen sulphide, generated from ferrous sulphide and sulphuric acid, was fractionated through traps at -78°, -96°, -145° and -196°, the fraction collecting at -145° being retained.

Ethylene, obtained from a cylinder (C.I.G. brand), was fractionated as above, the last fraction being retained.

Tetrafluoroethylene was prepared by pyrolysis of Teflon and fractionated as for ethylene, the fraction condensing at -196° being retained.

1,1-Difluoroethylene, obtained from a cylinder supplied by Dupont de Nemours Company, was fractionated as for ethylene, the last fraction being retained.

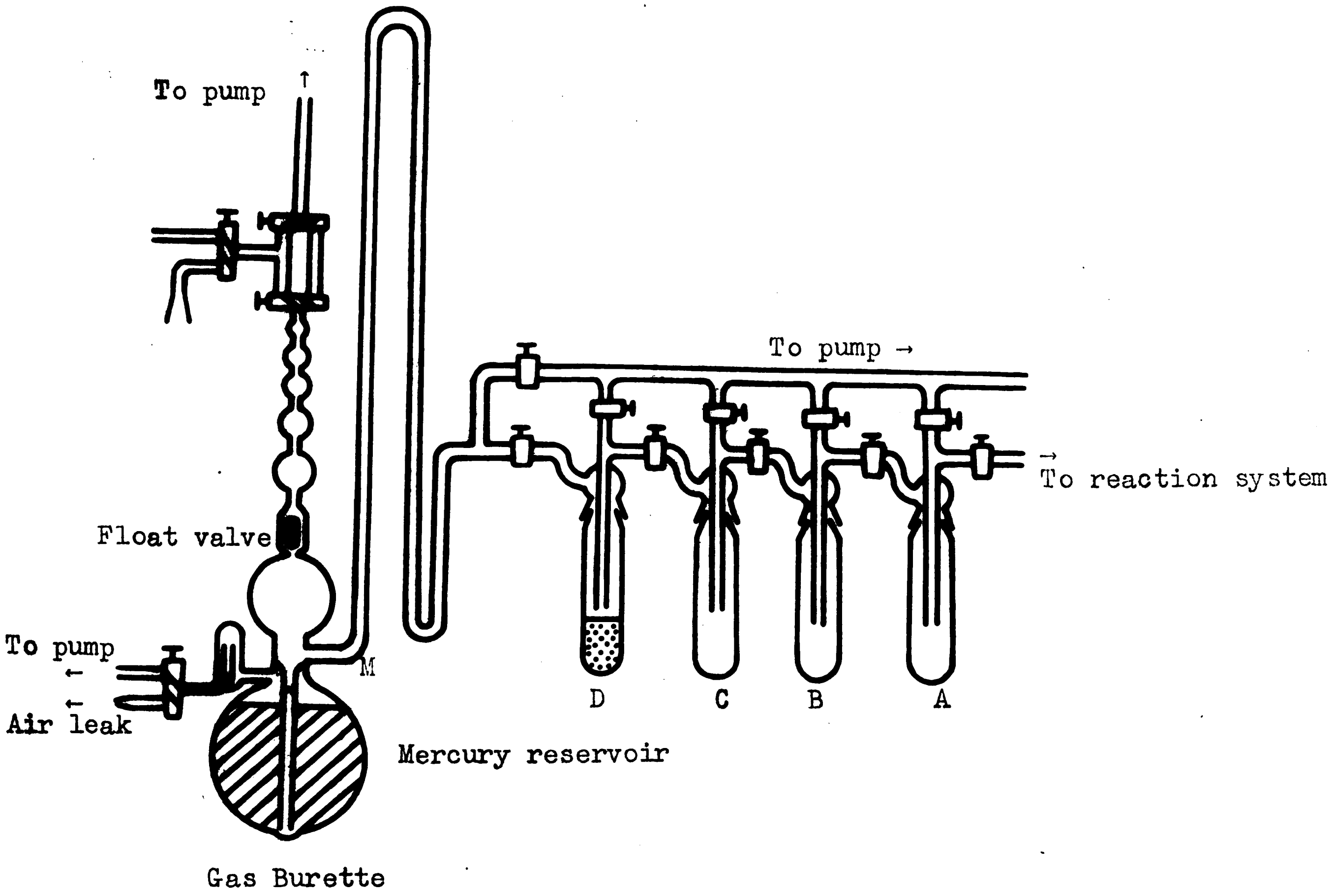
All materials were thoroughly degassed before use.

Apparatus

A conventional high-vacuum apparatus was used to handle reactants and products. The gas analysis system, illustrated in Fig. 1, consisted of a series of traps each of which could be connected to a gas burette.

Photolyses were carried out in a silica vessel, volume 130 ml. After being dosed with reactants the vessel was placed in a thermostat bath at 30°, and during irradiation was rotated at 30 r.p.m. The source of radiation was a Hanovia UVS 500, medium-pressure

Fig. 1. The Gas Analysis System.



mercury arc lamp, unfiltered. The arrangement of the photolysis system is shown in Fig. 2.

Between runs the reaction vessel was washed with carbon disulphide, hot water containing detergent, distilled water; then oven dried and degassed under vacuum.

Products were analysed by means of a Perkin-Elmer model 21 infrared spectrometer and a Perkin-Elmer model 154-C gas-chromatograph. The latter was fitted with either a 2-m. silica gel column at 25°, or a 2-m. diisodecyl phthalate column at 70°. Nitrogen or hydrogen was used as carrier gas.

Irradiation of Hydrogen Sulphide with Ethylene

(1) Identification of Products

A series of experiments was performed in which mixtures of hydrogen sulphide and ethylene, total pressure 500 mm., were irradiated at 30° for 8 hrs., the $H_2S:C_2H_4$ ratio being varied from 10:1 to 6:1. The volatile products from each run were fractionated through traps at -96° (fraction A), -145° (fraction B), -196° (fraction C), and a trap containing charcoal at -196° (fraction D); the last to absorb non-condensable products. The involatile products (fraction E) remained in the reaction vessel.

Fractions, A, B and C were subjected to gas chromatography on a 2-m. diisodecyl phthalate column at 70°, hydrogen carrier, flow rate 95 ml./min. Fraction A yielded two peaks whose retention times were identical with those of standard samples of ethanethiol

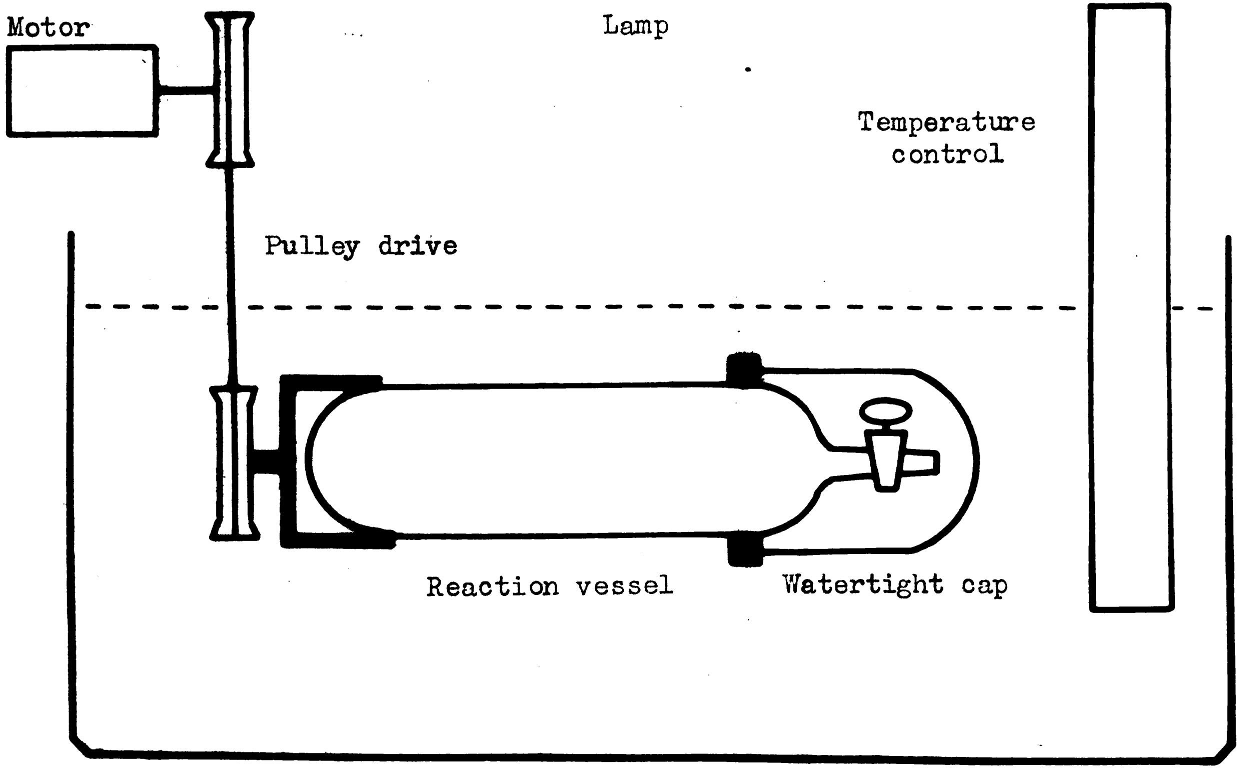


Fig. 2. The Irradiation Apparatus.

and diethyl sulphide; fraction B yielded one peak corresponding in retention time to hydrogen sulphide; fraction C yielded two peaks corresponding to ethylene and hydrogen sulphide, the latter being in small quantity. No buthanethiol was detected in any of these fractions.

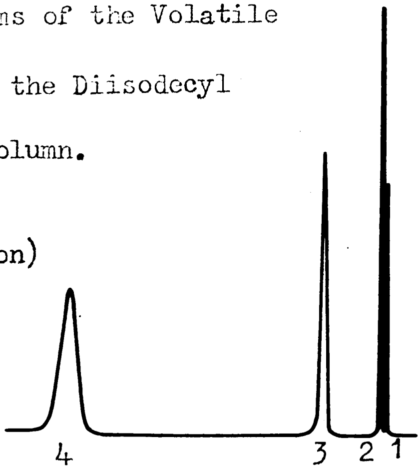
Fractions C and D were subjected to gas chromatography on a 2-m. silica gel column at 25°. Fraction C, with hydrogen carrier, flow rate 55 ml/min. yielded two peaks with retention times characteristic of ethylene and ethane, the small amount of hydrogen sulphide being absorbed; fraction D, with hydrogen carrier, gave no peaks, but with nitrogen carrier one peak with a retention time characteristic of hydrogen, was recorded.

Typical chromatograms of the volatile products on the diisodecyl phthalate column, and of fraction C on the silica gel column are reproduced in Figs. 3 and 4 respectively.

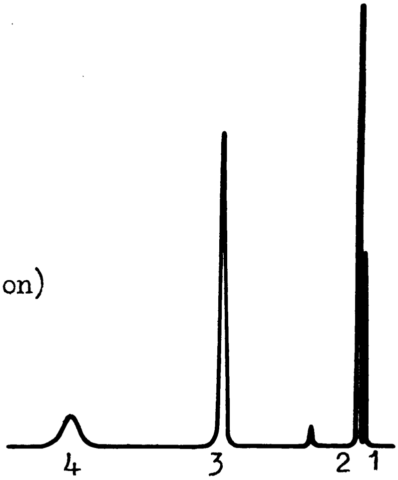
The involatile products consisted of a white deposit on the walls of the reaction vessel and a liquid residue; both were soluble in carbon disulphide and the liquid residue in carbon tetrachloride. The infrared spectrum of the solution in carbon tetrachloride was identical with that of a standard sample of diethyl disulphide, and agreed with that obtained by Trotter and Thompson[17] for diethyl disulphide. The carbon tetrachloride solution was tested for the presence of SH and $>$S groups by the very sensitive sodium nitroprusside test;[18] this proved to be negative. The white deposit was presumed to be sulphur.

Fig. 3. Chromatograms of the Volatile Products on the Diisodecyl Phthalate Column.

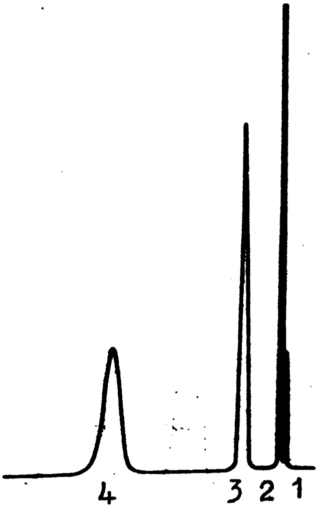
A (C_2H_4 - H_2S reaction)



B (CF_2CH_2 - H_2S reaction)



C (C_2F_4 - H_2S reaction)



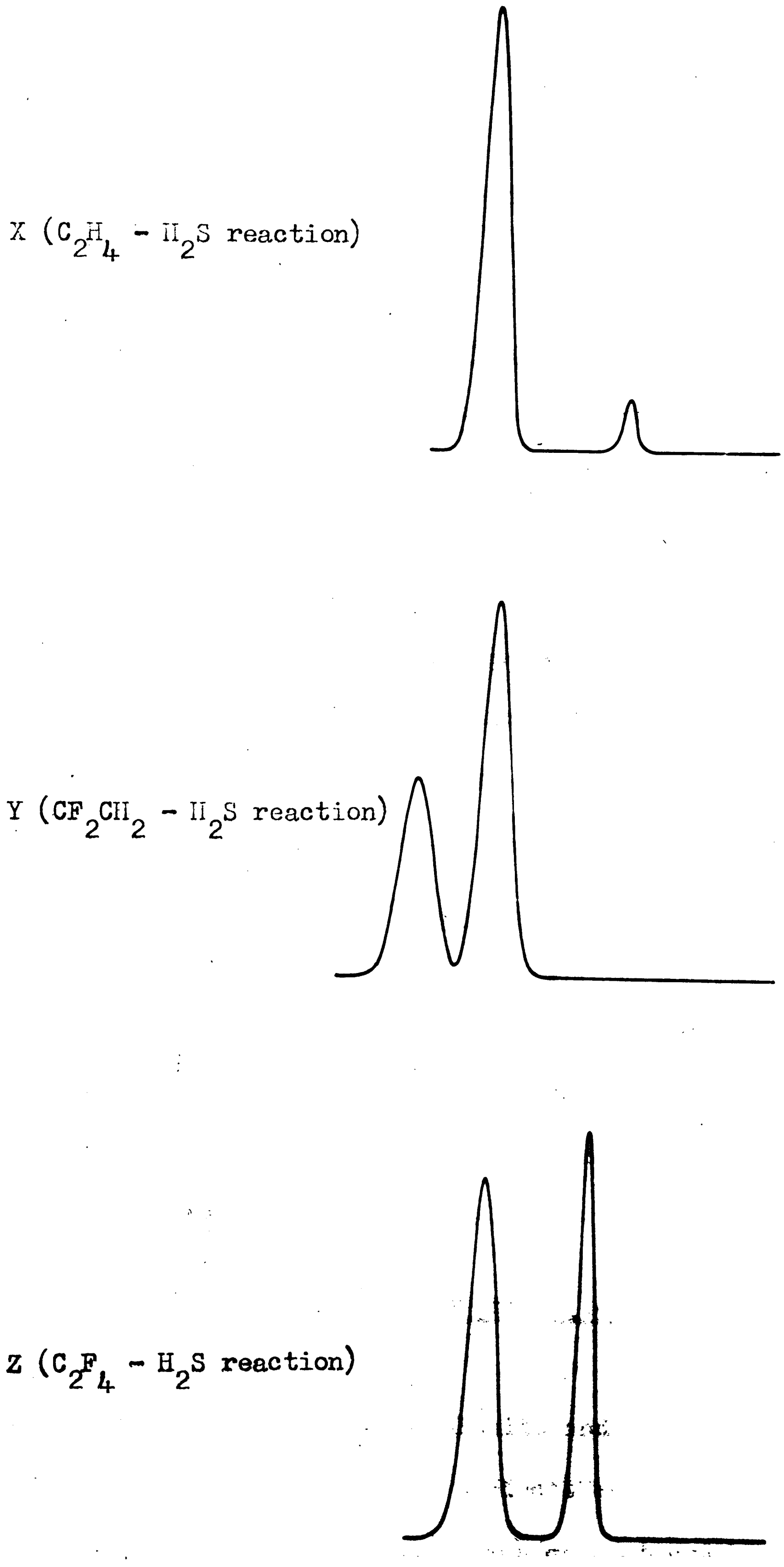


Fig. 4. Chromatograms of Fraction C on the Silica Gel Column.

It was concluded, therefore, that the products from irradiation of mixtures of hydrogen sulphide and ethylene in ratios from 10:1 to 6:1 were ethanethiol, diethyl sulphide, diethyl disulphide, ethane, hydrogen, and sulphur.

(2) Variation of Product Concentrations with Time

A series of runs at 30° was carried out with initial pressures of hydrogen sulphide 434 mm. and ethylene 71 mm., giving an $H_2S:C_2H_4$ ratio of 6.1:1. The time of irradiation was varied between 0 and 8 hrs. The products from each run were fractionated in the manner previously described and the volume of each fraction measured in the gas burette. The small amount of hydrogen sulphide in fraction C was measured by absorbing it in a mixture of silver nitrate and ethylene glycol on firebrick, and noting the reduction in volume of this fraction. The ratio $C_2H_4:C_2H_6$ in fraction C was determined by gas chromatography on silica gel, and the ratio $C_2H_5SH:(C_2H_5)_2S$ in fraction A by gas chromatography on diisodecyl phthalate. Sulphur and diethyl disulphide were not determined quantitatively.

The results are given in Table 1, and are graphed as a composition time curve in Fig. 5.

Irradiation of Hydrogen Sulphide with 1,1-Difluoroethylene and Tetrafluoroethylene

6:1 mixtures of hydrogen sulphide and each olefin were irradiated at 30° for 8 hrs. The volatile products were fractionated as previously described, and analysed by gas chromatography. The involatile

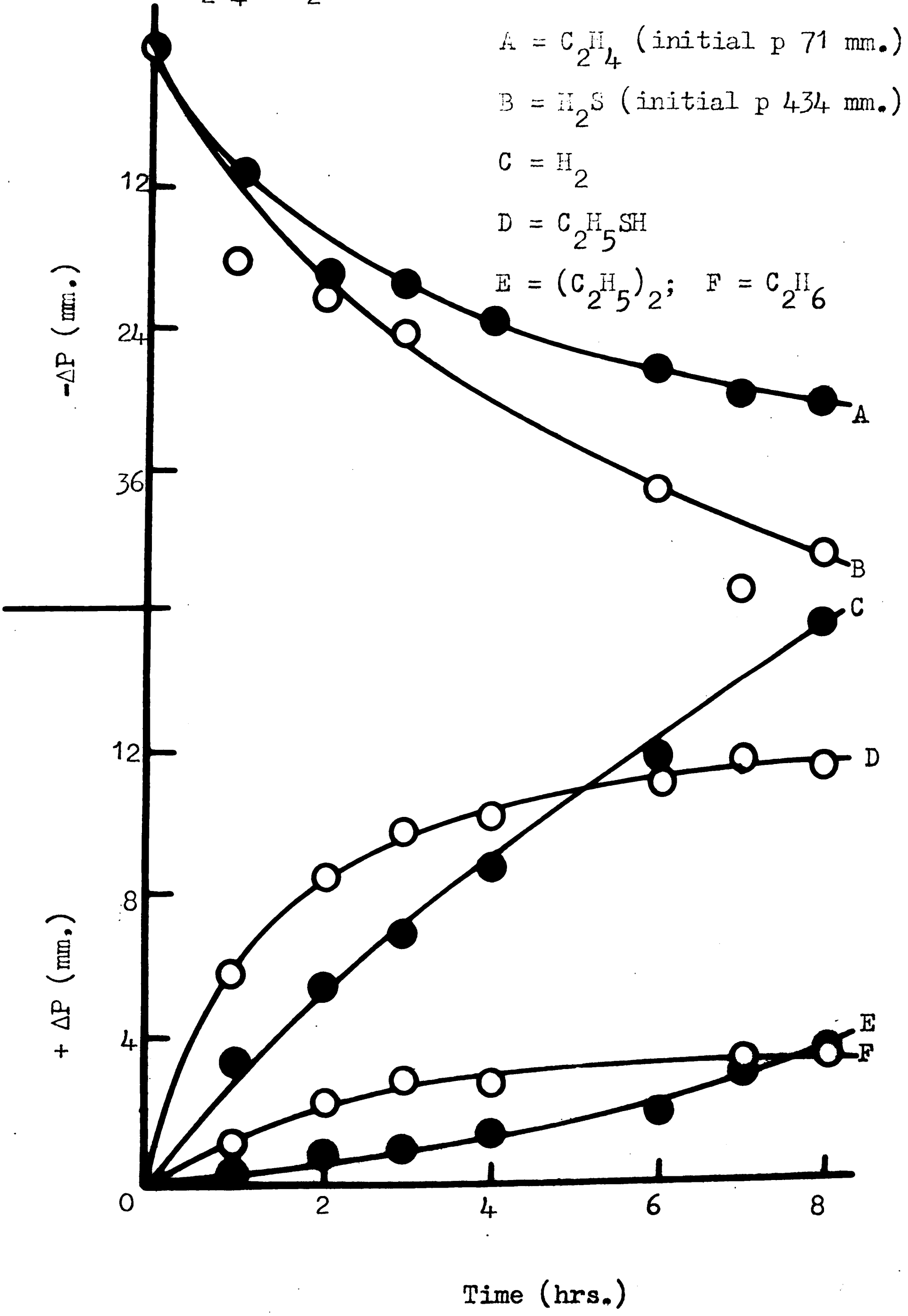
Table 1

Variation of Amounts of Reactants and Products with Time (H_2S-C_2H_4 reaction, temperature 30°)

All quantities given as mm. pressure in reaction vessel at 30°.

Time (hrs.)	C_2H_4	H_2S	C_2H_5SH	$(C_2H_5)_2S$	H_2	C_2H_6
0	71.2	433.9	0	0	0	0
1	66.5	415.7	5.85	0.30	3.43	1.13
2	51.6	412.5	8.57	0.95	5.54	2.26
3	50.9	409.6	9.86	1.00	6.89	2.86
4	47.5	-	10.20	1.40	8.86	2.62
6	43.9	396.5	11.20	1.87	11.96	-
7	41.4	-	11.84	2.91	-	3.33
8	40.5	390.6	11.54	3.85	15.61	3.45

Fig. 5. Variation of Reactant and Product Concentrations with Time (C_2H_4 - H_2S reaction).

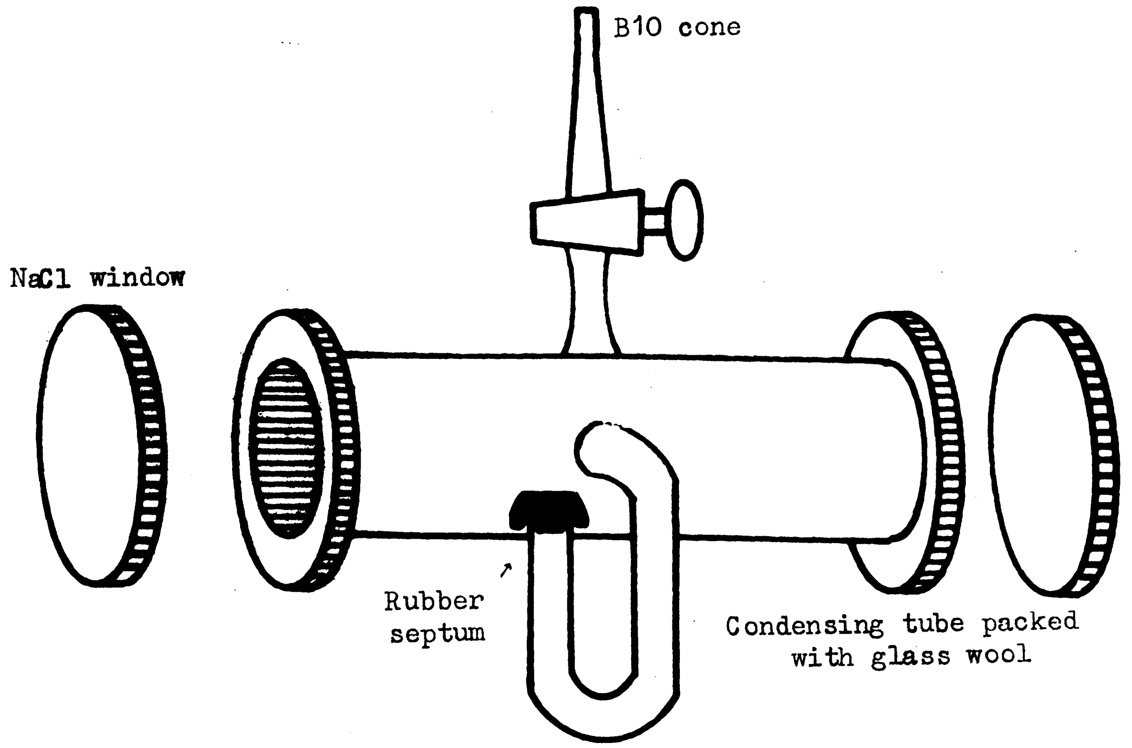


fraction found in these reactions was dissolved in carbon disulphide and its infrared spectrum taken.

Typical chromatograms of the volatile products on the diisodecyl phthalate column, and of fraction C on the silica gel column, are compared with the corresponding chromatograms from the hydrogen sulphide-ethylene reaction in Figs. 3 and 4 respectively.

The infrared spectra of individual products were obtained by collecting each product directly from the fractometer in a combined fraction collector and infrared gas cell (illustrated in Fig. 6).

Fig. 6. Combined Fraction Collector and Infrared Gas Cell.



Chapter 3

Discussion

Irradiation of Hydrogen Sulphide with Ethylene

On the basis that the photochemical decomposition of hydrogen sulphide results in formation of hydrogen atoms and hydrosulphide radicals, the following free radical mechanism is proposed to account for the products of the hydrogen sulphide-ethylene reaction.

$$H_2S \xrightarrow{h\nu} \cdot H + \cdot SH \qquad [1]$$

$$\cdot H + H_2S \rightarrow H_2 + \cdot SH \qquad [2]$$

$$\cdot H + C_2H_4 \rightarrow \cdot CH_2CH_3 \qquad [3]$$

$$\cdot CH_2CH_3 + H_2S \rightarrow C_2H_6 + \cdot SH \qquad [4]$$

$$\cdot SH + C_2H_4 \rightarrow \cdot CH_2CH_2SH \qquad [5]$$

$$\cdot CH_2CH_2SH + H_2S \rightarrow C_2H_5SH + \cdot SH \qquad [6]$$

$$C_2H_5SH \xrightarrow{h\nu} C_2H_5S\cdot + \cdot H \qquad [7]$$

$$C_2H_5SH + \cdot R \rightarrow C_2H_5S\cdot + RH \qquad [8]$$

$$C_2H_5S\cdot + C_2H_4 \rightarrow \cdot CH_2CH_2SC_2H_5 \qquad [9]$$

$$\cdot CH_2CH_2SC_2H_5 + H_2S \rightarrow (C_2H_5)_2S + \cdot SH \qquad [10]$$

$$C_2H_5S\cdot + C_2H_5S\cdot \rightarrow C_2H_5S\text{-}SC_2H_5 \qquad [11]$$

$$\cdot SH + \cdot SH \rightarrow H_2S + S \qquad [12]$$

$$\cdot SH + \cdot SH \rightarrow H_2 + S_2 \qquad [13]$$

(The species •R in step [8] is a free radical)

Steps [1], [2], [12], and [13] were proposed by Darwent and Roberts to describe the photolysis of hydrogen sulphide. From measurements of the quantum yield of hydrogen formation, Φ, over a wide range of pressure, they deduced that 13% of reactions between two SH radicals proceed via [13], however the following recalculation of their data indicates that this figure should be 26%. Considering steps [1], [2], [12] and [13], at the steady state:

$$\frac{d[H]}{dt} = I_a - k_2[H][H_2S] = 0 \qquad (1)$$

$$\frac{d[SH]}{dt} = I_a + k_2[H][H_2S] - 2k_{12}[SH]^2 - 2k_{13}[SH]^2 = 0 \qquad (2)$$

Solving these equations simultaneously gives

$$[SH] = \left\{\frac{I_a}{k_{12}+k_{13}}\right\}^{\frac{1}{2}}$$

Therefore the rate of formation of hydrogen is given by

$$\frac{d[H_2]}{dt} = k_2[H][H_2S] + k_{13}[SH]^2$$

$$= I_a + \frac{k_{13}I_a}{k_{12}+k_{13}}$$

and the quantum yield by

$$\Phi = 1 + \frac{k_{13}}{k_{12}+k_{13}} \qquad (3)$$

Thus the quantum yield should be greater than unity and be independent of pressure. Experimentally the limiting quantum yield, which was independent of pressure above 200 mm., was 1.26. Hence $k_{13}/k_{12}+k_{13} = 0.26$, that is 20% of reactions between two SH radicals proceed via [13] and 74% via [12]. It should be noted that in

Darwent and Roberts' calculation, equation (2) is written incorrectly as

$$\frac{d[SH]}{dt} = I_a+k_2[H][H_2S]-k_{12}[SH]^2-k_{13}[SH]^2 = 0$$

which leads to $2k_{13}/k_{12}+k_{13} = 0.26$, and hence to a 13% contribution of [13] to SH radical termination.

Steps [3]-[11] are normal radical reactions and a consideration of their energetics shows that they are either exothermic or thermoneutral. Since no butanethiol was detected, the polymerisation step

$$\bullet CH_2CH_2SH + C_2H_4 \rightarrow \bullet CH_2CH_2CH_2CH_2SH$$

is evidently unimportant under the prevailing experimental conditions.

The ready detection and amounts of hydrogen, ethane and diethyl disulphide formed suggest that under the conditions of these experiments chains are short, in contrast to the liquid phase experiments of Vaughan and Rust, Harris and Stacey, and Sugimoto and Ando, where the occurrence of long chains prevented these products from being detected.

In addition to accounting for all of the products formed, the postulated mechanism explains satisfactorily several aspects of the quantitative results in Fig. 5. The mechanism suggests that the formation of diethyl sulphide is dependent on the formation of ethanethiol; this is borne out by the experimental results which show that diethyl sulphide is formed at the expense of ethanethiol. If chain termination by SH radical combination is assumed to occur predominantly by step [12], then initially, when [7] and [8] are negligible, steps [2]-[4] will account for the hydrogen and ethane formed. The initial rate of formation of hydrogen is given by

$$R_{H_2} = k_2[H][H_2S] \tag{4}$$

and the rate of formation of ethane by

$$R_{C_2H_6} = k_4[C_2H_5][H_2S]$$

But $$\frac{d[C_2H_5]}{dt} = k_3[H][C_2H_4]-k_4[CH_2CH_3][H_2S] = 0$$

Therefore $$R_{C_2H_6} = k_3[H][C_2H_4] \tag{5}$$

Hence $$\frac{R_{H_2}}{R_{C_2H_6}} = \frac{k_2[H_2S]}{k_3[C_2H_4]} \tag{6}$$

Therefore $$\frac{k_2}{k_3} = \frac{R_{H_2}[C_2H_4]}{R_{C_2H_6}[H_2S]} \tag{7}$$

From Fig. 5, $R_{H_2}/R_{C_2H_6}$ 2.4 and therefore k_2/k_3 0.5. This value is only approximate because of the considerable error involved in estimating the amount of ethane in fraction C. Making the reasonable assumption that A_2/A_3 is 10, $k_2/k_3 = 0.5$, yields an activation energy difference, E_2-E_3, of 1.8 k.cal.mole^{-1}. Darwent and Roberts[19] have studied the kinetics of hydrogen atom addition to olefins relative to hydrogen atom abstraction from hydrogen sulphide by hydrogen atoms. They deduced for ethylene that E_2-E_3 is 0.9 k.cal.mole^{-1} which is of a similar order of magnitude to the value calculated above.

If it is assumed that the quantum yields of steps [1] and [7] are similar, competition for light quanta should be in favour of [1] because of the great excess of hydrogen sulphide over ethanethiol ($[H_2S]:[C_2H_5SH$ is initially infinity and after 8 hrs. is 40). Hence C_2H_5S radicals are formed mainly by step [8].

From equation (6), as the ratio $[H_2S]:[C_2H_4]$ increases, $k_2[H_2S]/k_3[C_2H_4]$ must increase. Initially the ratio $[H_2S]:[C_2H_4]$ is 6:1 and after 8 hrs., 10:1. Hence, as the reaction time increases the ratio of the rate of formation of hydrogen to the rate of formation of ethane is expected to increase, and from Fig. 5 this is seen to occur.

From the postulated mechanism the stoicheiometry of the formation of products in the $H_2S-C_2H_4$ reaction is:

$$\begin{aligned}
1 \text{ mol. } C_2H_4 + 1 \text{ mol. } H_2S &= 1 \text{ mol. } C_2H_5SH \\
2 \text{ mol. } C_2H_4 + 1 \text{ mol. } H_2S &= 1 \text{ mol. } (C_2H_5)_2S \\
2 \text{ mol. } C_2H_4 + 2 \text{ mol. } H_2S &= 1 \text{ mol. } (C_2H_5)_2S_2 \\
1 \text{ mol. } C_2H_4 &= 1 \text{ mol. } C_2H_6 \\
1 \text{ mol. } H_2S &= 1 \text{ mol. } H_2 + 1 \text{ mol. } S
\end{aligned}$$

This stoicheiometry may be tested with the experimental results in Fig. 5 by comparing the actual loss of ethylene and hydrogen sulphide with that expected from the amounts of the measured products. These figures, read from the smoothed curves in Fig. 5 are given in

Table 2

All quantities given as mm. pressure in reaction vessel at 30°.

Time (hrs.)	1	2	3	4	5	6	7	8
C_2H_4 loss	10.6	17.0	21.1	23.8	26.1	27.9	29.5	31.0
Predicted C_2H_4 loss	7.65	11.65	14.3	16.15	17.75	19.05	20.6	22.25
ΔC_2H_4	2.95	5.35	6.8	7.65	8.35	8.85	8.9	8.75
H_2S loss	12.3	19.9	25.0	29.3	33.2	36.8	40.0	43.4
Predicted H_2S loss	9.1	14.15	17.8	20.75	23.35	25.7	28.1	30.55
ΔH_2S	3.2	5.75	7.2	8.55	9.85	11.1	11.9	12.85
$\Delta H_2S:\Delta C_2H_4$	1.08	1.07	1.06	1.12	1.18	1.26	1.34	1.49

Table 2. The differences, ΔH_2S and ΔC_2H_4, between the actual losses of H_2S and C_2H_4, and the losses accounted for by the formation of the measured products, are also shown in Table 2. The discrepancy observed is considered to be due to the formation of diethyl disulphide. The proposed stoicheiometry indicates that hydrogen sulphide and ethylene should be consumed in a 1:1 ratio in forming diethyl disulphide. Table 2 shows that this is in good agreement with the $\Delta H_2S:\Delta C_2H_4$ ratio for the first 5 hours, but thereafter agreement is less satisfactory.

Hydrogen sulphide is lost at a greater rate than ethylene, and this can be explained by the photochemical decomposition of hydrogen sulphide according to the stoicheiometry:

$$H_2S = H_2 + S$$

Irradiation of Hydrogen Sulphide with 1,1-Difluoroethylene and Tetrafluoroethylene

If the chromatograms of the volatile products from the C_2H_4-H_2S, CF_2CH_2-H_2S, and C_2F_4-H_2S reactions, obtained with the diisodecyl phthalate column are designated A, B, and C respectively, it can be seen from Fig. 3 that A, B, and C conform to the same pattern. In each case four main peaks designated 1, 2, 3, and 4, were recorded. In chromatogram A (C_2H_4-H_2S products), peaks 1 and 2 correspond to the reactants, peak 3 to ethanethiol, and peak 4 to diethyl sulphide. It was found that peaks 1 and 2 in chromatograms B and C were also produced by the reactants, and it was therefore concluded that in each case peak 3 corresponded to a polyfluoroethanethiol and peak 4 to a dipolyfluoroethyl sulphide.

The volatile organosulphur products from C_2F_4 will be 1,1,2,2-tetrafluoroethanethiol and bis-1,1,2,2-tetrafluoroethyl sulphide. This is in agreement with the results of Harris and Stacey[12] on the X-ray initiated C_2F_4-H_2S reaction.

Chromatogram B (CF_2CH_2-H_2S products), shows the presence of a small quantity of a third product. This is not unexpected since the addition of H_2S to CF_2CH_2 could feasibly yield five products, viz. CF_2HCH_2SH, $(CF_2HCH_2)_2S$, CH_3CF_2SH, $(CH_3CF_2)_2S$, and $CF_2HCH_2SCF_2CH_3$. Nevertheless, by analogy with the free radical addition of HBr[20], CF_3I[21], CF_3SH[13], CH_3SH[13], and $SiHCl_3$[22], to CF_2CH_2, the main products are expected to be those with fluorine atoms in the β position. Thus the two major peaks in chromatogram B are assigned to 2,2-difluoroethanethiol and bis-2,2-difluoroethyl sulphide. The small quantity of third product is presumed to be 1,1-difluoroethanethiol. Harris and Stacey also found only CF_2HCH_2SH and $(CF_2HCH_2)_2S$ in the analogous X-ray initiated CF_2CH_2-H_2S reaction.

In Fig. 4, chromatogram X refers to fraction C (liquid air fraction) of the products from the products from the C_2H_4-H_2S reaction; correspondingly chromatograms Y and Z, refer to the same product fraction from the CF_2CH_2-H_2S and C_2F_4-H_2S reactions respectively. All show only two peaks. The second peak in each case corresponds to the olefin, and the first to the alkanes, C_2H_6 in X,

CF_2HCH_3 in Y, and CF_2HCF_2H in Z.

By analogy with the C_2H_4-H_2S reaction it is reasonable to suggest that the involatile liquid formed in the CF_2CH_2-H_2S reaction is bis-2,2-difluoroethyl disulphide, and the involatile liquid from the C_2F_4-H_2S reaction is bis-1,1,2,2-tetrafluoroethyl sulphide.

Study of the infrared spectra of the products from the C_2F_4-H_2S reaction provides some evidence in favour of the structures proposed for them. All of the products of the C_2F_4-H_2S reaction show a peak, corresponding to the C-H stretching vibration, at around 3,000 $cm.^{-1}$ The position of the peak varies from compound to compound. In the spectrum of the fluorocarbon, considered to be CF_2HCF_2H, it appears at 3,010 $cm.^{-1}$; in the spectrum of the product considered to be CF_2HCF_2SH it appears at 2,970 $cm.^{-1}$, and in the corresponding sulphide and disulphide spectra the peak occurs at 2,920 $cm.^{-1}$

C-F stretching is known to give rise to intense absorption in the range 1,000-1,400 $cm.^{-1}$ [23] The product spectra all show an intense band at 1,380 $cm.^{-1}$ and a band around 1,150 $cm.^{-1}$

The position of the bands in the spectrum of the fluorocarbon is in excellent agreement with the published spectrum of 1,1,2,2-tetrafluoroethane.[24]

The SH group is known to absorb weakly in the range 2,550-2,650 $cm.^{-1}$ [25] No peak was recorded in this range for the product assigned the structure CF_2HCF_2SH, but this is not surprising in view of the low concentration of the sample and the very low intensity of SH absorption. C-S and S-S[25] stretching frequencies were too low (less than 700 cm.$^{-1}$) to assist in structure determination with the infrared instrument available.

Of the products of the CF_2CH_2-H_2S reaction, only the involatile disulphide was examined spectroscopically. The usual strong C-F bands appeared and the C-H stretching vibration occurred at 2,930 cm.$^{-1}$

SECTION II

THE THERMAL DECOMPOSITION OF TRIFLUOROACETALDEHYDE.

Chapter 4

Introduction

The thermal decomposition of trifluoroacetaldehyde is similar in many respects to that of acetaldehyde. The kinetics of the acetaldehyde decomposition are therefore discussed, and this is followed by a review of the literature relating to the order of methyl radical combination. Relevant aspects of the photolysis of trifluoroacetaldehyde are also presented, and the results of the thermal decomposition of trifluoroacetaldehyde are summarised.

The Thermal Decomposition of Acetaldehyde

The thermal decomposition of acetaldehyde yields mainly methane and carbon monoxide in accordance with the stoicheiometry[1-7]:

$$CH_3CHO = CH_4 + CO$$

The kinetics of the reaction were first studied by Hinshelwood and Hutchison[1] (1926) in the temperature range 430-592°. Their results could be fitted to a second order rate plot, and gave an activation energy of 45.5 k.cal./mole. Fletcher and Hinshelwood[8,9] (1933) found that a plot of half-life against initial pressure showed abrupt changes in slope over the pressure range 0.2-1100 mm. This led them to postulate that the acetaldehyde molecule existed in different activated states which decomposed by virtually independent bimolecular processes.

The pyrolysis of acetaldehyde was also investigated by Kassell[10,11] (1928), who obtained a reaction order of 5/3. However, recalculation[7,12] of the data of Hinshelwood et al. and of Kassell, by plotting the logarithm of initial rate against the logarithm of pressure, yielded an order of 1.5 exactly.

Rice and Herzfeld[12] (1934) suggested that the experimental facts could be explained on the basis of the following free radical chain mechanism:

$$CH_3CHO \rightarrow CH_3 + CHO \qquad [1']$$

$$CHO \rightarrow H + CO \qquad [2]$$

$$H + CH_3CHO \rightarrow H_2 + CH_3CO \qquad [3]$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \qquad [4]$$

$$CH_3CO \rightarrow CH_3 + CO \qquad [5]$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad [6']$$

Steps [4] and [5] constitute the chain with methyl and acetyl radicals as the chain carriers. Application of the steady state treatment to this mechanism leads to the rate expression:

$$\frac{-d[CH_3CHO]}{dt} = 2k_1'[CH_3CHO] + k_4\left\{\frac{k_1'}{k_6'}\right\}^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}}$$

Under the conditions of long chain length found in this reaction, the first term may be neglected, hence

$$\frac{-d[CH_3CHO]}{dt} = k_4\left\{\frac{k_1'}{k_6'}\right\}^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}}$$

Thus the Rice-Herzfeld mechanism satisfactorily accounted for both the composition of the reaction products and the overall order of reaction.

A number of papers on the pyrolysis of acetaldehyde were published by Letort[7,14,14] (1937). He found the order of the reaction to be exactly 1.5 for pressures between 0.3 and 1160 mm. and temperatures between 473 and 564°, and an activation energy of 45.7 k.cal./mole was obtained. Letort explained these results in terms of the Rice-Herzfeld mechanism.

The studies summarised above led to a conflict of opinion concerning the relative importance of the radical chain and intramolecular mechanisms in the decomposition of acetaldehyde. A number of investigators studied various aspects of the reaction in an effort to elucidate the exact nature of the mechanism, and the results obtained, more often in conflict than in agreement, are summarised below.

Detection of Free Radicals in the Reaction: Letort demonstrated the presence of methyl radicals in the products of pyrolysis of acetaldehyde at 700-1100° by the Paneth technique of metallic mirror removal. Patat and Sasche[15-17] (1935) measured the stationary concentration of hydrogen atoms in the reaction at 550° and obtained clear evidence for the production of free radicals. However, they calculated that the concentration of radicals was too low to support a chain mechanism of the kind envisaged by Rice and Herzfeld. Radicals were detected at the lower temperatures employed in kinetic studies by Burton, Ricci and Davis[18] (1940) using a modified

Paneth technique involving the transport of radioactivity from a radio-lead mirror.

The Induced Decomposition: Another approach to the investigation of the acetaldehyde pyrolysis mechanism was provided by studies of its induced decomposition. Methyl radicals, produced photochemically[19,20] and thermally,[21] were able to induce the decomposition at temperatures where acetaldehyde alone was quite inert. This was explained by postulating that the methyl radicals initiated a chain decomposition of acetaldehyde, and this was taken to support the Rice-Herzfeld mechanism for the thermal decomposition. The decomposition was also induced by radicals from ethylene oxide[22,23] diethyl ether[24,25], vinyl ether[26], biacetyl[27,28], tert-butyl peroxide[29,30], and by the decomposition of products of ethyl bromide and ethyl iodide[31,32]. Traces of oxygen strongly accelerated the reaction.[7,33-37] The effect of a number of inorganic compounds[38] on the decomposition has also been investigated.

Inhibition of the Reaction: Early work on the influence of nitric oxide and propylene on the kinetics of the thermal decomposition of acetaldehyde produced contradictory results.[26,39-42] Smith and Hinshelwood[43] (1942) re-examined the problem in greater detail and found that for 50 mm. or less of acetaldehyde, the first 2 mm. of nitric oxide appreciably retarded the decomposition while larger quantities accelerated it; for pressures of acetaldehyde greater than 50 mm. no inhibition was observed. The reaction was also inhibited by propylene,[37,43] increasing quantities of propylene causing the rate to decrease to a limiting value. These results were interpreted on the assumption that the inhibitable part of the decomposition was a chain reaction and the residual reaction at maximum inhibition was an independent molecular process.

Rice and Varnerin[44] (1954) pyrolysed $CH_3CHO-C_2D_6$ and $CF_3CDO-C_2H_6$ mixtures in the presence and absence of nitric oxide and propylene. The extent of isotopic mixing, measured by the ratios CH_3D/CH_4 and CD_3H/CD_4 respectively, indicated that both CH_3CHO and CD_3CDO decomposed by a chain process unaccompanied by any contribution from a molecular reaction.

In order to account for the kinetics of the foundation of the minor products from the reaction in the presence of nitric oxide, namely, ethane, hydrogen and hydrogen cyanide, Freeman, Danby and Hinshelwood[45] (1958) postulated that nitric oxide, besides initiating a chain process, also stimulated the molecular rearrangement.

Re-examination of the reaction by Eusuf and Laidler[46] (1964) substantiated the results of Smith and Hinshelwood, and showed that as the nitric oxide concentration was increased, the reaction order with respect to acetaldehyde rose above 1.5 and then fell to 1.5 again. They confirmed the result of Freeman et al. that at higher nitric oxide concentrations the rate varied with $[CH_3CHO]^{\frac{3}{2}}[NO]^{\frac{1}{2}}$. These observations were shown to be consistent with a free radical mechanism in which it was postulated that initiation occurred by a reaction originally proposed by Rice and

Polly[37]

$$CH_3CHO + NO \rightarrow CH_3CO + HNO$$

together with those processes occurring in the absence of nitric oxide. The observed increase in ethane production in the presence of nitric oxide was explained by introducing the additional chain termination reactions,

$$CH_3 + CH_3NO \rightarrow C_2H_6 + NO$$

$$CH_3NO + CH_3NO \rightarrow C_2H_6 + 2NO$$

in which nitric oxide was described as acting as a "chaperon" for the combination of methyl radicals.

<u>Isotopic-Mixing Experiments</u>: Morris[47,48] (1941) devised a method of distinguishing between the free radical and intramolecular reactions by measuring the isotopic composition of the methanes resulting from pyrolysis of CH_3CHO-CD_3CDO mixtures. It was expected that a chain mechanism would lead to the formation of isotopically mixed methanes while an intramolecular reaction would yield only methane and methane-d_4. Mixed methanes were obtained in quantities which indicated a chain mechanism contribution of 50%, but when the aldehydes were purified from oxygen this reduced to 10-20%. Morris concluded that the radical chain was caused by a superimposed induced decomposition initiated by oxygen.

Zemany and Burton[49] (1951), and Wall and Moore[50,51] (1951) monitored the decomposition products of CH_3CHO-CD_3CDO mixtures by mass spectrometry. Isotopically mixed methanes were formed, and the intramolecular reaction contribution was calculated by Zemany and Burton to be around 20%, and by Wall and Moore to be negligible. By showing that the thermal exchange of CH_4 and CD_4 at 600° was negligible, Wall and Moore excluded the possibility that the isotopically mixed methanes might have resulted from secondary reactions.

The experiments of Rice and Varnerin, described above, led to the conclusion that CH_3CHO and CD_3CDO decomposed solely by a radical chain mechanism.

The Effect of Foreign Inert Gases: Some aspects of the decomposition mechanism of acetaldehyde have been clarified by studying the reaction in the presence of inert gases. In early investigations it appeared that hydrogen[52,53], nitrogen[54], helium[55], and carbon dioxide[56] increased the reaction rate, while carbon monoxide and methane[56,57] decreased the rate.

Letort et al.[58,59,60] (1950), in a theoretical investigation, established identities relating mechanism to reaction order for a homogeneous gas phase thermal decomposition involving radical chains. Identities, predicting an order of 1.5, were derived for several mechanisms applicable to the acetaldehyde decomposition. The various modes of initiation and termination appropriate to these mechanisms are summarised in Table 3. A distinction was made between β radicals (radicals which do not decompose), and μ and μ_2 radicals (radicals which decompose via first and second order processes respectively), both types being important in chain propagation. Chain termination by collision of two β radicals was designated a $\beta\beta$ process, collision of β and μ radicals a $\beta\mu$ process, and collision of two μ radicals, a $\mu\mu$ process. This terminology has been extended by Laidler et al.[62] to the description of a complete radical mechanism; for example, the original Rice-Herzfeld mechanism is written $^{1}\beta\beta_{3/2}$, where the superscript refers to the order of the initiation process, the subscript to the overall reaction order, and $\beta\beta$ to the termination reaction.

Table 3

Mechanisms Predicting 1.5 Order for the Decomposition of Acetaldehyde.

Unimolecular Initiation

	Termination Reaction	Acetyl Radical Decomposition
$\beta\beta$	$CH_3 + CH_3 \rightarrow C_2H_6$	$CH_3CO \rightarrow CH_3 + CO$
$\beta\mu_2$	$CH_3 + CH_3CO \rightarrow CH_3COCH_3$	$CH_3CO + X \rightarrow CH_3 + CO + X$
$\mu_2\mu_2$	$CH_3CO + CH_3CO \rightarrow$ products	$CH_3CO + X \rightarrow CH_3 + CO + X$

Bimolecular Initiation

	Termination Reaction	Acetyl Radical Decomposition
$\beta\mu$	$CH_3 + CH_3CO \rightarrow CH_3COCH_3$	$CH_3CO \rightarrow CH_3 + CO$
$\beta\beta(X)$	$CH_3 + CH_3 + X \rightarrow C_2H_6 + X$	$CH_3CO \rightarrow CH_3 + CO$
$\beta\mu_2(X)$	$CH_3 + CH_3CO + X \rightarrow CH_3COCH_3 + X$	$CH_3CO + X \rightarrow CH_3 + CO + X$
$\mu_2\mu_2(X)$	$CH_3CO + CH_3CO + X \rightarrow$ products $+ X$	$CH_3CO + X \rightarrow CH_3 + CO + X$

X = third body, initially CH_3CHO.

In order to distinguish between these possibilities Letort et al.[59,60] studied the effect of the inert gases, hydrogen, nitrogen and carbon dioxide on the reaction. It was found that each gas slightly inhibited the reaction. The mechanism predicting this inhibition was determined by assuming that a chemically inert gas added to a decomposing substrate could have a purely physical action. By acting as a third body in chain terminating triple collisions it could decrease the reaction rate, or by participating in chain initiating bimolecular collisions it could increase the rate. Letort et al. derived relations which showed that if R_o is the initial rate of decomposition of pure acetaldehyde, and R_x is the initial rate in the presence of inert gas X, the form of the dependence of R_x/R_o on $[CH_3CHO]$ and $[X]$ found experimentally, viz.

$$\left\{\frac{R_x}{R_o}\right\}^2 = \frac{1 + r_i[X]/[CH_3CHO]}{1 + r_t[X]/[CH_3CHO]}$$

was in agreement with that predicted by the ${}^2\beta\beta(x)_{3/2}$ mechanism with the inclusion of steps [1x] and [6x]:

$$CH_3CHO + CH_3CHO \rightarrow CH_3 + CHO + CH_3CHO \qquad [1]$$

$$CH_3CHO + X \rightarrow CH_3 + CHO + X \qquad [1x]$$

$$CHO \rightarrow H + CO \qquad [2]$$

$$H + CH_3CHO \rightarrow H_2 + CH_3CO \qquad [3]$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \qquad [4]$$

$$CH_3CO \rightarrow CH_3 + CO \qquad [5]$$

$$CH_3 + CH_3 + CH_3CHO \rightarrow C_2H_6 + CH_3CHO \qquad [6]$$

$$CH_3 + CH_3 + X \rightarrow C_2H_6 + X \qquad [6x]$$

The expressions for R_x and R_o predicted by this mechanism are:

$$R_o = k_4\left\{\frac{k_1}{k_6}\right\}^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}} \tag{1}$$

$$R_x = k_4\left\{\frac{k_1[CH_3CHO] + k_{1x}[X]}{k_6[CH_3CHO] + k_{6x}[X]}\right\}^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}} \tag{2}$$

$$\text{Hence} \quad \left\{\frac{R_x}{R_o}\right\}^2 = \frac{1 + k_{1x}[X]/k_1[CH_3CHO]}{1 + k_{6x}[X]/k_6[CH_3CHO]} \tag{3}$$

Thus $r_i = k_{1x}/k_1$ and $r_t = k_{6x}/k_6$, and therefore r_i and r_t are the relative efficiencies of X compared with CH_3CHO in chain initiation and chain termination respectively. If $r_i < r_t$, inert gases will retard the reaction; if $r_i > r_t$ inert gases will accelerate the reaction. The values of r_i and r_t obtained for each inert gas by Letort et al. are listed in Table 4.

Recent Work on the Mechanism of Reaction (Formation of Minor Products and Effect of Inert Gases)

Small amounts of hydrogen and ethane were detected in the pyrolysis products of acetaldehyde by Letort, and Freeman, Danby and Hinshelwood.[45] The kinetics of hydrogen formation have been studied by Trenwith[61] (1963). According to the original Rice-Herzfeld mechanism the rate of hydrogen production, equal to the rate of the initiation step

$$CH_3CHO \rightarrow CH_3 + CHO \qquad [1']$$

is given by

$$\frac{d[H_2]}{dt} = k_1'[CH_3CHO].$$

However, if the mechanism involves the bimolecular initiation step

$$CH_3CHO + CH_3CHO \rightarrow CH_3 + CHO + CH_3CHO \qquad [1]$$

the rate of hydrogen production will be given by

$$\frac{d[H_2]}{dt} = k_1[CH_3CHO]^2.$$

Trenwith found that plots of log R_{H_2} against log $[CH_3CHO]$, for different temperatures, were straight lines of slope very nearly two, which indicated that over the experimental pressure range, the chain initiating step was a second order process. An activation energy of 73.8 k.cal./mole was obtained for reaction [1]. The graphs of hydrogen formed against time showed a short induction period, which varied with the temperature and the surface area of the reaction vessel, but was independent of the acetaldehyde pressure. The conclusion drawn was that the decomposition of the formyl radical

$$CHO \rightarrow H + CO \qquad [2]$$

proceeded at such a rate that a measurable time elapsed before the formyl radical concentration attained the steady state value. From the lengths of the induction periods, k_2 was calculated to be $10^{5.3}$ exp(-26,300/RT)sec.$^{-1}$, which was taken to imply that the decomposition of the formyl radical was a heterogeneous process occurring at the walls of the reaction vessel.

The kinetics and mechanism of the pyrolysis of acetaldehyde have recently been reinvestigated by Eusuf and Laidler[62] (1964). They showed that an order of 1.5 held accurately for pressures between 30 and 580 mm. and temperatures between 480 and 525°; the overall rate constant was given by:

$$k = 1.16 \times 10^{13} \exp(-47,600/RT) \text{ cc.}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{sec.}^{-1}.$$

Added foreign gases decreased the rate and increased the order to approximately 1.6, CO_2, CH_4 N_2, CO, and C_2H_6 having essentially the same effect. The rate of ethane formation was measured and found to be dependent on $[CH_3CHO]^2$, and to be increased by added nitrogen. This was taken to be strong evidence for the initiation being a second order process, in agreement with the results of Trenwith on the rate of hydrogen production.

The $^1\beta\beta_{3/2}$ mechanism, the original Rice-Herzfeld mechanism, was rejected because it predicts no inert gas effect, while the $^2\beta\mu_{3/2}$ mechanism was rejected because it predicts acceleration in the presence of inert gases. The $^2\beta\beta(X)_{3/2}$ mechanism in the form proposed by Letort et al. was considered by Eusuf and Laidler to be unsatisfactory because it seemed to them unreasonable to suppose that inert gases should be effective in transferring energy from an activated ethane molecule by collision, but ineffective in transferring energy to an acetaldehyde molecule. This apparent difficulty was overcome by postulating that initiation occurred by the hydrogen transfer reaction,

$$CH_3CHO + CH_3CHO \rightarrow CH_3CO + CH_3CHOH \qquad [1a]$$

followed by

$$CH_3CHOH \rightarrow CH_3CHO + H \qquad [2a]$$

together with the energy transfer processes:

$$CH_3CHO + CH_3CHO \rightarrow CH_3 + CO + CH_3CHO \qquad [1]$$

$$CH_3CHO + X \rightarrow CH_3 + CO + X \qquad [1x]$$

The overall initiation process would therefore be second order.

This modified $^2\beta\beta(X)_{3/2}$ mechanism leads to the following expressions for R_o, the rate in the absence of foreign gas, and R_x, the rate in the presence of foreign gas:

$$R_o = k_4\left\{\frac{k_1+k_{1a}}{k_6}\right\}^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}} \qquad (4)$$

$$R_x = k_4\left\{\frac{(k_1+k_{1a})\ [CH_3CHO] + k_{1x}[X]}{k_6[CH_3CHO] + k_{6x}[X]}\right\}^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}} \qquad (5)$$

The ratio R_x/R_o is therefore given by:

$$\left\{\frac{R_x}{R_o}\right\}^2 = \frac{1 + k_{1x}[X]/(k_1+k_{1a})[CH_3CHO]}{1 + k_{6x}[X]/k_6[CH_3CHO]} \qquad (6)$$

$$= \frac{1 + r_i[X]/[CH_3CHO]}{1 + r_t[X]/[CH_3CHO]}$$

The values of r_i and r_t obtained by Eusuf and Laidler are listed in Table 4.

Trenwith and Dexter[63] (1964) have made a detailed analysis of the minor products from the pyrolysis of acetaldehyde, and reinvestigation of the effect of carbon dioxide and ethane on the reaction. The relative amounts of hydrogen, acetone, ethane, ethylene and carbon dioxide, detected, indicated that both acetone and ethane were chain ending products, and that reactions [6] and [7] were the only significant chain termination reactions.

$$CH_3 + CH_3 + CH_3CHO \rightarrow C_2H_6 + CH_3CHO \qquad [6]$$

$$CH_3CO + CH_3 \rightarrow CH_3COCH_3 \qquad [7]$$

Trenwith and Dexter found that the initial rate in the presence of carbon dioxide was unchanged, but the rate in the presence of ethane was decreased and the reaction order rose to 1.65. The rates of hydrogen and ethane formation were increased by added carbon dioxide, but the rate of acetone formation was unaffected.

These observations were accounted for by the proposal that both the $^2\beta\beta(X)_{3/2}$ and $^2\beta\mu_{3/2}$ mechanisms were applicable to the decomposition of acetaldehyde. The expressions given by the $^2\beta\beta(X)_{3/2}$ mechanism for R_o, R_x, and R_x/R_o are given in equations (1), (2) and (3) respectively. The $^2\beta\mu_{3/2}$ mechanism (steps [1] - [5], [7] and [1x]) leads to the relations:

$$R_o = \left\{\frac{k_1 k_4 k_5}{k_7}\right\}^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}} \qquad (7)$$

$$R_x = k_4\left\{\frac{k_1 k_5 [CH_3CHO] + k_{1x} k_5 [X]}{k_4 k_7 [CH_3CHO]}\right\}^{\frac{1}{2}} [CH_3CHO]^{\frac{3}{2}} \qquad (8)$$

Therefore

$$\left\{\frac{R_x}{R_o}\right\}^2 = \frac{1 + k_{1x}[X]}{k_1 [CH_3CHO]} \qquad (9)$$

The values of r_i and r_t, obtained from the rates of formation of hydrogen and ethane respectively, are compared with those found by Letort et al. and Eusuf and Laidler in Table 4.

Table 4

Values of r_i and r_t for Acetaldehyde in the Presence of Inert Gases.

	Letort et al.			Eusuf and Laidler	Trenwith and Dexter
X	H_2	CO_2	$CO + CH_4$	$CO, CO_2, N_2, CH_4, C_2H_6$	CO_2
r_i	?	v. small	0.06	0.19	0.12
r_t	0.10		0.33	1.02	0.28

These differences are no doubt due to the large error involved in calculating r_i and r_t from the effect of inert gases on the initial rate. Laidler states that an upper limit for r_i of 0.3 is possible, while Trenwith estimates an error of ± 60%.

The negligible effect of carbon dioxide on the rate of reaction was explained by Trenwith and Dexter as being due to balancing of the retardation predicted by the $^2\beta\beta(X)_{3/2}$ mechanism (where $r_i < r_t$) in equation (3), with the acceleration predicted by the $^2\beta\mu_{3/2}$ mechanism in equation (9). The retarding effect of ethane is due to the larger value of r_t relative to that for carbon dioxide, and the rise in order with respect to acetaldehyde to 1.65 follows from equation (2) if X is present in sufficient quantity.

A serious objection to the occurrence of reactions [1a] and [2a], postulated by Eusuf and Laidler, arises from consideration of the effect of inert gases on the rates of formation of the minor products. The rate of ethane formation was found by both Trenwith and Dexter, and Eusuf and Laidler to increase with added inert gas. Since the rate of termination must equal the rate of initiation, the rate of initiation must increase, and Trenwith finds that the rate of hydrogen formation is greater in the presence of carbon dioxide. This can only occur if the energy transfer initiation processes [1] and [1x] are much more important than the hydrogen transfer reaction [1a]. Comparing equations (1)and (2) with (4) and (5) shows that reaction [1a] is not needed to explain the overall kinetics, and in fact complicates the kinetic treatment unnecessarily.

Eusuf and Laidler consider that acetone is formed, not by reaction [7] as proposed by Trenwith and Dexter, but by addition of a methyl radical to the carbonyl bond of acetaldehyde, followed by decomposition of the resultant radical, represented by reaction [7a].

$$CH_3 + CH_3CHO \rightarrow CH_3CH\dot{O}CH_3 \rightarrow CH_3COCH_3 + H \qquad [7a]$$

This mechanism is criticised by Trenwith and Dexter on the grounds that it predicts the rate of hydrogen formation to be dependent on $[CH_3CHO]^{\frac{3}{2}}$, rather than $[CH_3CHO]^2$ found experimentally. Trenwith's explanation that the induction period for hydrogen formation results from the heterogeneous decomposition of the formyl radical is rejected by Eusuf and Laidler, who argue that the homogeneous decomposition of the formyl radical is so fast as to make an induction period seem unlikely. They explain the induction period in terms of the slow decomposition of the intermediate radical in reaction [7a].

In summary, the recent work of Trenwith and Dexter, and Eusuf and Laidler, on the acetaldehyde decomposition, is in agreement on the order of the initiation process, but differs as to its mechanism. On one hand an energy transfer mechanism is proposed, and on the other, a hydrogen atom transfer reaction, independent of added inert gas, is also postulated. Both workers consider that termination occurs through the third order combination of methyl radicals, and Trenwith and Dexter consider that combination of methyl and acetyl radicals to form acetone is also a chain terminating step. The usual chain steps are common to both.

The Order of Methyl Radical Combination

The order of the combination of methyl radicals is a matter of some controversy. The rate of methyl radical combination has been measured by a number of investigators,[64-67] all of whom assumed that the reaction was second order under their experimental conditions.

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad [1]$$

Using the rotating sector technique, Kistiakowsky and Roberts[68] found that at 165° the second order rate constants for methyl radical combination fell by a factor of three or four when the acetone pressure was lowered below 10 mm. A similar pressure dependence was observed by Dodd and Steacie[69] in the photolysis of acetone at 247°. In Brinton's[70] study of the photolysis of acetone, the plot of $\log(k_2/k_1^{\frac{1}{2}})$ v. $1/T$, obtained at low acetone

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2 \qquad [2]$$

concentrations, showed marked upward curvature at temperatures between 400 and 435°, with a corresponding increase in activation energy from 10 to 14.6 k.cal./mole. From the assumption that $E_1 = 0$ at low temperatures, E_2 was calculated to be -9.2 k.cal. in agreement with the negative activation energy of -11.7 k.cal. predicted theoretically by Gill and Laidler.[71] On the other hand the data of Danby, Buchanan and Henderson[72] on the photolysis of acetaldehyde gave no indication of the pressure dependence of methyl radical combination in the temperature range 212-340° and pressure range 19-317 mm. Dodd[73], measuring the recombination rate constant by the rotating sector method, found that although the plot of $\log(k_1/k_2)$ v. $1/T$ showed no curvature at temperatures between 150 and 450° and in the pressure range 200-400 mm., an activation energy of 10.7 k.cal. was obtained; this gave a negative activation energy for [1] of -3.2 k.cal. which was taken to indicate a slight pressure dependence.

Studies of the pyrolysis of ethane have provided further information as to the order of methyl radical combination. The Rice-Herzfeld[12] mechanism which explained the overall first order kinetics was:

$$C_2H_6 \rightarrow 2\ CH_3 \qquad [-1]$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \qquad [3]$$

$$H + C_2H_5 \rightarrow C_2H_6 \qquad [4]$$

In order to account for the accelerating effect of inert gases Küchler and Theile[74] proposed a ${}^2\mu\mu_1$ type mechanism:

$$C_2H_6 + M \rightarrow 2\ CH_3 + M \qquad [-1']$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \qquad [3]$$

$$C_2H_5 \rightarrow C_2H_4 + H \qquad [5]$$

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \qquad [6]$$

$$2\ C_2H_5 \rightarrow C_4H_{10} \text{ or } C_2H_6 + C_2H_4 \qquad [7]$$

Evidence in support of this mechanism was obtained by Laidler and Wojciechowski[75] who predicted that a change to 3/2 order kinetics would occur at temperatures above 640° and pressures below 60 mm. as [7] was replaced by [4] as the main chain terminating reaction. Such a transition was observed at approximately the predicted pressure, and this confirmation of the second order dissociation of ethane required, by the principle of microscopic reversibility, that the combination of methyl radicals be third order. The rate of formation of methane in the pyrolysis of ethane was shown by Quinn[76] to be first order in ethane at pressures as low as 60 mm.; this implied that the dissociation was first order. Quinn accepted [7] to be the main chain terminating step and explained the overall first order kinetics by suggesting that the decomposition of the ethyl radical could be expressed as $k_5[C_2H_5][M]^x$, where $x = \frac{1}{2}$ and initially $M = C_2H_6$; this implied that C_2H_5 was half way between a μ and a β radical. Quinn's mechanism explained the inert gas effect, since inert gases would accelerate the decomposition of the ethyl radical, but Laidler contended that it would not explain the sharpness of the observed transition to 3/2 order kinetics. Quinn's observations have been confirmed by Lin and Back[77] and by Gordon.[78] The former examined the rate of formation of methane and butane and amended the mechanism by proposing a small contribution from [4] to account for the order of butane formation and $R_{CH_4}/R_{C_4H_{10}}$ being greater than predicted by Quinn's mechanism. The latter found evidence for hydrogen atom quenching on the surface. Küchler and Thiele[74] and Spall et al.[79] found that inert gases had very little effect on the rate of ethane decomposition maximally inhibited by nitric oxide. Laidler et al.[80] argued that this could not be explained in terms of Quinn's mechanism since it required the decomposition of ethyl radicals to be first order which meant that the dissociation of ethane had to be second order to explain the overall kinetics.

Recently Trenwith and Dexter[81] showed that the experimental first order rate constants began to fall from the high pressure value at pressures around 100 mm. and that the order of the reaction rose to approximately 1.2 at 10 mm.

The related problem of the order of decomposition of the ethyl radical was studied by Eusuf and Laidler[82] in the decomposition of propionaldehyde at temperatures between 520 and 560°. The rate of ethylene formation was unaffected by added inert gas and since ethylene arose only from

$$C_2H_5 \rightarrow C_2H_4 + H$$

the decomposition of ethyl radicals was presumed to be in its first order region. The effect of pressure on the rate of ethylene formation in the pyrolysis of n-butane was attributed by Purnell and Quinn[83] to the pressure dependence of the decomposition of ethyl radicals. Laidler et al.[80] have shown that these results can be explained by invoking a molecular component to the reaction.

Evidence for the third order combination of methyl radicals (Letort et al.,[58-60] Trenwith and Dexter,[61,63] and Eusuf and Laidler[62]) has been reviewed above.

These conflicting conclusions could be reconciled if the pressure dependence of the combination of methyl radicals were a function of the differences between the energy levels available for coupling with different third bodies. If this were the case the pressure at which the order of the process changed would vary with the third body.

The Photolysis of Trifluoroacetaldehyde

An investigation of the photolysis of trifluoroacetaldehyde was made by Dodd and Smith[84] (1957). The products of irradiation at 3130 Å, and temperatures between 150 and 400°, were trifluoromethane, carbon monoxide, hexafluoroethane, and hydrogen. Quantum yields of carbon monoxide and trifluoromethane, designated Φ_{CO} and Φ_{CF_3H} respectively, were as high as 60, and the rate of formation of carbon monoxide (R_{CO}) was proportional to the square root of the light intensity (I_a). These facts were accounted for by the following free radical chain mechanism:

$$CF_3CHO \xrightarrow{h\nu} CF_3 + CHO \qquad [1]$$

$$CF_3 + CF_3CHO \rightarrow CF_3H + CF_3CO \qquad [2]$$

$$CF_3CO \rightarrow CF_3 + CO \qquad [3]$$

$$CF_3 + CF_3 \rightarrow C_2F_6 \qquad [4]$$

On the assumption that CF_3H resulted only from [2] and C_2F_6 only from [4], then

$$\frac{R_M}{R_E^{\frac{1}{2}}[CF_3CHO]} = \frac{k_2}{k_4^{\frac{1}{2}}} \qquad (1)$$

where R_M is the rate of formation of CF_3H, and R_E, that of C_2H_6. As predicted by (1), $k_2/k_4^{\frac{1}{2}}$ was independent of I_a and $[CF_3CHO]$, and an Arrhenius plot of log $k_2T^{-\frac{1}{4}}/k_4^{\frac{1}{2}}$ against $1/T$ gave $(E_2 - \frac{1}{2} E_4) = 8.2 \pm 0.5$ k.cal./mole, so that E_2 8.2 k.cal./mole.

Arguments based on material balance led Dodd and Smith to postulate the occurrence of [5] and [6] above 250°,

$$CHO \rightarrow H + CO \qquad [5]$$

$$H + CF_3CHO \rightarrow H_2 + CF_3CO \qquad [6]$$

but at lower temperatures they considered the heterogeneous decomposition of CHO more likely. The Arrhenius plot deviated from linearity below 150° and this was taken to indicate a contribution to R_M from the primary intramolecular reaction

$$CF_3CHO \xrightarrow{h\nu} CF_3H + CO \qquad [1']$$

Hence
$$\Phi_M = \frac{R_M}{I_a} = \frac{k_2}{k_4^{\frac{1}{2}}} \frac{R_E^{\frac{1}{2}}[CF_3CHO]}{I_a} + k_1' \qquad (3)$$

A plot of Φ_M against $R_E^{\frac{1}{2}}[CF_3CHO]/I_a$ showed that equation (3) was obeyed and $k_1' = 0.021$. However the slope was greater than the value of $k_2/k_4^{\frac{1}{2}}$ obtained by extrapolation of the linear portion of the Arrhenius plot, and instead of the quantity $\Phi_M - (k_2/k_4^{\frac{1}{2}}) R_E^{\frac{1}{2}}[CF_3CHO]/I_a$ being constant, it was found to be proportional to $R_E^{\frac{1}{2}}[CF_3CHO]/I_a$. This suggested a reaction between CF_3 radicals and aldehyde molecules adsorbed on the walls:

$$CF_3 + CF_3CHO\text{ (wall)} \rightarrow CF_3H + \text{products} \qquad [7]$$

Equation (3) then became

$$\Phi_M - \frac{k_2}{k_4^{\frac{1}{2}}} R_E^{\frac{1}{2}} \frac{[CF_3CHO]}{I_a} = k_1' + \left\{\frac{k_7}{k_4^{\frac{1}{2}}[CF_3CHO]} \cdot \frac{R_E^{\frac{1}{2}}[CF_3CHO]}{I_a}\right\} \qquad (4)$$

A value of k_7 was deduced for room temperature and equation (4) used to correct all points below 150° on the Arrhenius plot, causing them to fall on the extrapolated linear portion.

Equation [8] was not needed to explain their results and mass spectrometric analysis gave no evidence for the formation of hexafluoroacetone

$$CF_3 + CF_3CO \rightarrow CF_3COCF_3 \qquad [8]$$

The pressure dependence of the trifluoromethyl radical combination was also studied. It was expected that if a pressure dependence existed, and was similar to that shown by methyl radical combination in that photolysis of acetone at low pressures, then $k_2/k_4^{\frac{1}{2}}$ would increase as the aldehyde pressure decreased. Experiments at 124° showed that, after applying the above-mentioned correction, there was no indication of dependence upon pressure down to 0.5 mm. of trifluoroacetaldehyde.

The Thermal Decomposition of Trifluoroacetaldehyde

The thermal decomposition of trifluoroacetaldehyde at pressures between 20 and 180 mm. and temperatures between 470 and 519° yields mainly carbon monoxide and trifluoromethane in accordance with the stoicheiometry:

$$CF_3CHO = CF_3H + CO$$

Small quantities of hydrogen and hexafluoroethane were also detected.

The order of the reaction is 1.5 and carbon monoxide and carbon dioxide both increase the rate of reaction.

The experimental observations are explained in terms of a free radical chain mechanism involving second order initiation, and termination by the third order combination of trifluoromethyl radicals.

Chapter 5

Results

Reaction Products: The products from a number of runs at 480° with initial trifluoroacetaldehyde pressures of 150 mm. and reaction times of 20 mins. were fractionated through traps at -96° (fraction A), -245° (fraction B), -196° (fraction C) and a trap containing activated charcoal at -196° (fraction D); the last to absorb non-condensable products. Gas chromatographic analysis of fractions B and C on a 2-m. diisodecyl phthalate column at 70°, hydrogen carrier, flow rate 35 ml./min., showed B to contain the residual trifluoroacetaldehyde, and C to contain trifluoromethane. Analysis of fraction C on a 1-m. silica gel column at 50°, hydrogen carrier, flow rate 90 ml./min., showed that it contained, besides trifluoromethane, trace quantities of hexafluoroethane and an unidentified compound; this compound, presumed to be a fluorocarbon, was smaller in quantity than the hexafluoroethane. The identity of the products was confirmed by collecting each fraction from the chromatogram, and taking its infrared spectrum. Analysis of fraction D on silica gel with hydrogen carrier showed that it contained carbon monoxide; on changing to nitrogen carrier fraction D was also shown to contain a trace of hydrogen.

Carbon monoxide and trifluoromethane were thus established as the main reaction products, and hydrogen and hexafluoroethane as minor products.

The possibility of small quantities of hexafluoroacetone being formed was not overlooked, but its presence or absence could not be ascertained because of the lack of a suitable analytical method. The complexity of the infrared spectrum of each fraction precluded its identification by this method. Gas chromatography was also unsuccessful in that the column materials, diisodecyl phthalate, tetraethylene glycol dimethyl ether, squalane, carbowax 1500 and polypropylene glycol, failed to give a peak after injection of a sample of hexafluoroacetone.

Small amounts of silicon tetrafluoride were detected through the presence of a peak at 9.75 μ in the infrared spectrum of the products. Presumably its formation was due to attack on silica by CF_3 radicals at high temperature.

Stoicheiometry: The stoicheiometry of the reaction was determined by conducting a series of runs at 480° with initial trifluoroacetaldehyde pressures of 116 mm. and reaction times between 1 and 20 mins. Fractions C and D were measured in the gas burette and, after checking the efficiency of fractionation by gas chromatography, were assigned to the products trifluoromethane and carbon monoxide respectively. Attempts to measure the residual trifluoroacetaldehyde were hampered by its tendency to polymerise. This difficulty was overcome by collecting the trifluoroacetaldehyde in a previously tared, evacuated trap, and weighing. The results are given in Table 5, and are graphed as a composition time curve in Fig. 7, in which, for the sake of clarity, alternate results for each of

Table 5

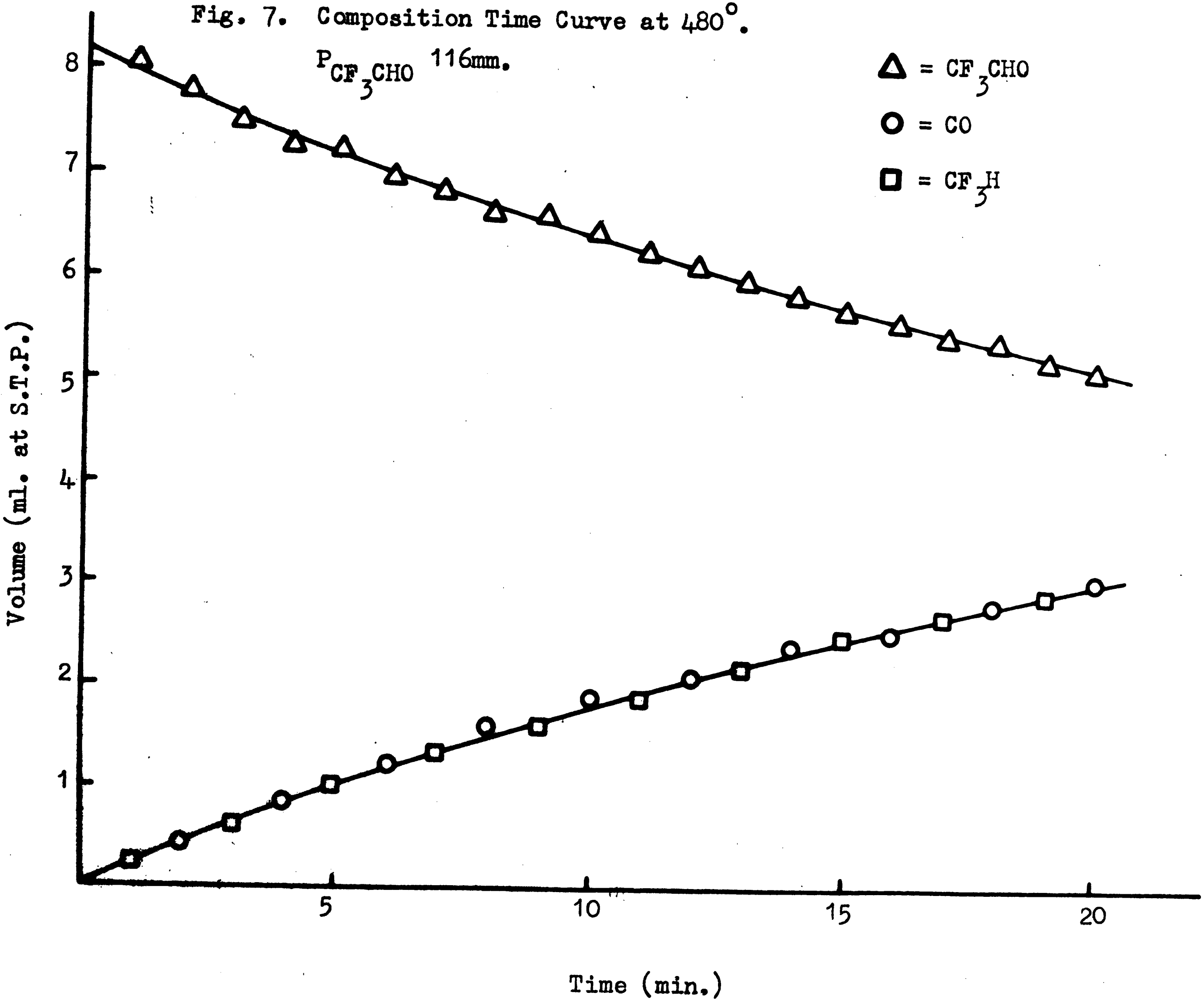
Analysis of Reaction Products

P_{CF_3CHO} = 116 mm. Temp. 480°C

All quantities in ml. at S.T.P. Time in mins.

Reaction Time	Residual CF_3CHO	CO formed	CF_3H formed
0	8.37	0	0
1	8.07	0.25	0.24
2	7.80	0.38	0.38
3	7.52	0.69	0.61
4	7.28	0.83	0.80
5	7.24	0.96	0.99
6	6.99	1.22	1.14
7	6.86	1.30	1.34
8	6.65	1.58	1.51
9	6.66	1.65	1.57
10	6.48	1.88	1.85
11	6.28	1.92	1.86
12	6.18	2.10	2.05
13	6.00	2.21	2.18
14	5.87	2.41	2.38
15	5.73	2.52	2.50
16	5.61	2.54	2.53

Fig. 7. Composition Time Curve at 480°.
P_{CF_3CHO} 116mm.



the products carbon monoxide and trifluoromethane are omitted.

It can be seen that within experimental error the amounts of carbon monoxide and trifluoromethane formed are identical and equal to the amount of trifluoroacetaldehyde consumed. Hence the decomposition, taken to 36% completion may be represented by the stoicheiometry,

$$CF_3CHO \rightarrow CF_3H + CO$$

Therefore $-d[CF_3CHO]/dt = d[CF_3H]/dt = d[CO]/dt = dP/dt = R$, and accordingly all initial rates were derived by measuring the rate of change of pressure.

Rate Equation: The variation of initial rate with trifluoroacetaldehyde pressure was investigated at temperatures of 471.5, 480, 488.5, 496, 502.5, 510.5 and 519°. At each temperature initial rates were measured for a series of runs in which the pressure of trifluoroacetaldehyde was varied between 15 and 190 mm. The results are given in Table 6 and in Fig. 8 where initial rates (R) in mm./min. are plotted against initial pressure of trifluoroacetaldehyde in mm. Plots of $\log_{10}R$ against $\log_{10}[CF_3CHO]$ gave a series of straight lines of slope 1.5 ± 0.03, and plots of R against $[CF_3CHO]^{1.5}$, shown in Fig. 9, gave a series of straight lines through the origin.

The overall order of reaction is therefore 1.5 and the rate of decomposition may be expressed by the equation

$$R = k[CF_3CHO]^{\frac{3}{2}}$$

Fig. 8. Variation of Initial Rate with P_{CF_3CHO}.

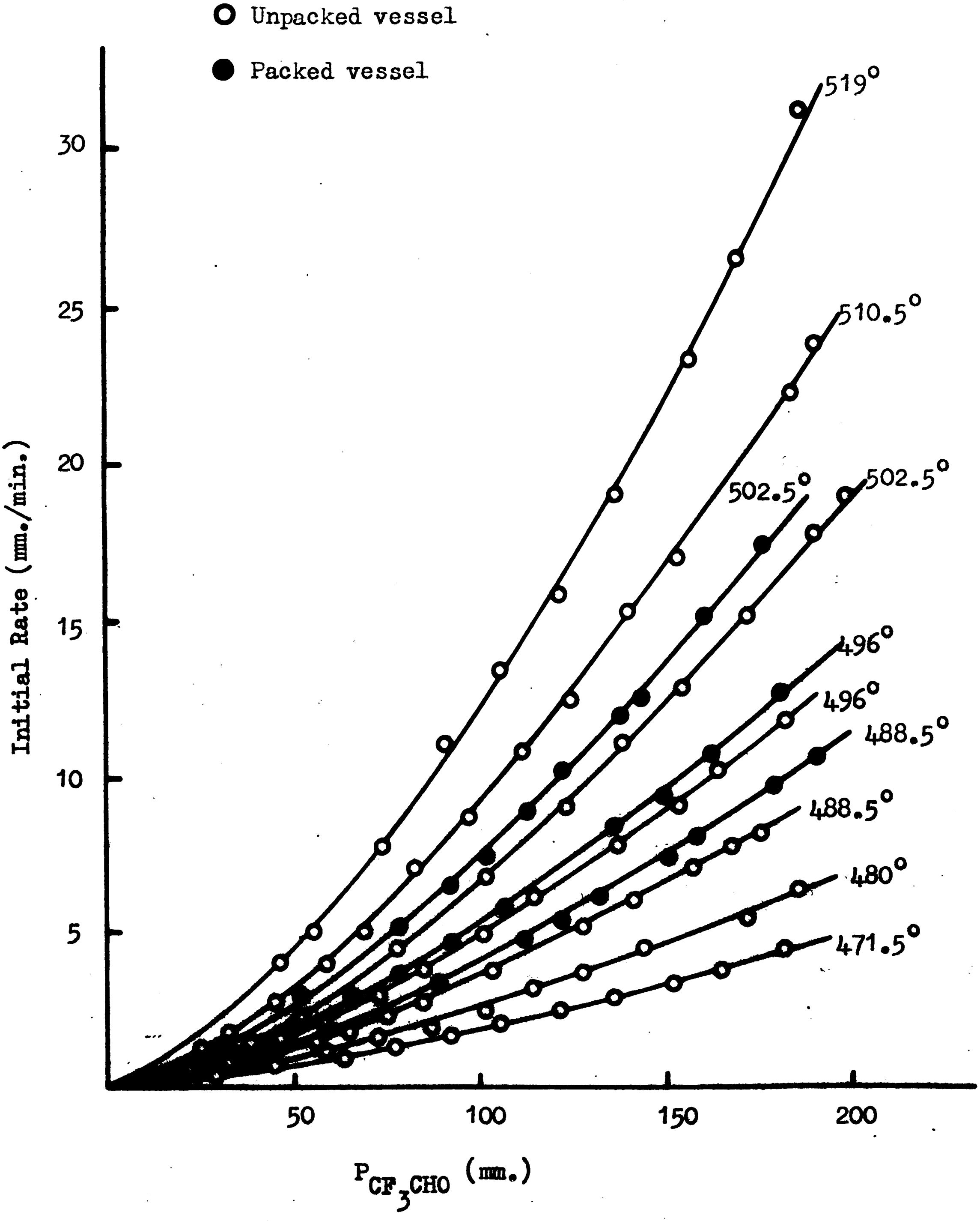
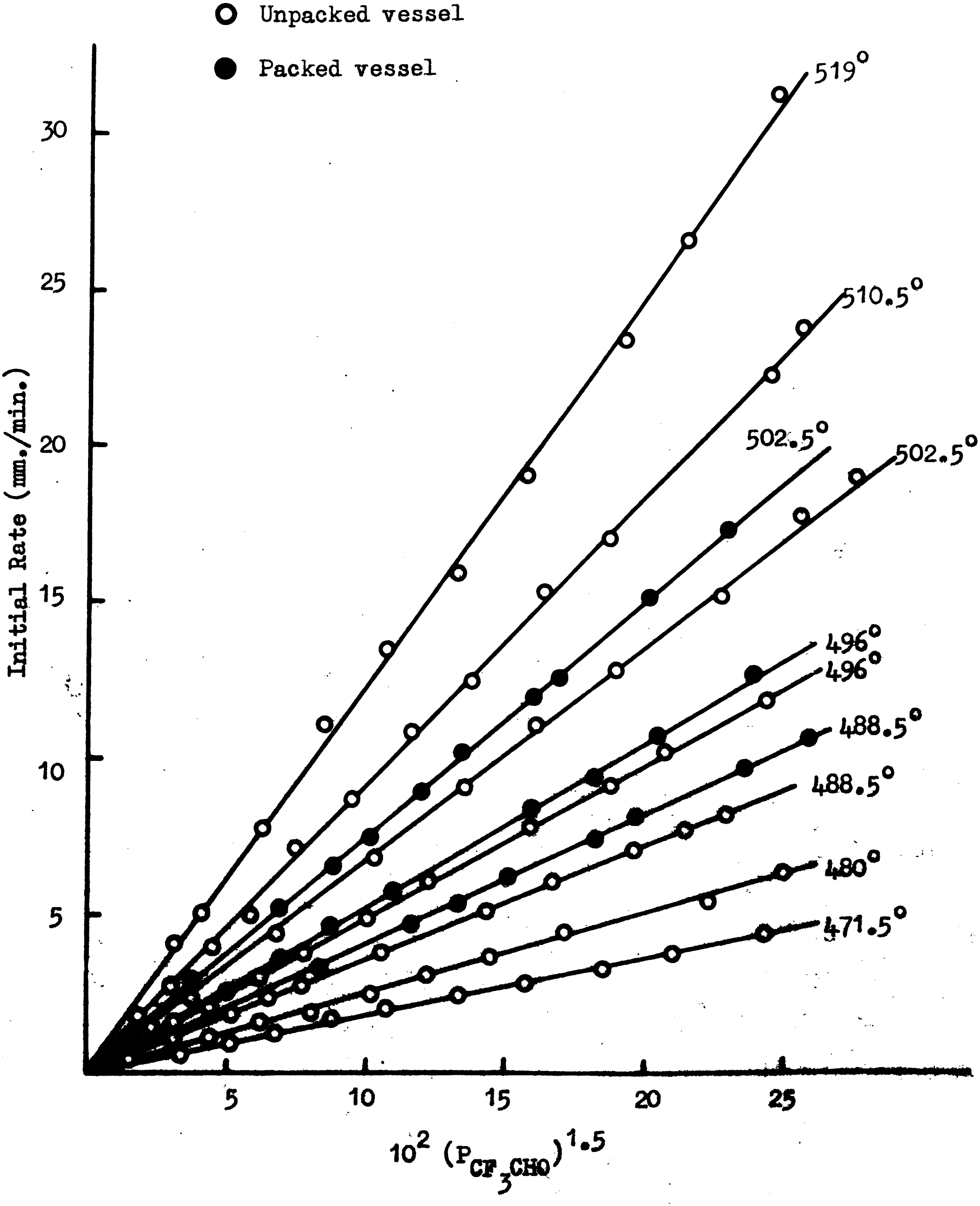


Fig. 9. Variation of Initial Rate with $(P_{CF_3CHO})^{1.5}$.



Effect of Surface Area: The effect of packing the reaction vessel with silica quill tubing was studied at three temperatures, 488.5, 496 and 502.5°. In each case an increase in rate was observed (Table 7, Figs. 8 and 9) the average increase being 8%.

Activation Energy: The experimental rate constants k, obtained from the slopes of the plots in Fig. 9, are given in Table 8. An Arrhenius plot of the results in Fig. 10, yielded by the method of least squares:

$$k = 10^{12.2} \exp(-49{,}000/RT) \text{ l.}^{\frac{1}{2}}\text{mole}^{-\frac{1}{2}}\text{sec.}^{-1}$$

The estimated precisions of the activation energy and pre-exponential factor are respectively

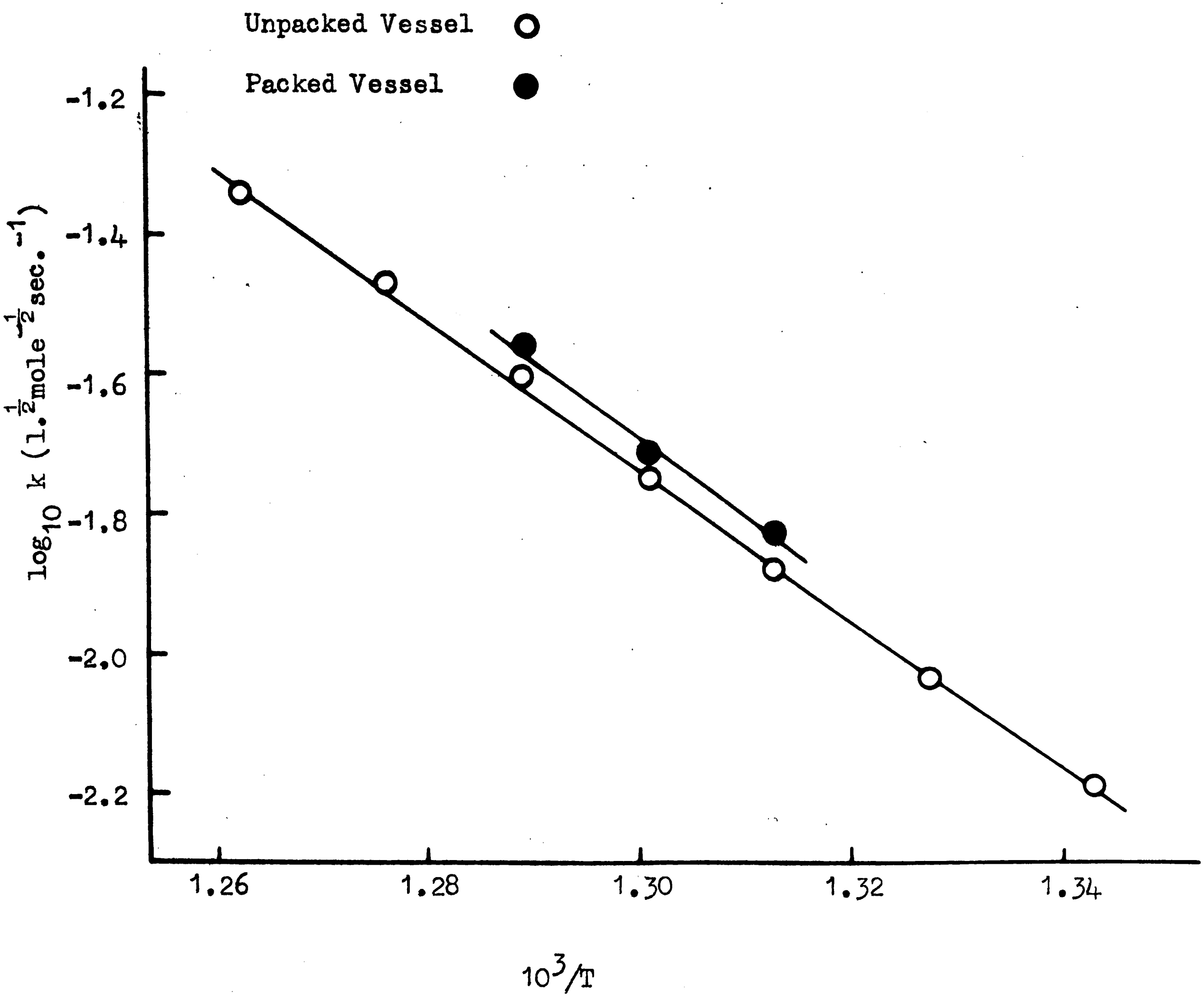
$$E = 49.0 \pm 0.9 \text{ k.cal./mole}$$

$$\log A = 12.2 \pm 0.3$$

The activation energy corresponding to the three points shown in Fig. 10 for the packed vessel could not be calculated because of insufficient results.

Rate of Formation of Hexafluoroethane: The rate of formation of hexafluoroethane was measured at 499° for pressures of trifluoroacetaldehyde between 80 and 250 mm. The products from each run were fractionated through traps at -96°, -145°, -196° and activated charcoal at -196°. Gas chromatographic analysis of the fraction collecting at -196° on a 1-m. molecular sieve (5A) column at 30°, hydrogen carrier, flow rate 60 ml./min., gave a sharp peak corresponding to hexafluoroethane, trifluoromethane being adsorbed on the

Fig. 10. Arrhenius Plot of $\log_{10} k$ against $1/T$.



column. Calibration of the column with samples of hexafluoroethane measured in the gas burette enabled the quantity of hexafluoroethane formed in the reaction to be estimated from the height of the hexafluoroethane peak.

From a series of runs at trifluoroacetaldehyde pressures of 100 and 200 mm. and reaction times between 1 and 5 mins., it was found that the amount of hexafluoroethane produced in the first minute of reaction was a good measure of the initial rate of hexafluoroethane formation. Accordingly a second series of runs was undertaken in which amounts of hexafluoroethane produced in one minute were measured at several pressures of trifluoroacetaldehyde. The results are given in Table 9 and Fig. 11. A log-log plot (Fig. 12) of the results gave a straight line the slope of which was found to be 2.0.

<u>Chain Length</u>: The chain length, Φ, was measured at 499° by determining the amounts of trifluoromethane and hexafluoroethane formed after 1 min. from 200 mm. of trifluoroacetaldehyde. The products from each run were fractionated as above and the fraction collecting at -196° measured in the gas burette. The quantity of hexafluoroethane in the fraction was obtained by gas chromatography using the method described above. On the assumption that Φ is equal to $R_{CF_3H}/2\,R_{C_2F_6}$, the average value of Φ was found to be 1,250.

Fig. 11. Variation of $R_{C_2F_6}$ with P_{CF_3CHO}.

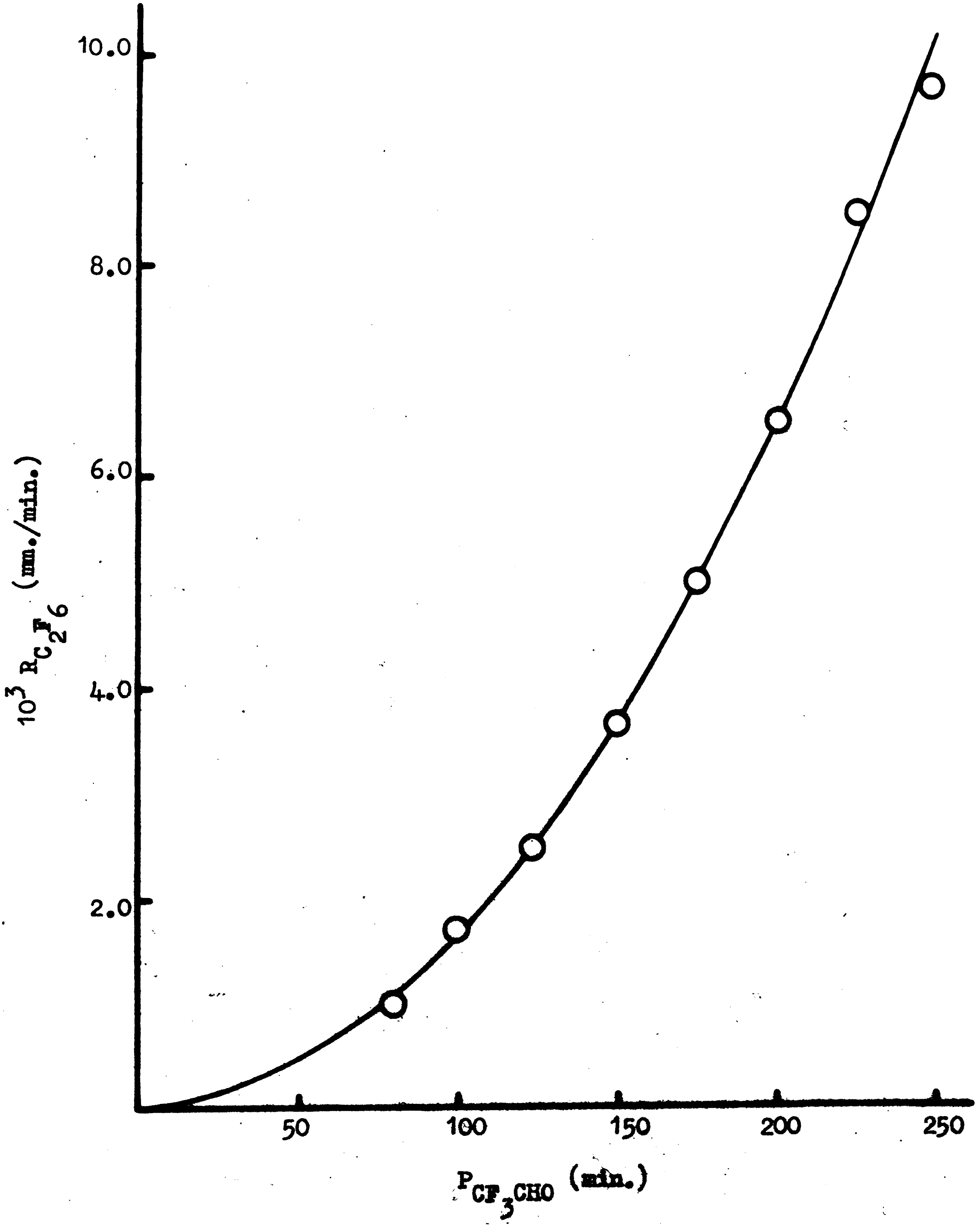


Fig. 12. Variation of $\log_{10} R_{C_2F_6}$ with $\log_{10} P_{CF_3CHO}$.

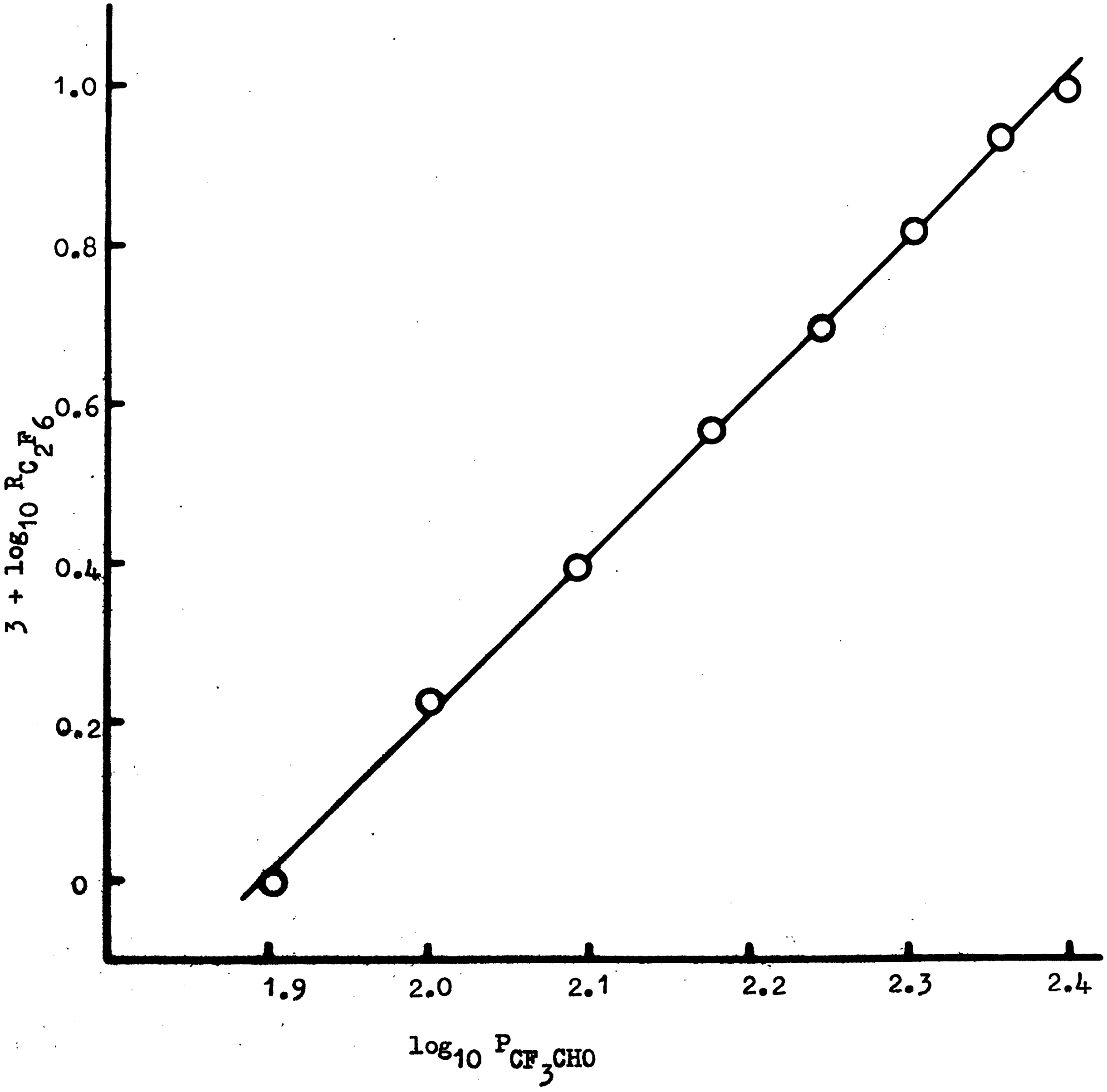


Table 6

Variation of Initial Rate (R) with Initial Pressure of CF_3CHO (P_{CF_3CHO}).

R in mm./min. P_{CF_3CHO} in mm. Temp. in °C.

471.5°		480°		488.5°		496°	
P_{CF_3CHO}	R	P_{CF_3CHO}	R	P_{CF_3CHO}	R	P_{CF_3CHO}	R
33.1	0.41	17.8	0.21	21.1	0.35	22.6	0.65
36.1	0.42	19.8	0.21	29.3	0.62	32.8	0.81
47.4	0.56	29.1	0.43	45.8	1.07	45.8	1.55
63.2	0.92	32.3	0.40	46.8	1.13	57.8	2.04
76.9	1.22	39.8	0.63	56.2	1.44	72.4	2.98
91.8	1.62	44.6	0.68	64.5	1.83	84.8	3.77
105.1	2.03	58.8	1.09	75.0	2.38	100.6	4.87
121.3	2.43	72.6	1.62	84.1	2.75	114.4	6.12
136.1	2.84	86.7	1.90	103.2	3.78	136.3	7.85
150.9	3.30	101.0	2.48	110.0	4.32	152.1	9.11
164.0	3.80	114.0	3.14	127.3	5.18	162.5	10.28
181.3	4.46	127.7	3.71	140.9	6.05	181.3	11.93
		143.3	4.47	156.6	7.13		
		155.2	4.56	166.8	7.78		
		171.2	5.51	174.3	8.21		
		184.2	6.41				

(contd.)

Table 6, contd - Variation of R with P_{CF_3CHO}.

502.5°		510.5°		519°	Temp.
P_{CF_3CHO}	R	P_{CF_3CHO}	R	P_{CF_3CHO}	R
17.6	0.44	14.5	0.40	32.9	1.95
37.9	1.42	16.8	0.55	46.3	4.03
51.6	2.30	20.8	0.88	55.6	5.03
77.5	4.51	25.4	1.29	73.7	7.80
101.7	6.83	32.6	1.77	90.3	11.18
122.8	9.02	45.5	2.74	105.4	13.52
137.4	11.09	58.9	3.97	121.0	15.86
153.3	12.89	69.4	5.01	135.9	18.98
171.1	15.21	82.3	7.09	155.4	23.40
187.8	17.79	96.8	8.79	167.3	26.52
197.2	19.01	111.0	10.87	183.5	31.20
		124.0	12.47		
		139.2	15.31		
		152.2	17.01		
		182.0	22.30		
		188.2	23.91		

Table 7

Variation of R with P_{CF_3CHO} for Packed Vessel.

R in mm./min. P_{CF_3CHO} in mm. Temp. in °C.

488.5°		496°		502.5°	
P_{CF_3CHO}	R	P_{CF_3CHO}	R	P_{CF_3CHO}	R
88.7	3.37	27.0	0.75	51.4	2.95
102.8	4.20	36.7	1.35	77.6	5.18
111.6	4.71	45.1	1.57	92.0	6.52
120.9	5.20	52.3	1.75	100.7	7.45
132.1	6.16	63.2	2.52	112.2	8.94
134.4	6.40	78.4	3.60	121.6	10.28
149.4	7.41	92.0	4.67	137.0	12.00
157.5	8.10	106.1	5.75	142.5	12.60
177.5	9.80	136.3	8.45	159.8	15.19
189.3	10.77	148.7	9.43	174.5	17.27
		161.4	10.78		
		179.3	12.76		

Table 8

Variation of k with Temperature.

k in $l.^{\frac{1}{2}}mole^{-\frac{1}{2}}sec.^{-1}$ Temp. in ^{o}C.

Temp.	471.5	480	488.5	496	502.5	510.5	519
10^3k (Empty vessel)	6.47	9.25	13.15	17.81	24.93	33.90	45.64
10^3k (Packed vessel)			14.97	19.24	27.69		

Table 9

Variation of $R_{C_2F_6}$ with P_{CF_3CHO}.

$R_{C_2F_6}$ in mm./min. P_{CF_3CHO} in mm. Temp. 499°C Reaction time 1 min.

P_{CF_3CHO}	$10^{-4}\ R_{C_2F_6}$
80	9.9
100	16.8
123	24.7
150	36.5
175	49.3
200	65.1
227	84.8
250	96.6

Effect of Inert Gases: The effect of the inert foreign gases carbon monoxide and carbon dioxide on the rate of reaction was investigated at 488.5°. A series of experiments were carried out in which a fixed pressure of trifluoroacetaldehyde was pyrolysed in the presence of varying pressures of carbon monoxide or carbon dioxide. The data obtained is given in Table 10. From Fig. 13, in which observed rates are plotted against pressure of inert gas, it can be seen that both carbon monoxide and carbon dioxide increase the rate of decomposition of trifluoroacetaldehyde, the effect of carbon dioxide being considerably greater than that of carbon monoxide.

Table 10

Variation of Rate with Pressure of CO.

Temp. 488.5°

P_{CF_3CHO} = 100 mm.			P_{CF_3CHO} = 75 mm.		
P_{CO}	R	R^2	P_{CO}	R	R^2
30	3.63	13.18	31	2.43	5.90
35	3.63	13.18	38	2.43	5.90
69	3.72	13.84	56	2.49	6.20
70	3.70	13.69	60	2.45	6.00
99	3.82	14.59	71	2.49	6.20
109	3.84	14.76	75	2.47	6.10
114	3.82	14.59	83	2.49	6.20
133	3.82	14.59	84	2.51	6.30

(contd.)

Table 10, contd. - Variation of Rate with Pressure of CO.

P_{CF_3CHO} = 100 mm.

P_{CO}	R	R^2
134	3.86	14.90
156	3.90	15.21
159	3.89	15.13

P_{CF_3CHO} = 75 mm.

P_{CO}	R	R^2
104	2.52	6.35
114	2.56	6.55
140	2.56	6.55
168	2.65	7.02

P_{CF_3CHO} = 50 mm.

P_{CO}	R	R^2
28	1.27	1.61
31	1.29	1.66
52	1.34	1.80
60	1.38	1.90
93	1.36	1.85
99	1.41	1.99
101	1.36	1.85
109	1.51	2.28
132	1.41	1.99
149	1.42	2.02
172	1.53	2.34

Table 10 (contd.)

Variation of Rate with Pressure of CO_2.

Temp. = 488.5°

P_{CF_3CHO} = 100 mm.

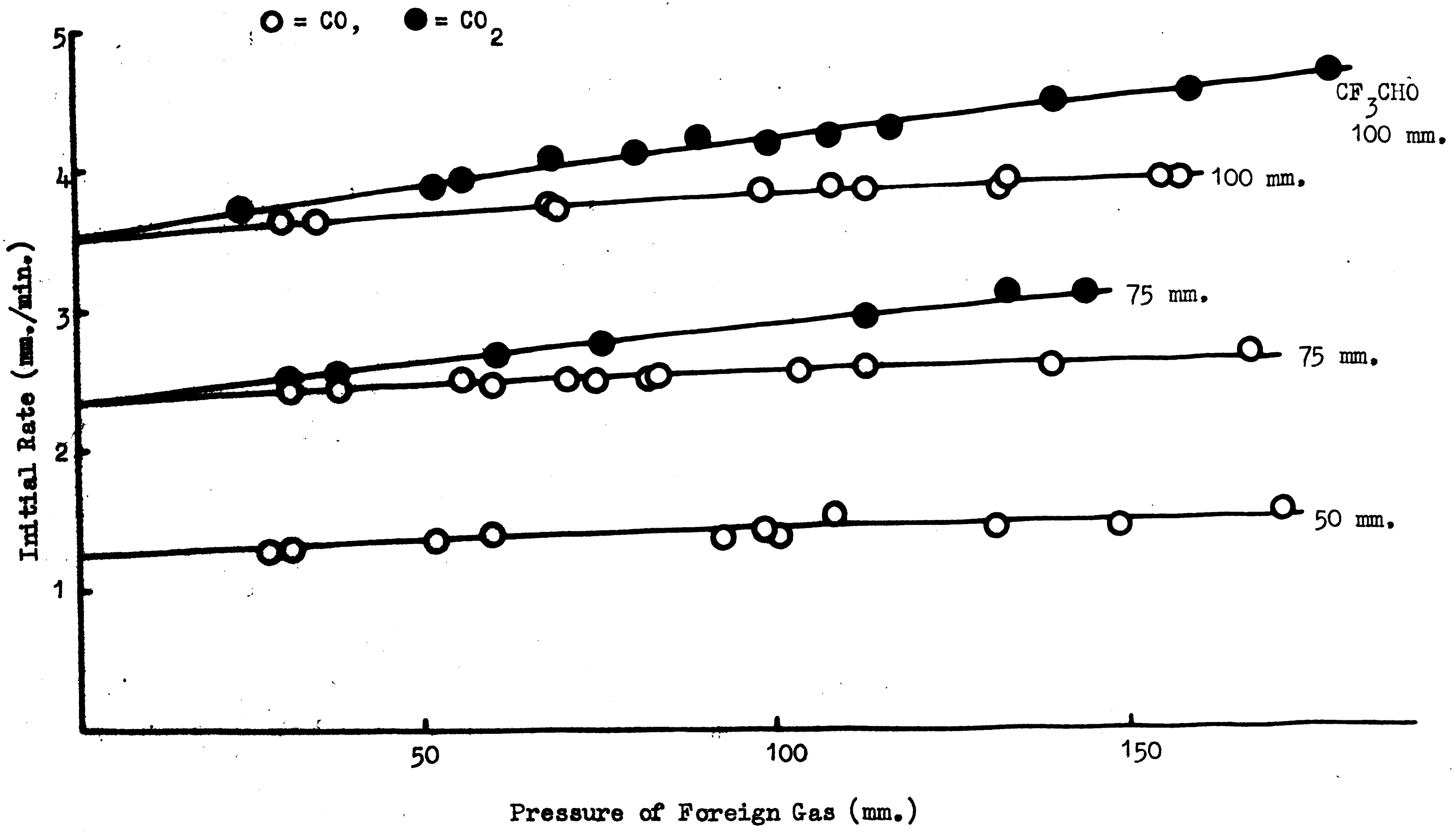
P_{CO}	R	R^2
24	3.72	13.84
52	3.86	14.90
56	3.90	15.21
69	4.06	16.48
81	4.10	16.81
90	4.10	16.81
100	4.18	17.47
109	4.20	17.64
118	4.25	18.06
141	4.44	19.71
160	4.50	20.25
180	4.63	21.44

P_{CF_3CHO} = 75 mm.

P_{CO}	R	R^2
31	2.50	6.25
38	2.53	6.40
61	2.66	7.08
76	2.75	7.56
114	2.91	8.47
134	3.09	9.55
145	3.08	9.49

Fig. 13. Variation of Initial Rate with Pressure of Foreign Gas.

P_{CF_3CHO} indicated on graph. Temperature 488.5°



Chapter 6

Discussion

The experimental order of 1.5 for the decomposition of trifluoroacetaldehyde can be explained by either a ${}^{1}\beta\beta_{3/2}$, ${}^{2}\beta\beta(X)_{3/2}$, or ${}^{2}\beta\mu_{3/2}$ mechanism. The accelerating effect of foreign gases must result from pressure dependent initiating and terminating reactions, and therefore a ${}^{2}\beta\beta(X)_{3/2}$ mechanism involving second order initiation and termination by the third order combination of trifluoromethyl radicals is postulated. The second order dependence of the rate of hexafluoroethane formation on the pressure of trifluoroacetaldehyde, and the overall kinetics of the decomposition, are shown to be predicted by such a mechanism. The products formed, namely trifluoromethane, carbon monoxide, hexafluoroethane, and hydrogen, are accounted for by conventional reactions of the intermediate radicals. Since attempts to find a suitable method for detection of hexafluoroacetone were unsuccessful, no allowance for its formation is made in the mechanism. This omission is justified to some extent by the fact that the trifluoroacetyl radical is less stable than the acetyl radical,[85,86,87] so that $\beta\mu$ termination would be most unlikely.

The observed surface effect is probably due to molecules of trifluoroacetaldehyde decomposing on the walls of the reaction vessel, but since the effect is small, this possibility is not included in the mechanism.

The following mechanism is postulated.

$$CF_3CHO + CF_3CHO \rightarrow CF_3 + CHO + CF_3CHO \qquad [1]$$

$$CF_3CHO + X \rightarrow CF_3 + CHO + X \qquad [1x]$$

$$CHO \rightarrow H + CO \qquad [2]$$

$$H + CF_3CHO \rightarrow H_2 + CF_3CO \qquad [3]$$

$$CF_3 + CF_3CHO \rightarrow CF_3H + CF_3CO \qquad [4]$$

$$CF_3CO \rightarrow CF_3 + CO \qquad [5]$$

$$CF_3 + CF_3 + CF_3CHO \rightarrow C_2F_6 + CF_3CHO \qquad [6]$$

$$CF_3 + CF_3 + X \rightarrow C_2F_6 + X \qquad [6x]$$

X represents a foreign gas molecule.

The rate equation predicted by this mechanism is derived in the following manner. At the steady state:

$$d[CF_3]/dt = k_1[CF_3CHO]^2 + k_{1x}[CF_3CHO][X] - k_4[CF_3][CF_3CHO] + k_5[CF_3CHO] - 2k_6[CF_3]^2[CF_3CHO] - 2k_{6x}[CF_3]^2[X] = 0$$

$$d[CHO]/dt = k_1[CF_3CHO]^2 + k_{1x}[CF_3CHO][X] - k_2[CHO] = 0$$

$$d[H]/dt = k_2[CHO] - k_3[H][CF_3CHO] = 0$$

$$d[CF_3CO]/dt = k_3[H][CF_3CHO] + k_4[CF_3][CF_3CHO] - k_5[CF_3CO] = 0$$

Solving these equations gives:

$$[CF_3] = \left\{\frac{k_1[CF_3CHO] + k_{1x}[X]}{k_6[CF_3CHO] + k_{6x}[X]}\right\}^{\frac{1}{2}} [CF_3CHO]^{\frac{1}{2}} \qquad (1)$$

Under conditions of long chain length the rate of loss of trifluoroacetaldehyde is given by:

$$-d[CF_3CHO]/dt = k_4[CF_3][CF_3CHO]$$

Hence the rate in the presence of foreign gas (X), R_x, is given by,

$$R_x = k_4\left\{\frac{k_1[CF_3CHO] + k_{1x}[X]}{k_6[CF_3CHO] + k_{6x}[X]}\right\}^{\frac{1}{2}}[CF_3CHO]^{\frac{3}{2}} \qquad (2)$$

and the rate in the absence of X, R, by:

$$R = k_4\left\{\frac{k_1}{k_6}\right\}^{\frac{1}{2}}[CF_3CHO]^{\frac{3}{2}} \qquad (3)$$

Experimentally it has been shown that $R = k[CF_3CHO]^{1.5}$. Hence k can be identified with $k_4k_1^{\frac{1}{2}}/k_6^{\frac{1}{2}}$, A with $A_4A_1^{\frac{1}{2}}/A_6^{\frac{1}{2}}$, and E with $E_4 + \frac{1}{2}E_1 - \frac{1}{2}E_6$. Insertion into this expression of 8.2 k.cal./mole for E_4 (Dodd and Smith[84]), and assuming E_6 to be zero, yields E_1 = 81.4 k.cal./mole. If the C-C bond strength in trifluoroacetaldehyde is similar to that in acetaldehyde (82.4 k.cal./mole), the value of 81.6 for E_1 is in excellent agreement. This may be compared with a similar calculation for acetaldehyde. The overall activation energy of Eusuf and Laidler[62] (47.6 k.cal.) and the value of 7.5 k.cal./mole for E_4 (Brinton and Volman[88]), yields E_1 = 80.2 k.cal./mole. Trenwith,[63] on the other hand, obtained a value of 70.5 k.cal. from experiments on the rate of hydrogen production.

Chain Length

The chain length in the absence of foreign gas can be calculated from the experimental results. From the postulated mechanism:

$$\text{Chain length} = \Phi = R_{CF_3H}/2\,R_{C_2F_6} = k_4/2k_1^{\frac{1}{2}}k_6^{\frac{1}{2}}[CF_3CHO]^{\frac{1}{2}}.$$

The data on the rate of formation of hexafluoroethane at 499°, with P_{CF_3CHO} = 200 mm., gives:

$$R_{C_2F_6} = 6.5 \times 10^{-3} \text{ mm./min.}$$

Interpolation on the Arrhenius plot at 499° gives:

$$R_{CF_3H} = dP/dt = k[CF_3CHO]^{\frac{3}{2}} = 15.9 \text{ mm./min.}$$

Hence $\Phi = 1200.$

This value agrees well with the average value of 1250 obtained by direct measurement of the trifluoromethane and hexafluoroethane in several runs.

The Rate of Hexafluoroethane Formation

The observed second order dependence of $R_{C_2F_6}$ on $[CF_3CHO]$ is also in agreement with the postulated mechanism. From the mechanism, in the absence of X,

$$R_{C_2F_6} = k_6[CF_3]^2[CF_3CHO]$$

From (1), $[CF_3]$ in the absence of X is given by:

$$[CF_3] = \left\{\frac{k_1}{k_6}\right\}^{\frac{1}{2}} [CF_3CHO]^{\frac{1}{2}}$$

Hence $R_{C_2F_6} = k_1[A]^2$

The Decomposition in the Presence of Inert Gases

A limiting case of equation (2) arises when $k_{6x}[X]$ is small compared with $k_6[CF_3CHO]$. This will be particularly true at low pressures of inert gas. Under these conditions (2) becomes:

$$R_x = k_4\left\{\frac{k_1}{k_6} + \frac{k_{1x}[X]}{k_6[CF_3CHO]}\right\}^{\frac{1}{2}} [CF_3CHO]^{\frac{3}{2}} \qquad (4)$$

When $[X] = 0$, (4) reduces to the expression for the rate in the absence of X, squaring (4) gives:

$$R_x^2 = \frac{k_1 k_4^2}{k_6} [CF_3CHO]^3 + \frac{k_{1x} k_4^2}{k_6} [CF_3CHO]^2[X] \qquad (5)$$

Hence, if the approximation made in deriving (4) is valid, a plot of R_x^2 against $[X]$ should be a straight line of slope $k_{1x}k_4^2[CF_3CHO]^2/k_6$. The results in Fig. 13 are plotted in this form in Fig. 14. Straight line characteristics are seen to hold, possibly fortuitously over the extended pressure range. Therefore the rate of decomposition in the presence of an inert gas can be expressed by:

$$R_x^2 = k'[CF_3CHO]^{\Upsilon} + k''[CF_3CHO]^{\Theta}[X] \qquad (6)$$

Since the first term in (6) represents the reaction when $[X] = 0$, Υ must take the value 3. The order Θ may be evaluated from the ratios of the slopes of the graphs in Fig. 14, making the assumption that k'' is independent of pressure in the experimental pressure range. The identity relating Θ to the slopes is:

$$\frac{\text{slope (1)}}{\text{slope (2)}} = \left\{\frac{[CF_3CHO\ (1)]}{[CF_3CHO\ (2)]}\right\}^{\Theta}$$

The values of Θ calculated from the various possible combinations of the graphs in Fig. 14 are given in Table 11. Small variations in the slopes markedly affect the value of Θ; the error involved is estimated to be approximately ± 25%.

Equation (6) may therefore be written:

$$_x^2 = k'[CF_3CHO]^3 + k''[CF_3CHO]^{2.2}[X] \qquad (7)$$

Fig. 14. Variation of R^2 with Pressure of Foreign Gas.

Temperature 488.5°

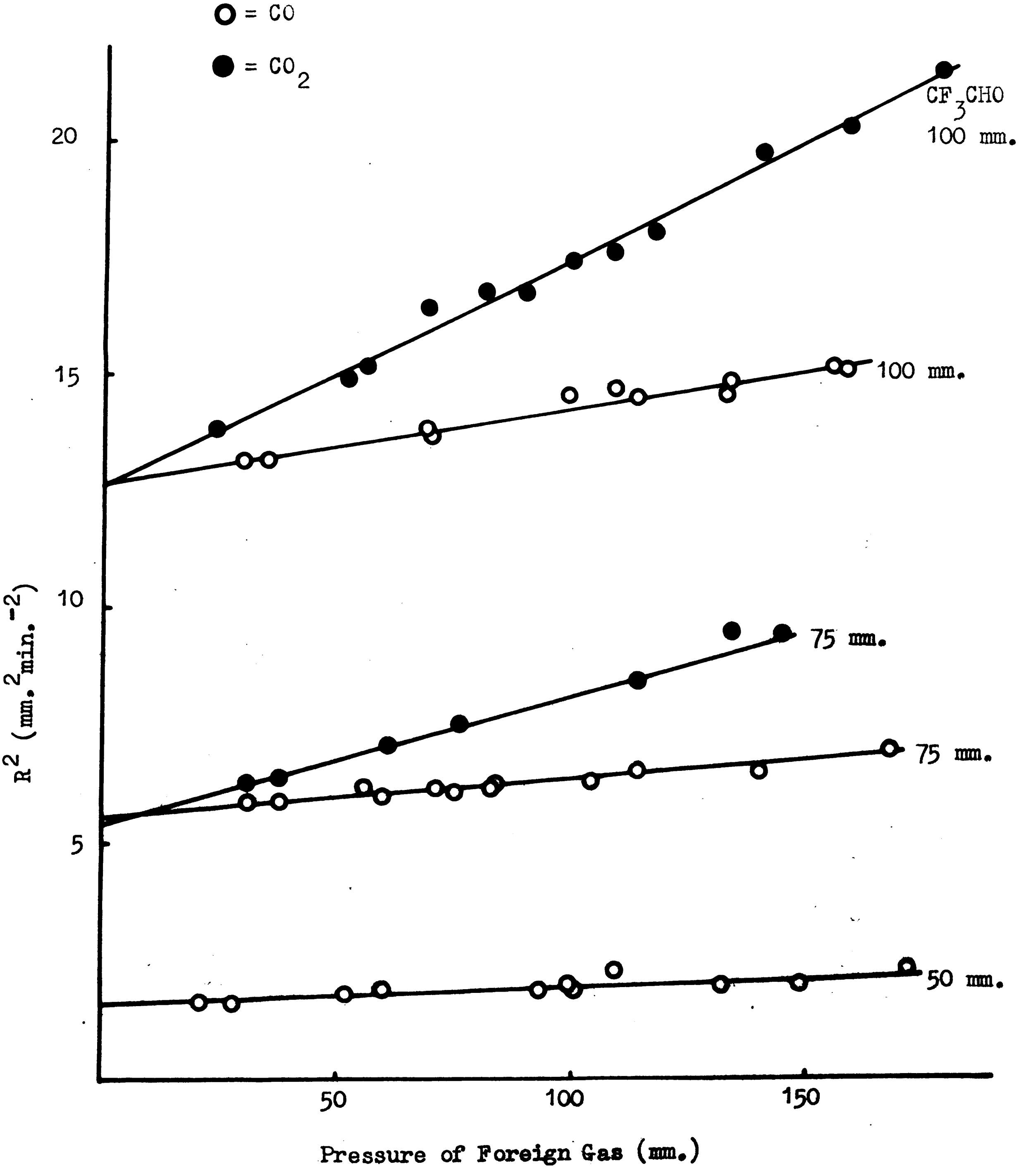


Table 11

Evaluation of the Order θ.

Inert gas	CO	CO	CO	CO_2
CF_3CHO (1)	100	100	75	100
CF_3CHO (2)	75	50	50	75
slope (1)/slope (2)	1.88	4.77	2.54	1.81
θ	2.2	2.25	2.3	2.1

which is of the same form as the theoretical expression (4) derived from the postulated mechanism.

From equations (2) and (3) the following relations for R_x/R can be derived:

$$\left(\frac{R_x}{R}\right)^2 = \frac{1 + k_{1x}[X]/k_1[CF_3CHO]}{1 + k_{6x}[X]/k_6[CF_3CHO]} \qquad (8)$$

$$= \frac{1 + r_i[X]/[CF_3CHO]}{1 + r_t[X]/[CF_3CHO]} \qquad (9)$$

If $k_{1x}/k_1 > k_{6x}/k_6$, equation (8) predicts an increase in rate with added foreign gas, and, for sufficiently high [X], equation (2) predicts a decrease in order with respect to trifluoroacetaldehyde. If $k_{1x}/k_1 < k_{6x}/k_6$, the rate is expected to decrease and the order to increase. Since both carbon monoxide and carbon dioxide accelerate the reaction, k_{1x}/k_1 must be greater than k_{6x}/k_6. The effect of inert gases on the order of reaction was determined for 100 mm. of inert gas by taking the square root of values read from Fig. 14, and plotting them in log-log form in Fig. 15. Because the variation of rate with foreign gas was investigated at only three CF_3CHO pressures, Fig. 15 cannot be considered accurate. Nevertheless, the slope of the line for results in the presence of carbon monoxide is less than 1.5, being approximately 1.35.

The relative efficiencies of CO and CO_2, compared with CF_3CHO, in initiation and termination can be obtained by evaluating r_i and r_t using equation (9). Values of r_i and r_t derived from Fig. 14 for an inert gas pressure of 100 mm. are shown in Table 12. Small variations in the slopes and intercepts of the graphs affect the values of r_i and r_t to such an extent that the error of ± 50% estimated by Laidler and Trenwith must be considered conservative.

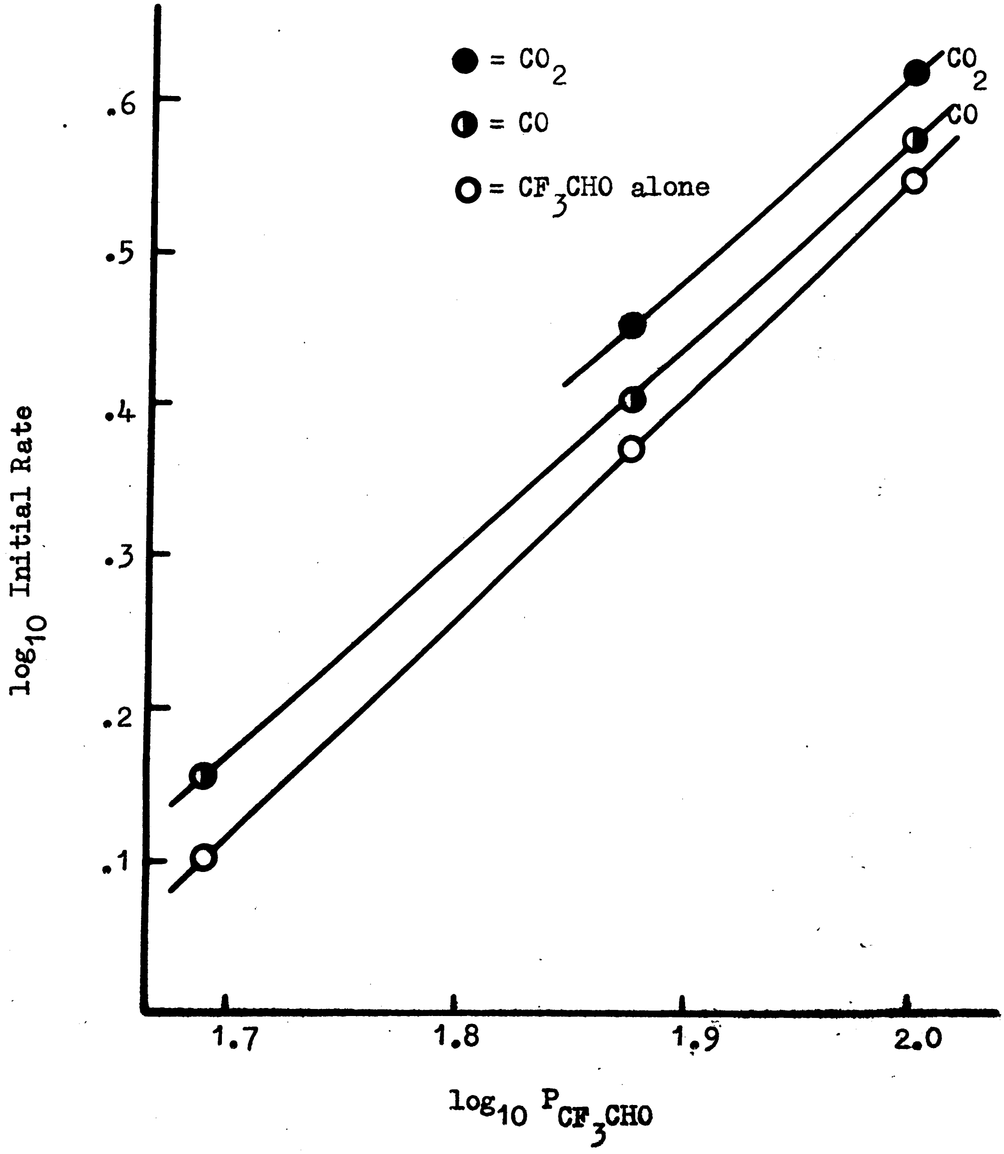
Table 12

Values of r_i and r_t.

Inert gas (100 mm.)	CO	CO	CO	CO_2
CF_3CHO (1)	100	100	75	100
CF_3CHO (2)	75	50	50	75
r_i	0.56	0.42	0.34	0.61
r_t	0.38	0.25	0.19	0.15

It is apparent that neither carbon monoxide nor carbon dioxide is as efficient as trifluoroacetaldehyde in promoting initiation and termination.

Fig. 15. Variation of $\log_{10}$ Rate with $\log_{10} P_{CF_3CHO}$ in the Presence of 100 mm. of Foreign Gas.



Chapter 7

Experimental

Materials

Trifluoroacetaldehyde, prepared from trifluoroacetaldehyde hydrate, supplied by the Columbia Organic Chemicals Co., by dehydration over phosphorus pentoxide, was fractionated through traps at -78°, -96°, -145°, and -196°. The fraction collecting at -145° was thoroughly degassed and stored at liquid air temperature.

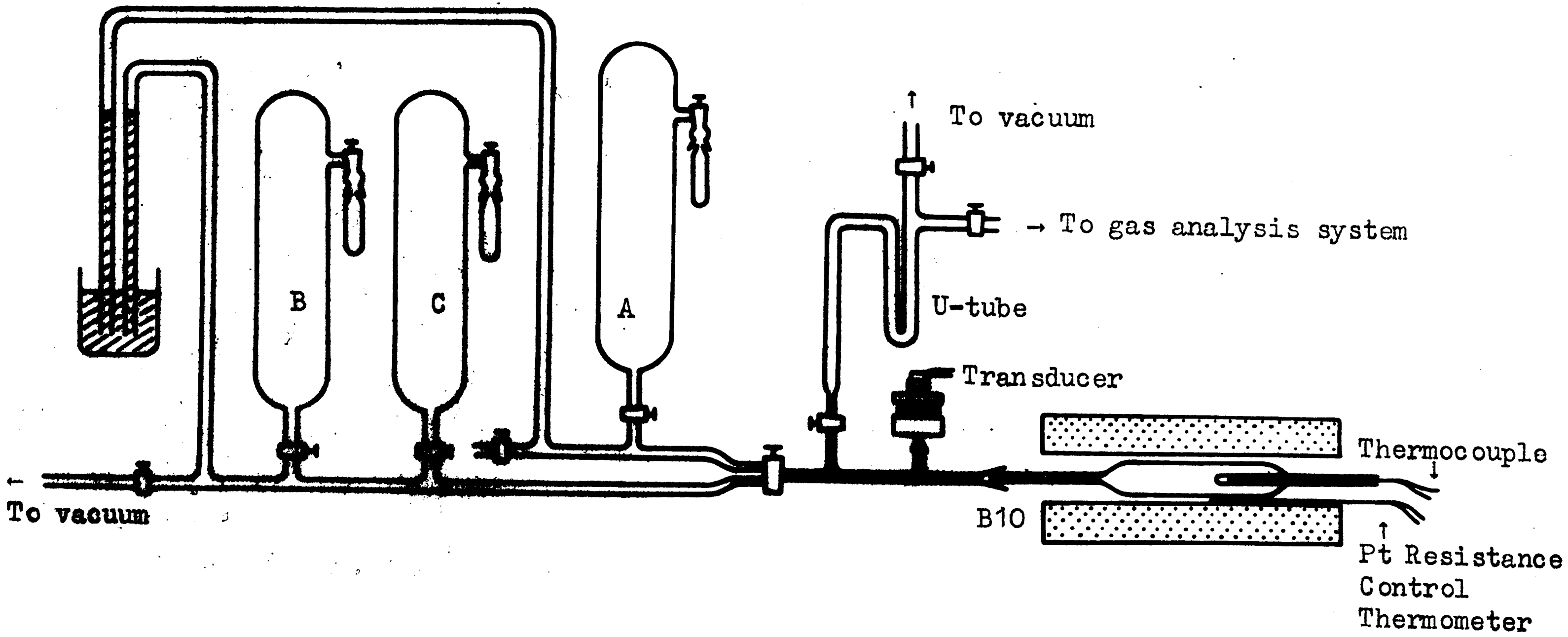
Carbon dioxide was obtained by the evaporation of "drikold". It was fractionated as for trifluoroacetaldehyde, the fraction collecting at -145° being retained after thorough degassing.

Carbon monoxide (High Purity Cylinder Grade) was passed through a liquid air trap, then over finely divided copper at 200° to remove any oxygen present, again through a liquid air trap, and stored ready for use.

Apparatus

A conventional high vacuum apparatus constructed of Pyrex glass was used. It consisted of a section for gas purification and storage, a reaction vessel with associated sampling bulbs (illustrated in Fig. 16), and a gas analysis section comprising a gas burette and six traps (illustrated in Fig. 1). These sections were connected by a main line to the pumping system which consisted of a mercury diffusion pump, backed by a two-stage rotary oil pump. Between the main line and the diffusion pump a trap cooled in liquid nitrogen prevented

Fig. 16. The Reaction System.



contamination of the pumps by condensable gases. The pressure in the main line was measured with a McLeod gauge.

The reaction vessels were of silica, capacity 155 ml., cylindrical in shape, and fitted with a thermocouple well extending to the centre of the vessel. One of the vessels was packed with short lengths of silica quill tubing. The reaction vessel was embedded in a tubular furnace and connected to the rest of the system through capillary tubing and a ground cone and socket joint sealed with Picein wax. Before use the reaction vessels were cleaned by etching with 10% hydrofluoric acid followed by washing with distilled water.

The reaction vessel was maintained at $\pm$ 0.5° of the required temperature with a Sunvic platinum resistance temperature controller, type RT2. The temperature of the reaction vessel was measured by means of a Chromel-Alumel thermocouple in conjunction with a Doran potentiometer. A second thermocouple was used as a reference for regular checking of the thermocouple in use.

Rate Measurement

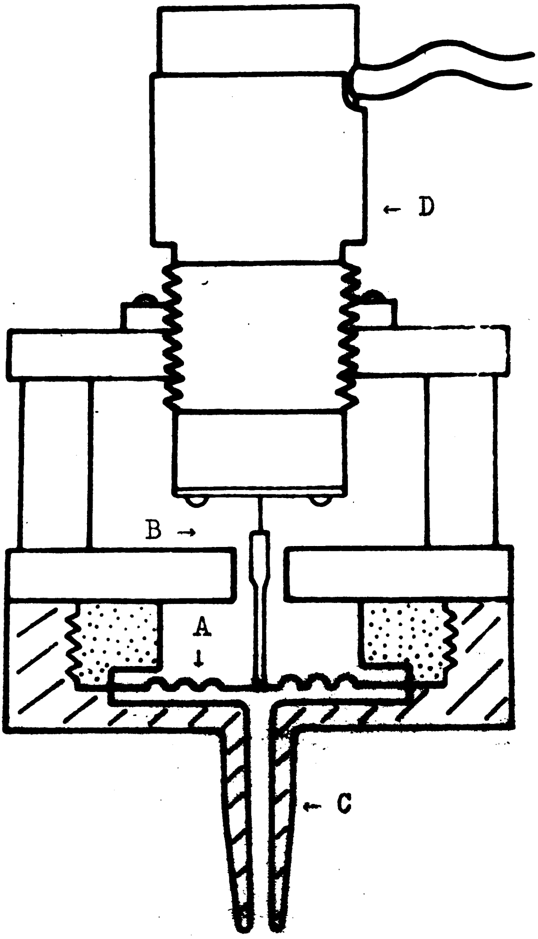
A diagrammatic representation of the reaction system is given in Fig. 16. The dead space outside the reaction vessel was reduced to a minimum by use of capillary tubing. The sampling bulbs, A, B, and C, were filled with trifluoroacetaldehyde, carbon monoxide, and carbon dioxide respectively. The gases were admitted separately to the reaction vessel, the time between successive additions being 4 seconds.

The reaction is accompanied by an increase in pressure, and it has been shown that the rate of change of pressure with time is a measure of the rate of reaction. Pressures in the reaction vessel were measured with a transducer arrangement consisting of an inductive displacement pick-up, Philips type PR9310, in conjunction with a Philips measuring bridge, type PR9300, and recorder, type PR2210. Pressure changes were transmitted to the transducer through a metal diaphragm, the probe of the pick-up being in direct contact with the centre of the diaphragm. The mounting arrangement is shown in Fig. 17, and the position of the transducer relative to the reaction vessel in Fig. 16.

The probe of the pick-up carries a small "Ferroxcube" core which moves axially in a non-magnetic tube on which a primary and two secondary coils are wound. Movement of the probe varies the degree of coupling between the primary coil (fed with an alternating voltage) and the two secondary coils, the connections of the latter being so arranged as to produce voltages which are opposite in phase. The differential voltage so produced is then measured by the bridge and recorded.

A number of materials were tried for the diaphragm; stainless steel and brass gave poor reproducibility, possibly through a hysteresis effect. Phosphor bronze sheet of uniform thickness in the range 5 to 10 thousands of an inch proved satisfactory, and reproducible calibrations were achieved using this material. The diaphragm was circular in shape, 4 cm. in diameter, and it was found

Fig. 17. Pressure Transducer Arrangement.



A Diaphragm

B Moving pin of transducer

C B10 cone

D Transducer

that its performance was improved if the diaphragm was indented with concentric circles.

In operation it was shown that the recorder deflection was linearly proportional to the pressure over a range of 25 mm. using the most sensitive bridge setting. Slight curvature of the calibration was observed over a range of one atmosphere using the least sensitive bridge setting. Frequent checks of the calibration were made during the work using carbon monoxide as the calibrant gas. With the variable sensitivity of the bridge and recorder, coupled with the recorder's variable chart speed, well defined pressure-time curves could be directly recorded for all experimental conditions. Initial rates were measured from the pressure-time curves, which could be made essentially linear in the early stages of reaction by suitable choice of bridge and recorder sensitivity, and chart speed.

Analytical Procedure

Reaction mixtures were analysed using the analysis train shown in Fig. 1. This consisted of five traps connected in series, and also individually to a back line, through which each could be opened either to the gas burette or to the pump. One of these traps contained activated charcoal which had been degassed by heating at 300° under vacuum.

The condensable gases from the reaction vessel were trapped in the U-tube cooled in liquid nitrogen, while the non-condensable gases were adsorbed on the charcoal cooled in liquid nitrogen. The volume of the non-condensable fraction was obtained by heating the charcoal trap to 300° and collecting the gas in the gas burette.

The gas burette acted as a Toepler pump; the gas entering the large bulb was pushed beyond the ground float-valve when the mercury was raised, and the valve sealed with a ring of mercury which prevented the gas returning when the mercury was lowered. By repeating this operation several times the gas was transferred from the trap to the calibrated bulbs; a small McLeod gauge indicated when transfer was complete. The pressure of the gas in the bulbs was measured with the manometer, M.

The condensable gases were fractionated through traps at -78°, -96°, -145°, and -196°, and the volume of any fraction could be measured in the gas burette using the above procedure.

Products were analysed by means of a Perkin-Elmer 154-C gas chromatograph, and a Perkin-Elmer model 21 infrared spectrometer.

Calculation of the Experimental Rate Constant, k, from Recorded Curves

The initial rate, R, in mm./min. is given by:

$$R = d.s.c.$$

where d is the slope of the recorded curve in chart divisions/cm., s is the chart speed in cm./min., and c is the diaphragm calibration in mm./chart division.

From the slopes of the plots of R against $(P_{CF_3CHO})^{1.5}$ in Fig. 9, k_m ($mm.^{-\frac{1}{2}}min.^{-1}$) may be obtained for each temperature. To convert k_m to k ($l.^{\frac{1}{2}}mole^{-\frac{1}{2}}sec.^{-1}$) involves conversion of concentration in mm. to moles/l. thus:

$$PV = nRT$$

Therefore $\frac{n}{V} = \frac{P}{RT}$

If $R = 82.057 \times 10^{-3}$ l.atm.deg.$^{-1}$mole^{-1}, then concentration in moles/l. is given by:

$$C = \frac{P}{82.057 \times 10^{-3} \times 760\ (T + 273.2)}$$

$$= \frac{0.01604\ P}{T + 273.2}$$

where P is in mm. and T is the temperature in ^{o}C. Hence $k = f.\ k_m$, where f is the conversion factor, then k (l.$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$sec.$^{-1}$) is given by:

$$k = \frac{k_m}{60}\left\{\frac{0.01604}{T + 273.2}\right\}^{\frac{1}{2}}$$

Therefore $f = \frac{1}{60}\left\{\frac{0.01604}{T + 273.2}\right\}^{\frac{1}{2}}$

SECTION III

THE ABSTRACTION OF HYDROGEN ATOMS FROM HYDROGEN SULPHIDE BY TRIFLUOROMETHYL RADICALS

Chapter 8

Introduction

Sources of Trifluoromethyl Radicals

Early kinetic studies of the reactions of trifluoromethyl radicals yielded little accurate data because of the lack of suitable radical sources. Attempts to use the pyrolyses of $(CF_3)_3As$ and $(CF_3)_3Sb$ to provide trifluoromethyl radicals[1] were limited by the occurrence of side reactions. The photolysis of trifluoroiodomethane[2-4] was complicated by the production of iodine atoms, and the fast back reaction with iodine led to a very low yield of trifluoromethyl radicals.

The most satisfactory source of trifluoromethyl radicals is the photolysis of hexafluoroacetone. Photolysis occurs readily at around 3000 Å with the production of carbon monoxide and hexafluoroethane in amounts approximating closely to the stoicheiometry (Ayscough and Steacie,[5] 1955):

$$(CF_3)_2CO = C_2F_6 + CO \qquad [1]$$

This stoicheiometry may be described by a mechanism involving reactions [2] and [3].

$$(CF_3)_2CO \xrightarrow{h\nu} 2\ CF_3 + CO \qquad [2]$$

$$2\ CF_3 \rightarrow C_2F_6 \qquad [3]$$

Thus carbon monoxide formation is a useful monitor of the rate of formation of trifluoromethyl radicals and of the primary photolytic act.

By analogy with the photolysis of acetone, the formation of the trifluoroacetyl radical might be expected to be important in the primary photochemical process,

$$(CF_3)_2CO \xrightarrow{h\nu} CF_3CO + CF_3 \qquad [4]$$

followed by decomposition of the trifluoroacetyl radical.

$$CF_3CO \rightarrow CF_3 + CO \qquad [5]$$

Perfluorobiacetyl would be expected to form through [6] if [4] occurred, but attempts to detect it have been unsuccessful.[5,6]

$$2\ CF_3CO \rightarrow (CF_3CO)_2 \qquad [6]$$

This indicates that even if [4] did occur, the trifluoroacetyl radical is more unstable than the acetyl radical and decomposes rapidly via [5] before reaction can occur. Thus reaction [2] adequately represents the primary process.

Some recent work on the photolysis in the presence of large amounts of the radical scavengers, bromine and chlorine (Tucker and Whittle,[6] 1965), has been interpreted in terms of the formation of trifluoroacetyl radicals. The trifluoroacetyl halide was formed, and it was proposed that this occurred by the reaction of trifluoroacetyl radicals with halogen molecules.

$$CF_3CO + Br_2 \rightarrow CF_3COBr + Br \qquad [7]$$

$$CF_3CO + Cl_2 \rightarrow CF_3COCl + Cl \qquad [7a]$$

When bromine atoms were produced in the presence of hexafluoroacetone there was no reaction, thus excluding the possibility that the trifluoroacetyl halide could be formed by a reaction not involving the trifluoroacetyl radical through addition of a halogen atom to the carbonyl bond of hexafluoroacetone.

$$(CF_3)_2CO + Br \rightarrow (CF_3)_2COBr \rightarrow CF_3COBr + CF_3 \qquad [8]$$

$$(CF_3)_2CO + Cl \rightarrow (CF_3)_2COCl \rightarrow CF_3COCl + CF_3 \qquad [8a]$$

A slight deviation of the stoicheiometry from that predicted by [1] has been observed, and the ratio C_2F_6:CO is probably closer to 0.96 (Boyd, Strachan, and Kutschke,[7] 1964). This discrepancy may in part be due to the formation of perfluoro t-butyl methyl ether, $(CF_3)_3COCF_3$, which has been found in the photolysis products (Gordon,[8] 1962). It was postulated that the ether is formed by addition of the trifluoromethyl radical to the carbonyl bond, followed by a radical combination reaction.

$$CF_3 + (CF_3)_2CO \rightarrow (CF_3)_2COCF_3$$

$$(CF_3)_2COCF_3 + CF_3 \rightarrow (CF_3)_3COCF_3$$

The quantum yield, based on carbon monoxide production approaches unity above 150° and at pressures of hexafluoroacetone up to 50 mm.[5] The quantum yield is reduced by foreign gases; this is expected if the absorption of radiation results in the formation of molecules in some vibrational level of an upper singlet electronic state, from which decomposition or collisional deactivation may occur. This is in accord with the fluorescence which accompanies the photolysis, the fluorescence occurring as a result of transitions from the zeroth vibrational level, reached through collisional deactivation, to the ground state.[7,9,10] Certain hydrocarbons, such as benzene and toluene, may be involved in chemical quenching, that is they appear capable of chemical reaction with the excited ketone molecule.[7]

In summary, the photolysis of hexafluoroacetone provides an almost ideal source of trifluoromethyl radicals for the study of their reactions with various substrates.

The photolysis of perfluoroazomethane has been used as a source of trifluoromethyl radicals, but this suffers from the disadvantage that the facile addition of trifluoromethyl radicals to the N=N bond competes strongly with substrate molecules for these radicals, reducing their stationary concentration to a low level.

$$CF_3N{=}NCF_3 \xrightarrow{h\nu} 2\ CF_3 + N_2$$

$$CF_3 + CF_3N{=}NCF_3 \rightarrow (CF_3)_2NNCF_3$$

The photolysis of trifluoroacetaldehyde, described in Chapter 4, has also been used as a source of trifluoromethyl radicals.

Abstraction Reactions of Trifluoromethyl Radicals

If CF_3 radicals are produced in the presence of a hydrogen-containing substrate, RH, trifluoromethane is formed by hydrogen abstraction,

$$CF_3 + RH \rightarrow CF_3H + R \qquad [9]$$

and the following reactions also occur.

$$CF_3 + R \rightarrow CF_3R \qquad [10]$$

$$R + R \rightarrow R_2 \qquad [11]$$

$$CF_3 + CF_3 \rightarrow C_2F_6 \qquad [3]$$

According to this scheme, the rate of formation of CF_3H is given by:

$$R_{CF_3H} = k_9[CF_3][RH]$$

and the rate of formation of C_2F_6 by,

$$R_{C_2F_6} = k_3[CF_3]^2$$

whence $$\frac{R_{CF_3H}}{R^{\frac{1}{2}}_{C_2F_6}[RH]} = \frac{k_9}{k_3^{\frac{1}{2}}} = \frac{A_9 \; 2^{-(E_9 - \frac{1}{2} E_3)/RT}}{A_3^{\frac{1}{2}}} \qquad (1)$$

It is therefore possible to determine k_9 if k_3 is known. k_3 has been measured by Ayscough as $k_3 = 2.3 \times 10^{13}$ cc.mole^{-1} sec.$^{-1}$, and the assumption is usually made that the energy of recombination of trifluoromethyl radicals, E_3, is zero.

Equation (1) has been used to obtain the Arrhenius parameters for hydrogen abstraction by trifluoromethyl radicals (produced by photolysis of hexafluoroacetone) from methane, ethane, propane, n-butane, isobutane, and the hydrogen isotopes (Ayscough et al.,[11,12,13] 1956).

Equation (1) was also used by Calvert et al. to obtain data on hydrogen abstraction from trifluoroacetone[14] and trifluoroacetophenone.[15] This method could not be applied to the study of secondary reactions of trifluoromethyl radicals produced by photolysis of perfluoroazomethane for reasons already discussed. An alternative procedure was devised in which the rate of a series of reactions of type [9] were compared with reaction [12],

$$CF_3 + D_2 \rightarrow CF_3D + D \qquad [12]$$

by measuring the ratio CF_3H/CF_3D when perfluoroazomethane was photolysed in the presence of RH and D_2 (Trotman-Dickenson et al.,[16,17] 1956).

Data on hydrogen abstraction from methane, isobutane, and acetaldehyde have also been obtained using the photolysis of trifluoroacetaldehyde as the source of trifluoromethyl radicals. In this system, CF_3H is formed by [9a] in addition to [9].

$$CF_3 + CF_3CHO \rightarrow CF_3H + CF_3CO \qquad [9a]$$

and k_9 may be obtained from the expression

$$\frac{R_{CF_3H}}{R^{\frac{1}{2}}_{C_2F_6}[CF_3CHO]} = \frac{k_{9a}}{k_3^{\frac{1}{2}}} + \frac{k_9[RH]}{k_3^{\frac{1}{2}}[CF_3CHO}$$

since k_{9a} is known from experiments on the photolysis of trifluoroacetaldehyde alone (Dodd and Smith,[18] 1957).

The activation energies, E_{CF_3}, for hydrogen abstraction from organic compounds by CF_3 radicals, obtained assuming $E_3 = 0$, are collected together in Table 13, where they are compared with the activation energies, E_{CH_3}, for the corresponding reactions of CH_3 radicals. E_{CH_3} are average values taken from the review of Pritchard and Miller.[19]

Alcock and Whittle[20] (1965) have studied the reactions of trifluoromethyl radicals, generated by the photolysis of hexafluoroacetone, with the methyl halides, CH_3X, where X = Cl, Br, I. It was found that trifluoromethyl radicals abstract the halogen from CH_3Br and CH_3I, but not from CH_3Cl; hydrogen was abstracted from all three.

$$CF_3 + CH_3X \begin{array}{ll} \nearrow CF_3H + CH_2X & \qquad [13] \\ \searrow CF_3X + CH_3 & \qquad [14] \end{array}$$

Equation (1) was used to obtain the Arrhenius parameters of the halogen and hydrogen transfer reactions, and the appropriate activation energies are listed in Table 14. The ratio k_{13}/k_{14} varied slightly

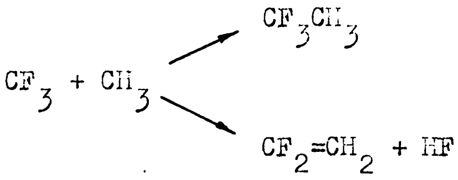
Table 13

Activation Energies for Hydrogen Abstraction by CF_3 and CH_3 Radicals.

	E_{CH_3} (k.cal./mole)	E_{CF_3} (k.cal./mole)
methane	13.9	9.5[16], 10.3[11], 10.4[18], 11.3[20]
ethane	11.0	7.3[17], 7.5[11]
propane	-	6.0[17], 6.5[12]
n-butane	8.3	5.1[12], 5.5[16]
isobutane	7.6	4.5[18], 4.7[12]
neopentane	10.0	7.4[17]
cyclopentane	8.8	4.5[29]
cyclohexane	8.3	5.0[17]
acetone	9.7	6.9[26], 7.8[17], 8.3[22]
trifluoroacetone	8.9	6.6[14]
trifluoroacetophenone	-	7.2[15]
acetaldehyde	7.2	4.0[18]
trifluoroacetaldehyde	-	8.2[18]
hydrogen	11.1	8.6[17], 9.5[13]
deuterium	12.0	10.2[13]
HD → CX_3H	10.0-10.7	10.5[13]
DH → CX_3D	10.7-11.3	10.5[13]

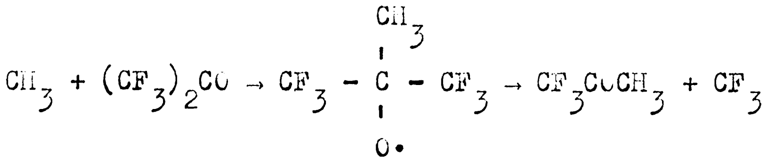
with CH_3Br pressure, and accordingly two sets of parameters were determined for low and high pressures of CH_3Br.

The reaction in the presence of CH_3I was more complicated than for the other halides in that as well as CF_3I, CO, C_2F_6 and CF_3H being formed, CF_3CH_3, $CF_2{=}CH_2$ and CF_3COCH_2 were detected in the products. CF_3CH_3 and $CF_2{=}CH_2$ were thought to result from the combination of trifluoromethyl and the methyl radicals formed in [14],



$$CF_3 + CH_3 \rightarrow CF_3CH_3 \qquad CF_3 + CH_3 \rightarrow CF_2{=}CH_2 + HF$$

and the formation of trifluoroacetone was postulated to occur by the addition of methyl radicals to the carbonyl bond of hexafluoroacetone



$$CH_3 + (CF_3)_2CO \rightarrow CF_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle O\cdot}{C}} - CF_3 \rightarrow CF_3COCH_3 + CF_3$$

rather than by βμ addition of radicals.

Table 14

Activation Energies of Halogen and Hydrogen Transfer Reactions.

CH_3X	E_{CF_3} for Abstraction of X	E_{CF_3} for Abstraction of H
CH_3Cl	>17	10.6
CH_3Br (low press.)	18.4	10.9
CH_3Br (high press.)	8.1	9.9
CH_3I	3.3	7.5
HBr		3.0

The reactions of trifluoromethyl radicals from photolysis of hexafluoroacetone with chlorine, bromine, iodine, and nitric oxide, have recently been investigated by Tucker and Whittle[6] (1965). CF_3COBr and CF_3COCl were found in the products of the reactions with Br_2 and Cl_2 respectively, and the amounts formed were in accord with the materials balance

$$R_{CF_3COBr} = R_{CF_3Br} - 2\,R_{CO}$$

expected from the reactions:

$$(CF_3)_2CO \xrightarrow{h\nu} 2\,CF_3 + CO$$

$$CF_3CO + Br_2 \rightarrow CF_3COBr + Br$$

$$CF_3CO \rightarrow CF_3 + CO$$

It is also possible that chemical quenching by the reaction of bromine with excited hexafluoroacetone molecules occurs:

$$CF_3COCF_3^* + Br_2 \rightarrow CF_3COBr$$

In experiments with iodine, no CF_3COI was found. Since trifluoromethyl radicals abstract iodine from iodides, this could have been due to the occurrence of:

$$CF_3 + CF_3COI \rightarrow CF_3I + CF_3CO$$

The reaction of trifluoromethyl radicals with nitric oxide produced only CF_3NO and CO, thus favouring [2] as the primary process in the photolysis of hexafluoroacetone rather than [4].

Hydrogen abstraction from hydrogen bromide by trifluoromethyl radicals has been compared with the reactions

$$CF_3 + I_2 \rightarrow CF_3I + I \qquad [15]$$

$$CF_3 + Br_2 \rightarrow CF_3Br + Br \qquad [16]$$

by Tucker and Whittle[21] (1965). If hexafluoroacetone is photolysed with a mixture of HBr and I_2, and if CF_3I and CF_3H are formed only by [15] and [17],

$$CF_3 + HBr \rightarrow CF_3H + HBr \qquad [17]$$

then

$$\frac{R_{CF_3I}}{R_{CF_3H}} = \frac{k_{15}[I_2]}{k_{17}[HBr]} \qquad (2)$$

Equation (2) was found to hold and the ratio k_{15}/k_{17} was obtained.

In the photolysis of mixtures of hexafluoroacetone, HBr, and Br_2 there are two sources of CF_3Br, [16] and [18]:

$$CF_3 + Br \rightarrow CF_3Br \qquad [18]$$

If, however, [19] predominates over [18],

$$Br + Br + M \rightarrow Br_2 + M \qquad [19]$$

then

$$\frac{R_{CF_3Br}}{R_{CF_3H}} = \frac{k_{16}[Br_2]}{k_{17}[HBr]} \qquad (3)$$

This equation was found to be valid and k_{16}/k_{17} was determined. The values of $E_{17} - E_{15}$ and $E_{17} - E_{16}$ obtained were 2.98 and 2.17 k.cal./mole respectively.

It can be seen from Table 13 that the activation energy of hydrogen abstraction by CF_3 radicals from a particular substrate is usually approximately 3 k.cal./mole less than that of the corresponding CH_3 radical reaction. It has been suggested[12] that, as these energies were measured with reference to the recombination of radicals, the observed differences in activation energies could be accounted for by the highly polar nature of the C-F bond which could give rise to a positive energy of activation for the recombination of trifluoromethyl radicals. However, current thought indicates that the activation energy for the recombination of trifluoromethyl radicals is close to zero.[21]

Trotman-Dickenson et al.[17] have explained the difference in reactivity in terms of the idea that activation energies and electronegativities are related. It was shown that an increase in electronegativity of the attacking radical for the series,

$$R + CH_4 \rightarrow RH + CH_3$$

where R = CH_3, CF_3, H, Cl, is paralleled by a decrease in activation energy.

The activation energy for hydrogen abstraction by trifluoromethyl radicals might be expected to be less than that for methyl radicals if the bond strength of the CF_3-H bond was greater than that of the CH_3-H bond, but sufficiently accurate data on both of these bond energies is not available to test this suggestion adequately.

It should be noted that the relative reactivities of trifluoromethyl and methyl radicals towards hydrogen abstraction is the reverse of that indicated by Table 13 where the substrate is hydrogen bromide, E_{CF_3} being 3.0 k.cal./mole and E_{CH_3} being 1.4 k.cal./mole.[23] This was explained by Tucker and Whittle in terms of the lower electron density on the carbon atom of the CF_3 radical leading to higher repulsion forces between the HBr molecule and the CH_3 radical.

The Recombination of Trifluoromethyl Radicals

The rate of recombination of trifluoromethyl radicals was determined by Ayscough[24] (1956) using the rotating sector technique. The rate constant was calculated to be 2.3×10^{13} cc.mole^{-1}sec.$^{-1}$ at 127°. This is similar to the rate of recombination of methyl radicals, 2.2×10^{13} cc.mole^{-1}sec.$^{-1}$ (Shepp,[25] 1956).

In order to determine the activation energy of the recombination of trifluoromethyl radicals, Pritchard and Dacey[26] (1960) photolysed mixtures of acetone and hexafluoroacetone and measured the relative rates of the reactions:

$$CF_3 + CH_3 \rightarrow CF_3CH_3 \qquad [20]$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad [21]$$

$$CF_3 + CF_3 \rightarrow C_2F_6 \qquad [3]$$

Using the relation

$$\emptyset = \frac{R_{CF_3CH_3}}{R^{\frac{1}{2}}_{C_2H_6}\,R^{\frac{1}{2}}_{C_2F_6}} = \frac{k_{20}}{k_{21}^{\frac{1}{2}}k_3^{\frac{1}{2}}}$$

$E_{20} - \frac{1}{2}(E_{21} + E_3)$ was found to be -1.07 k.cal./mole. If $E_{20} = E_{21} = 0$, $E_3 = 2.14$ k.cal./mole. Pritchard and Dacey pointed out that other combinations are possible and that the most general conclusion from their results was that all three recombination reactions have a small positive activation energy, the greatest being attributable to [3]. The values of $\emptyset$ obtained ranged between 1.8 and 3.5, while Dawidowicz and Patrick[27] deduced that $\emptyset = 1.7$ from the photolysis of trifluoroacetone.

Whether any of the reactions [20], [21] and [3], have an activation energy has recently been reinvestigated by Giles and Whittle[22] (1965) by photolysing mixtures of acetone and hexafluoroacetone. The products of the reaction were CO, CH_4, CF_3H, C_2F_6, CF_3CH_3, $CF_2{=}CH_2$, and CF_3COCH_3. It was postulated that $CF_2{=}CH_2$ resulted from the disproportionation of CF_3 and CH_3 radicals [22]

$$CF_3 + CH_3 \xrightarrow{[20]} CF_3CH_3^{*} \begin{cases} \xrightarrow{M} CF_3CH_3 & [20a] \\ \longrightarrow CF_2{=}CH_2 + HF & [22] \end{cases}$$

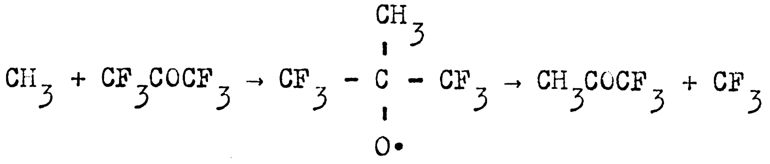
so that, assuming the same transition state for [20a] and [22], the preference for cross-combination of CF_3 and CH_3 radicals is described by:

$$\phi^{*} = \frac{R_{CF_3CH_3} + R_{CF_2=CH_2}}{R^{\frac{1}{2}}_{C_2H_6}\, R^{\frac{1}{2}}_{C_2F_6}} = \frac{k_{20}}{k_{21}^{\frac{1}{2}} k_3^{\frac{1}{2}}}$$

Using this identity, $E_{20} - \frac{1}{2}(E_{21} + E_3) = 0.17$ k.cal./mole, and it was concluded that it was no longer necessary to postulate $E_3 = 2$ k.cal./mole for trifluoromethyl radical combination.

The occurrence of reactions [20a] and [22] was supported by experiments in which the variation of $R_{CF_3CH_3}/R_{CF_2=CH_2}$ with pressure, temperature, and foreign gas was studied. It was found that as the temperature increased, [22] was favoured over [20a], and $E_{22} - E_{20a} = 1.1$ k.cal./mole. This explained the temperature dependence of ϕ and therefore the apparent activation energy deduced for [3].

Trifluoroacetone was considered to be formed by the addition of methyl radicals to the carbonyl group of hexafluoroacetone,



$$CH_3 + CF_3COCF_3 \rightarrow CF_3-\underset{O\bullet}{\overset{CH_3}{C}}-CF_3 \rightarrow CH_3COCF_3 + CF_3$$

rather than by βμ addition of radicals.

The Reaction of Trifluoromethyl Radicals with Nitrous Oxide

The photolysis of hexafluoroacetone in the presence of nitrous oxide was found by Bell and Kutschke[28] (1964) to yield carbon monoxide, hexafluoroethane, and nitrogen. The formation of nitrogen was explained in terms of the oxygen abstraction reaction

$$CF_3 + N_2O \rightarrow CF_3O + N_2 \qquad [23]$$

and the rate of [23] was measured by comparison with the recombination of trifluoromethyl radicals by means of the expression:

$$\frac{R_{CF_3H}}{R^{\frac{1}{2}}_{C_2F_6}[N_2O]} = \frac{k_{23}}{k_3^{\frac{1}{2}}}$$

The mass balance,

$$2\ CO = 2\ C_2F_6 + N_2$$

expected from reactions [2], [3], and [23], was found to hold. Because of the difficulty of measuring the small quantities of hexafluoroethane formed, the quantity $(CO - \frac{1}{2}N_2)$ was taken as a measure of the hexafluoroethane. Using Ayscough's value for [3], $k_{23} = 1.4 \times 10^{13} \exp(-24{,}000/RT)$ cc.mole^{-1}sec.$^{-1}$ Some uncertainty in k_{23} was introduced by the occurrence of the thermal decomposition of hexafluoroacetone at the temperature of the experiments (316-375°), and by the heterogeneous dark decomposition of nitrous oxide.

The work described in this section concerns the abstraction of hydrogen from hydrogen sulphide by trifluoromethyl radicals produced by photolysis of hexafluoroacetone, as part of a programme initiated to investigate the relative reactivities of CF_3, CD_3, and CH_3 radicals towards hydrogen abstraction from various inorganic substrates.

Chapter 9

Results and Discussion

A number of preliminary experiments were carried out in order to establish suitable conditions for rate studies. It was found that the efficiency of the abstraction process yielding trifluoromethane was such that sufficient hexafluoroethane for analysis was produced only at low pressures of hydrogen sulphide (less than 1.5 mm.) and at temperatures less than 110°, for pressures of hexafluoroacetone around 45 mm.

In order to determine whether the reaction was complicated by the photolysis of hydrogen sulphide, 14 mm. of hydrogen sulphide was photolysed at 95° for 45 mins. with the filtered radiation used in the rate determination. No hydrogen was detected indicating that the photolysis of hydrogen sulphide is unimportant in this work.

The possibility of the occurrence of a dark reaction was investigated by heating 39 mm. of hexafluoroacetone and 1 mm. of hydrogen sulphide for 9 mins. at 93.5°. Analyses for carbon monoxide, hexafluoroethane, and trifluoromethane proved to be negative.

A number of runs were carried out in which mixtures of hexafluoroacetone (approximately 45 mm.) and hydrogen sulphide (approx. 1 mm.) were photolysed at temperatures between 63 and 100.5° for periods of 5-15 mins. The volatile products were analysed by the method outlined in Chapter 10, and the results are given in Table 15. The non-condensable products contained carbon monoxide and hydrogen, while the volatile products passing through the absorption column

Table 15

The Photolysis of $(CF_3)_2CO$ in the Presence of H_2S.

P = pressure in mm. R = rate of formation in μ mole/min. $k_3/k_2^{\frac{1}{2}}$ in cc.$^{\frac{1}{2}}$mole$^{-\frac{1}{2}}$sec.$^{-\frac{1}{2}}$

Time in mins. Illuminated volume of reaction vessel = 173 ml.

Temp. °C	Time	P_{H_2S}	$P_{CF_3COCF_3}$	R_{CO}	R_{H_2}	$R_{C_2F_6}$	R_{CF_3H}	$\log(k_3/k_2^{\frac{1}{2}})$
63	12	0.91	38.9	-	-	0.00077	0.0625	2.447
73	12	0.92	40.6	-	-	0.00063	0.0359	2.522
73.5	15	1.05	44	-	-	0.00069	0.0419	2.510
81.5	15	1.05	44	0.0329	0.0027	0.00086	0.0538	2.579
87.5	9	1.05	43.7	0.0392	0.0030	0.0011	0.0623	2.596
99	6	1.00	42.4	-	-	0.00077	0.0625	2.716
100.5	9	1.05	43.8	0.0476	0.0008	0.0010	0.0737	2.698
100.5	6	1.04	43.6	0.0433	0.0017	0.00093	0.0658	2.678

Table 15 (contd.)

The Photolysis of $(CF_3)_2CO$ in the Presence of H_2S.

Temp. °C	$\frac{1}{2} R_{CF_3H} + R_{C_2F_6}$	$R_{CO} - (\frac{1}{2} R_{CF_3H} + R_{C_2F_6})$
63	0.0115	-
73	0.0185	-
73.5	0.0215	-
81.5	0.0278	0.0051
87.5	8.0323	0.0069
99	0.0321	-
100.5	0.0379	0.0097
100.5	0.0338	0.0095

consisted of trifluoromethane and hexafluoroethane. The formation of the products may be explained in terms of the following reactions:

$$(CF_3)_2CO \rightarrow 2\ CF_3 + CO \qquad [1]$$

$$2\ CF_3 \rightarrow C_2F_6 \qquad [2]$$

$$CF_3 + H_2S \rightarrow CF_3H + SH \qquad [3]$$

$$SH + SH \rightarrow H_2S + S \qquad [4a]$$

$$SH + SH \rightarrow H_2 + S_2 \qquad [4b]$$

The expected mass balance,

$$R_{CO} = \tfrac{1}{2} R_{CF_3H} + R_{C_2F_6}$$

is seen from Table 15 not to hold, not all the CF_3 radicals formed being accounted for in the products. The discrepancy, given by $R_{CO} - (\tfrac{1}{2} R_{CF_3H} + R_{C_2F_6})$ expressed as a percentage of R_{CO}, is about 18%. It is unlikely that the formation of $(CF_3)_3COCF_3$ could account for a deficiency of this size. However, the efficiency of reaction [3] will lead to the formation of a large number of SH radicals, so that the occurrence of the hetero radical recombination reaction [5] is highly probable.

$$CF_3 + SH \rightarrow CF_3SH \qquad [5]$$

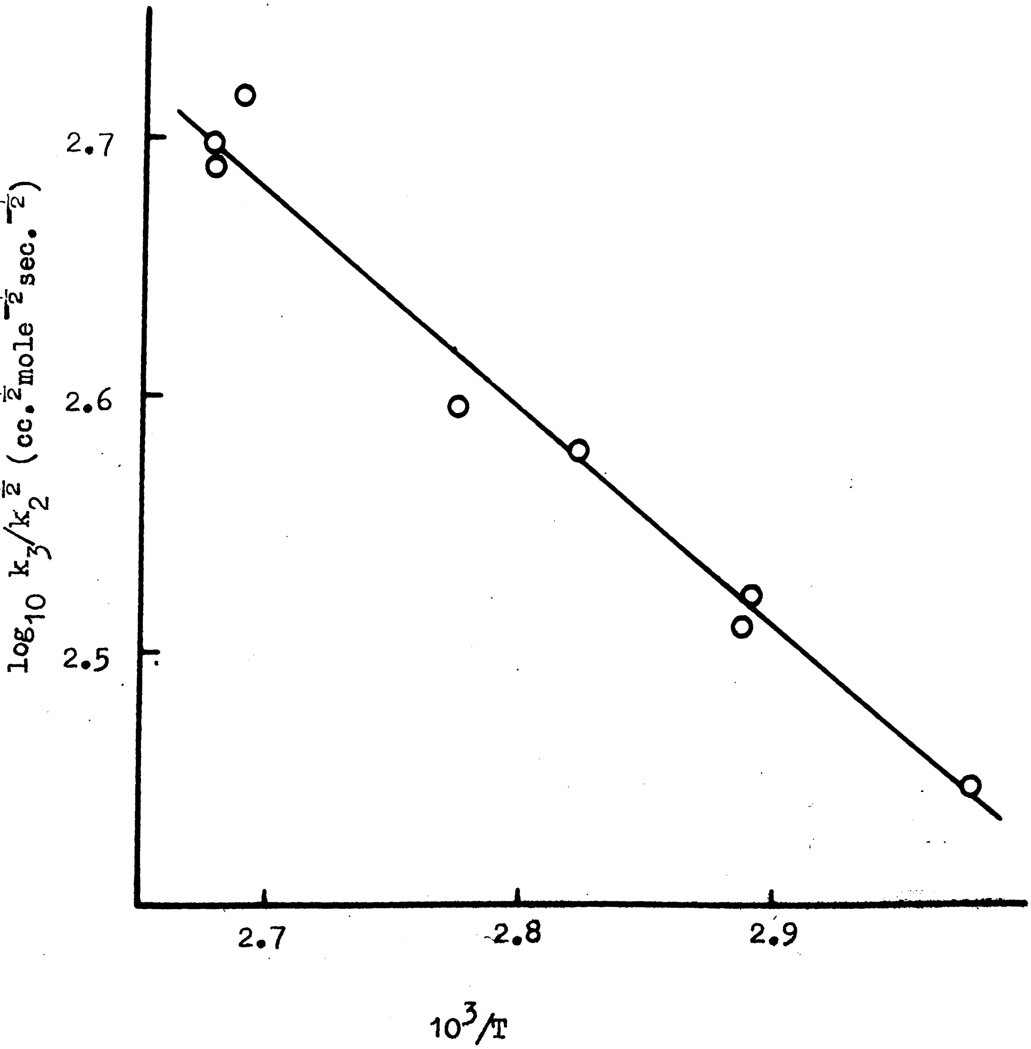
If reaction [5] plays a significant part in the reaction scheme, the expected mass balance would be,

$$R_{CO} = \tfrac{1}{2} R_{CF_3H} + \tfrac{1}{2} R_{CF_3SH} + R_{C_2F_6}$$

which could account for $(\tfrac{1}{2} R_{CF_3H} + R_{C_2F_6}) < R_{CO}$ in these experiments.

If trifluoromethane and hexafluoroethane are produced only by reactions [3] and [2] respectively, then

Fig. 18. Arrhenius Plot of $\log_{10} k_3/k_2^{\frac{1}{2}}$ against $1/T$.



$$\frac{R_{CF_3H}}{R^{\frac{1}{2}}_{C_2F_6}[H_2S]} = \frac{k_3}{k_2^{\frac{1}{2}}}$$

Thus measurement of R_{CF_3H} and $R_{C_2F_6}$ enables $k_3/k_2^{\frac{1}{2}}$ to be determined. The values of $k_3/k_2^{\frac{1}{2}}$ for various temperatures are given in Table 15. Even under the conditions described above, an extent of reaction (based on the ratio of CF_3H formed to H_2S present initially) of 5-8% was necessary to ensure sufficient hexafluoroethane for analysis.

An Arrhenius plot of log $k_3/k_2^{\frac{1}{2}}$ against 1/T is shown in Fig. 18. Evaluation of the data by the method of least squares leads to $E_3 - \frac{1}{2} E_2 = 3.88 \pm 0.26$ k.cal./mole. Using the value of $k_2 = 2.3 \times 10^{13}$ cc.mole^{-1}sec.$^{-1}$ obtained by Ayscough,[24] and assuming $E_2 = 0$, gives log $A_3 = 11.65 \pm 0.16$. Thus the rate constant for the abstraction of H atoms from H_2S by CF_3 radicals is given by:

$$k_3 = 10^{11.65 \pm 0.16}\, e^{(-3880 \pm 260)/RT} \text{ cc.mole}^{-1}\text{sec.}^{-1}$$

If A = pz, the steric factor, p, can be determined by calculating z, the collision number for CF_3-H_2S collisions. The collision number z', assuming one molecule of each kind per ml., is given by[30]:

$$z' = \frac{1}{4}(\sigma_{CF_3} + \sigma_{H_2S})^2 \left\{\frac{8\pi RT}{\mu}\right\}^{\frac{1}{2}}$$

where σ_{CF_3} and σ_{H_2S} are the collision diameters of CF_3 and H_2S respectively, R is the gas constant, T is the absolute temperature, and μ is the reduced mass, given by:

$$\mu = \frac{M_{CF_3} \cdot M_{H_2S}}{M_{CF_3} + M_{H_2S}}$$

M = molecular weight.

Substituting $\sigma_{CF_3} = 5$ Å (assumed), $\sigma_{H_2S} = 4.7$ Å (calculated), and $R = 8.314 \times 10^7$ ergs.deg.$^{-1}$ mole^{-1}, at 357 Å,

$$z' = \frac{1}{4}(5 + 4.7)^2\ 10^{-16} \left\{\frac{8\pi \times 8.314 \times 10^7 \times 357}{22.8}\right\}^{\frac{1}{2}}$$

$$= 4.25 \times 10^{-10} \text{ cc.sec.}^{-1}$$

The collision number z, for one mole of each species per ml., is therefore given by:

$$z = Nz' \text{ where } N = \text{Avogadro's number}$$

$$= 2.6 \times 10^{14} \text{ cc.mole}^{-1}\text{sec.}^{-1}$$

Experimentally,

$$A = 4.5 \times 10^{11} \text{ cc.mole}^{-1}\text{sec.}^{-1}$$

Hence $\qquad p = 1.7 \times 10^{-3}$

The collision diameter of H_2S, σ_{H_2S}, was calculated from the viscosity data of Rankine and Smith.[31] The viscosity, η, of a gas is given by the expression[32]

$$\eta = 0.499\ nm\bar{c}\lambda$$

where n = number of molecules per cc., m = mass of a molecule, $\bar{c}$ = mean molecular velocity, and λ = mean free path. From the relations:

$$\lambda = 1/\ 2\pi n\sigma^2$$

$$\bar{c} = \left\{\frac{8RT}{\pi M}\right\}^{\frac{1}{2}}$$

σ is given by:

$$\sigma^2 = \frac{0.499\ M}{2\pi\eta N}\left\{\frac{8RT}{\pi M}\right\}^{\frac{1}{2}}$$

$\eta = 116.6 \times 10^{-6}$ poises at 273° A and 1 atmosphere, hence

$$\sigma^2 = \frac{0.499 \times 34.1}{2\pi \times 116.6 \times 6.02 \times 10^{23}}\left\{\frac{8 \times 8.324 \times 10^7 \times 273.2}{34.1\ \pi}\right\}^{\frac{1}{2}}$$

$$= 22.5 \times 10^{-16}$$

Therefore

$$\sigma_{H_2S} = 4.7 \times 10^{-8} \text{ cm., i.e. } 4.7 \text{ Å}$$

The value of p is similar to the steric factors involved in hydrogen abstraction from many organic systems, and may be considered normal. The high rate of reaction is therefore due to the low activation energy which is considerably less than that for hydrogen abstraction from hydrocarbons by trifluoromethyl radicals. The ease of abstraction of hydrogen from the SH group is, however, well established. Kerr and Trotman-Dickenson[33] have estimated activation energies of 4.9 to 5.6 k.cal./mole for removal of this hydrogen from a series of thiols by methyl radicals. The reliability of these figures is difficult to assess owing to the lack of detail given in the paper; however, the figures are derived from an assumed A factor and rates were measured at one temperature only.

The reaction of methyl radicals with hydrogen sulphide is more directly comparable with the present results, and Imai and Toyama have made two studies of this abstraction. The first,[34] based on product analysis from the acetone-hydrogen sulphide system, gave:

$$k_6 = 10^{11.4}\ e^{-2600/RT}\ \text{cc.mole}^{-1}\text{sec.}^{-1}$$

for $$CH_3 + H_2S \rightarrow CH_4 + SH \qquad [6]$$

The second determination of k_6, from experiments in which acetaldehyde was photolysed in the presence of hydrogen sulphide, may be considered less reliable in that an overall rate of reaction based on pressure change was measured. The Arrhenius parameters of [6] were determined relative to the abstraction from acetaldehyde, reaction [7]

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \qquad [7]$$

A number of determinations of [7] have been[36] made allowing a range of possible values of E_6 between 2.8 and 4.0 k.cal./mole. A_6/A_7 was given as 1.7 ± 0.5. Reasonable agreement between the values of k_6 obtained by the different methods is apparent, and they are of the same order of magnitude as that found in this work for abstraction by trifluoromethyl radicals.

The abstraction of hydrogen from hydrogen sulphide by trifluoromethyl and methyl radicals can also be compared with the corresponding reactions of hydrogen bromide because of the similarity in physical properties of the two substrates. For example, hydrogen bromide has a bond length of 1.41 Å and a bond strength of 86.5 k.cal.,[37a] while hydrogen sulphide has a bond length of 1.34 Å,[37b] and values of 92 ± 2,[38a] 95.3,[38b] 89 ± 4,[38c] and < 90.6[38d] k.cal. have been obtained for its bond strength. On the assumption that iodine abstraction from I_2 has zero activation energy, Tucker and Whittle[21] obtained an activation energy of 3 k.cal./mole for [8].

$$CF_3 + HBr \rightarrow CF_3H + Br \qquad [8]$$

The activation energy for the corresponding methyl reaction, [9], was found by Fettis and Trotman-Dickenson[23] to be 1.4 k.cal./mole.

$$CH_3 + HBr \rightarrow CH_4 + Br \qquad [9]$$

It is noteworthy that the order of activation energies for CF_3 and CH_3 attack is the opposite of that shown by their reactions with hydrocarbons. This is considered by Tucker and Whittle to be due to the reduced electron density on the hydrogen atom of HBr (due to the polarity of the H-Br bond) in conjunction with the low electron density on the carbon atom of CF_3 compared with that of CH_3. Thus as the radicals approach an HBr molecule, repulsion forces will be greater for CF_3 than for CH_3; hence the increased activation energy for the CF_3 reaction.

If the value of 2.6 k.cal., obtained by Imai and Toyama for the activation energy of abstraction from hydrogen sulphide, is compared with the 3.9 k.cal. found in this work, the trend shown with HBr is also observed with hydrogen sulphide. The polarities of the S-H and H-Br bonds are similar (dipole moment, μ, for HBr is 0.78×10^{18} e.s.u., while μ for H_2S is 1.1×10^{18} e.s.u., giving μ for the S-H bond as 0.79×10^{18} e.s.u.) so that the relative reactivity of CF_3 and CH_3 towards hydrogen abstraction from hydrogen sulphide can also be explained in terms of the polarity of the substrate molecule.

Chapter 10

Experimental

Materials

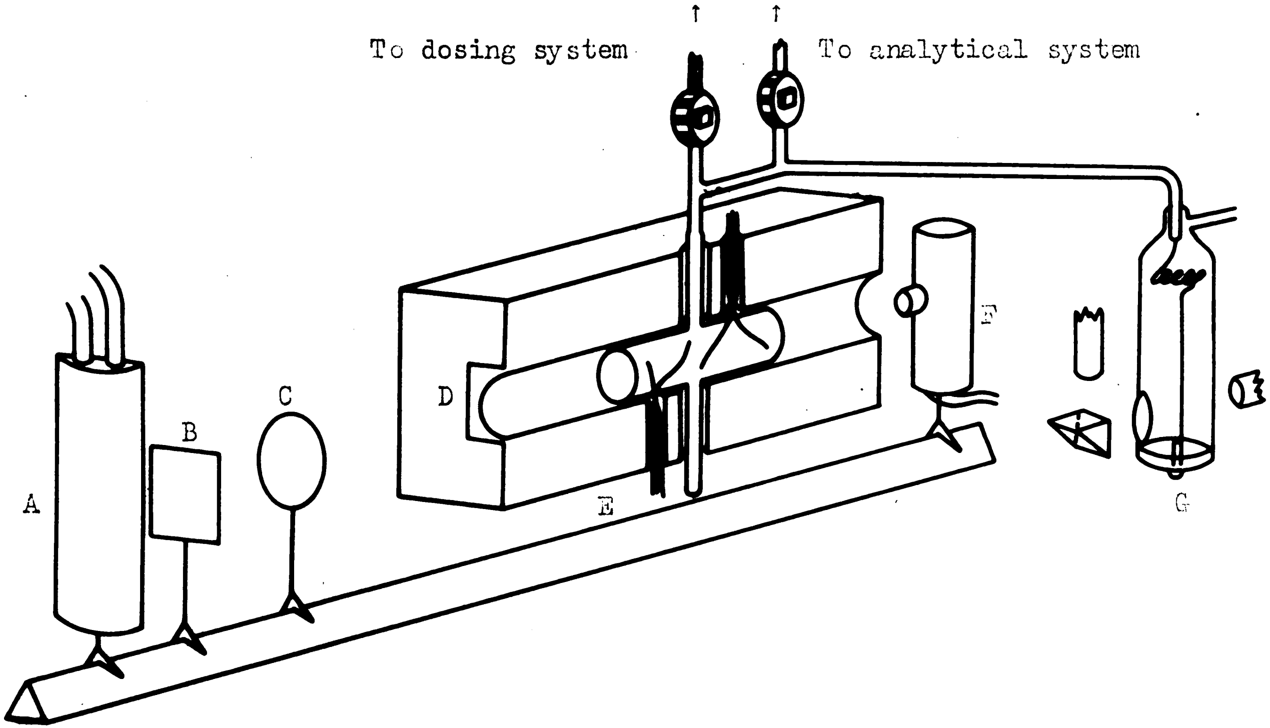
Hydrogen sulphide, generated from ferrous sulphide and sulphuric acid, was fractionated through traps at -78°, -96°, -145°, and -196°, the fraction collecting at -145° being retained and stored in a blackened bulb.

Hexafluoroacetone, obtained from a cylinder supplied by the Allied Chemical Corporation, was fractionated as above. The fraction condensing at -145° was thoroughly degassed at -145° in order to remove traces of CF_3H and C_2F_6, by repeatedly warming, and freezing and pumping. The hexafluoroacetone was stored in a blackened bulb at liquid nitrogen temperature.

Apparatus and Procedure

The photolysis was carried out in a quartz reaction vessel (illuminated volume 173 ml.) fitted with plane parallel windows, and suspended in a tubular furnace 15 inches long fitted with quartz end windows. Radiation was supplied by a Hanovia S500 mercury arc lamp filtered with Corning filters, colour specification 0-53 and 7-54, giving radiation in the range 2,800-4,200 Å. Light intensity was measured with an RCA 935 photocell and a Cambridge spot-galvanometer. Temperature was measured by six chromel-alumel thermocouples taped to the walls of the cell. Pressures in the reaction vessel were measured with a Pyrex spiral gauge used as a

Fig. 19. The Photolysis Apparatus.



A: Lamp and Housing, B: Filters, C: Lens, D: Quartz window,

E: Thermocouples, F: Photocell, G: Pressure Gauge system.

null instrument. The reaction vessel was connected through Hoke 413 stainless steel valves to the analytical and storage sections. The arrangement of the photolysis apparatus is illustrated in Fig. 19.

In operation, either fresh mixtures of the two reactants, or measured quantities of each reactant admitted singly, were introduced into the reaction vessel. The mixture was condensed into a small appendage protruding through the furnace and then pumped on for three minutes. After warming, a mixing time of 15 mins. was allowed.

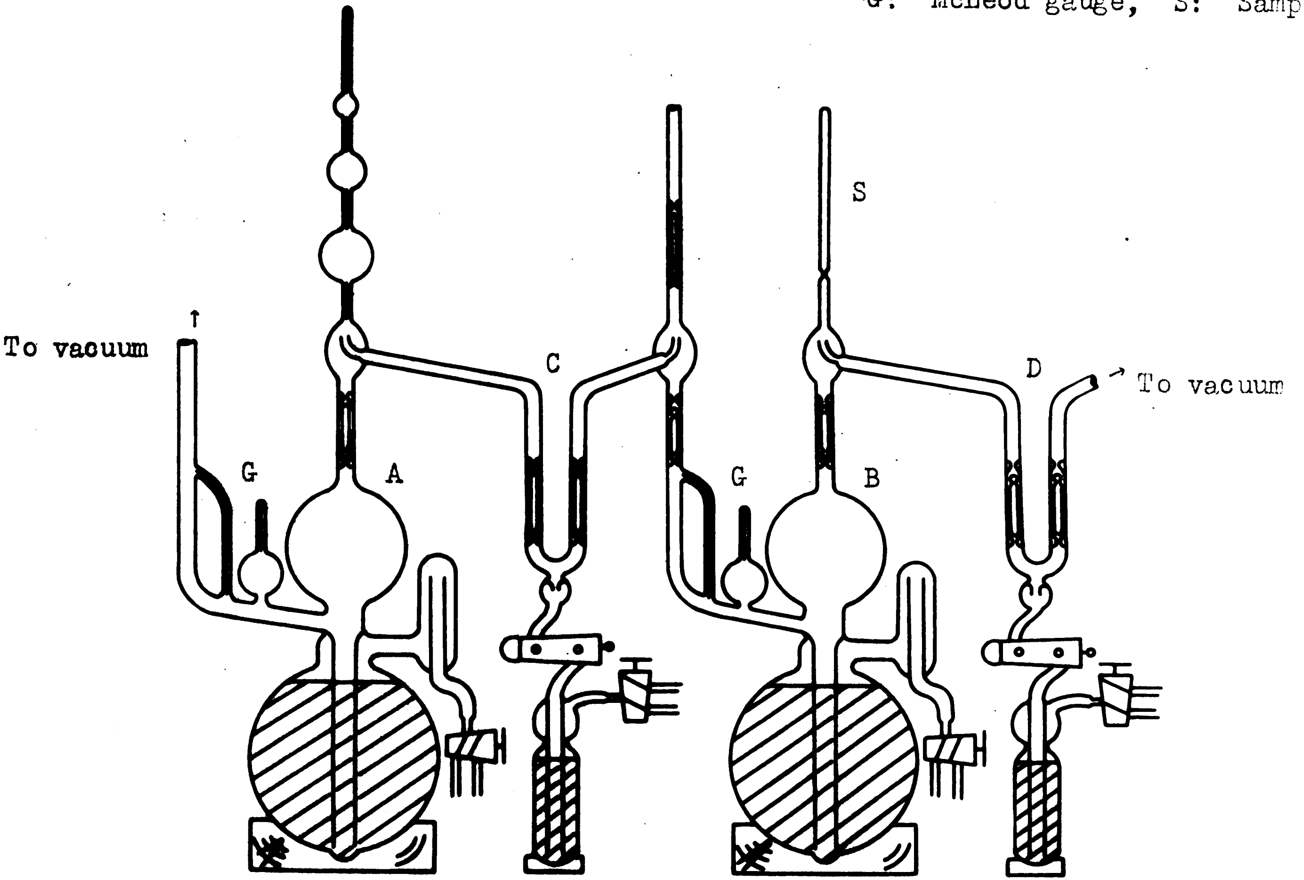
After reaction, the non-condensable products were measured by means of the apparatus illustrated in Fig. 20. This consisted of a combined toepler and gas burette, A, a toepler B, and two mercury cut-offs, C and D. With mercury filling C, the non-condensable products were transferred to A and measured. The mercury in C was then lowered, and the gas transferred from A to B by toeplering. The McLeod gauges, G, showed when the transfer was complete in each case. With mercury filling D, the mercury level in B was raised, compressing the gas into the sample tube, T, which was then sealed. The method of sealing involved freezing a mercury thread in T just above the constriction, withdrawing the rest of the mercury, and sealing below the frozen thread.

The condensable products were fractionated using the apparatus illustrated in Fig. 21. The condensable gases were collected in the U-tube, U, allowed to warm up, then swept onto an absorption column, C, with a stream of nitrogen, flow rate 25 ml./min. The

Fig. 20. Gas Burette and Toepler Arrangement.

A: Gas Burette, B: Toepler, C and D: Mercury Cut-offs,

G: McLeod gauge, S: Sample tube.

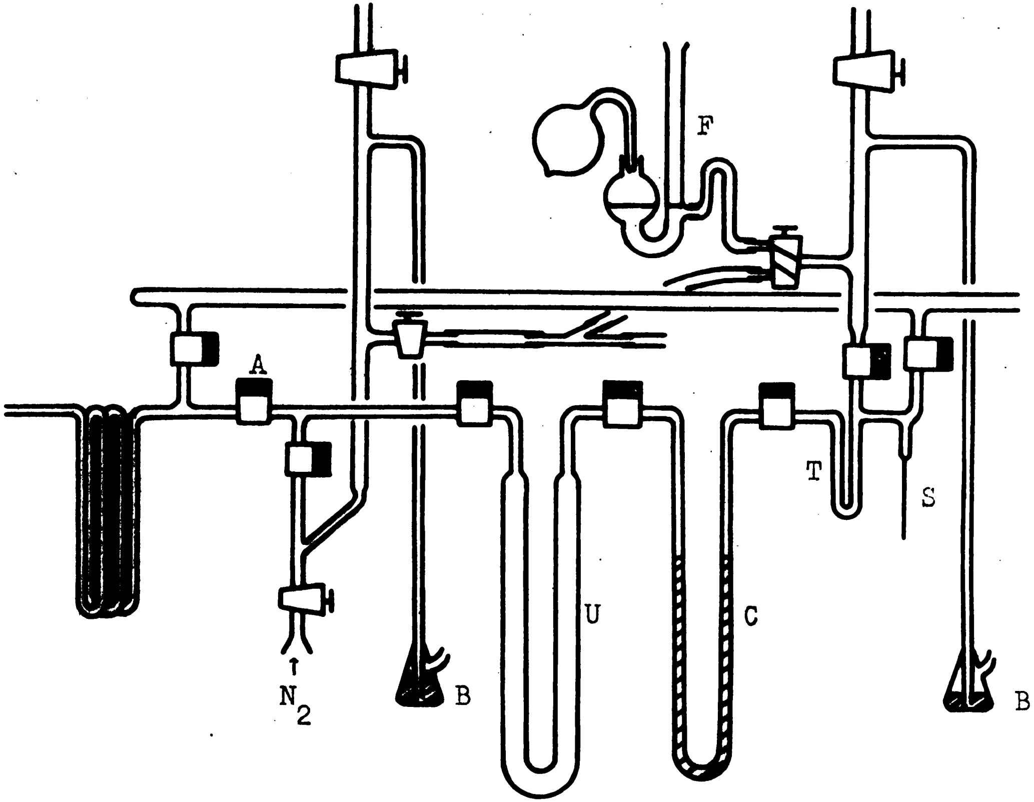


absorption column was $\frac{1''}{4}$ in diameter, and packed with alumina, silver nitrate - ethylene glycol on firebrick, and alumina, in series. The eluate was collected for 10 mins. in a trap, T, packed with glass wool. T was evacuated and the eluate transferred into a side arm, S, which was then sealed off ready for gas chromatographic analysis.

Using this method all reactants and products except trifluoromethane and hexafluoroethane were absorbed on the column. In the course of time two extra peaks appeared in the chromatographic analysis. Blackening of the silver nitrate packing indicated that hydrogen sulphide had reached this phase. Removal of the silver nitrate packing resulted in the elimination of the extra peaks, whence it was concluded that they were caused by a reaction between silver nitrate and hydrogen sulphide, possibly giving oxides of nitrogen. All rate measurements were carried out using an absorption column containing alumina only, which was found to be sufficiently retentive to absorb the small quantities of hydrogen sulphide used.

The non-condensable fraction was analysed by gas chromatography on a 1-m. charcoal column at 25°. Hydrogen was detected with nitrogen as carrier, and carbon monoxide estimated with hydrogen carrier, flow rate 50 ml./min. The condensable products, after the treatment described above, were analysed for CF_3H and C_2F_6 on an 1-m. alumina column, at 25°, hydrogen carrier, flow rate 60 ml./min.

Fig. 21. Apparatus for the Separation of CF_3H and C_2F_6 from the Products.



A: Springham greaseless tap, B: Blow-off, C: Absorption Column,

U: U-tube, T: Trap packed with glass wool, S: Sample tube, F: Soap bubble flow meter.

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Gas chromatographic analysis of ethylene and some fluoroethylenes

It was of interest in a recent investigation[1] to separate the C_2-olefius ethylene, 1,1-difluoroethylene and tetrafluoroethylene. Silica gel and silver nitrate–ethylene glycol packings show excellent separational properties for hydrocarbons and olefins[2,3], and in the present work these materials have been used to separate the C_2-olefins.

Using silica gel alone it is found that 1,1-difluoroethylene is separated from the ethylene and tetrafluoroethylene peak, while silver nitrate–ethylene glycol separates ethylene from the fluoroolefins. The quantitative separation of all three olefins is achieved by using both column materials in series.

Experimental and results

Silver nitrate in diethylene glycol on a firebrick support was purchased from the Perkin-Elmer Co., as was the silica gel. A Perkin-Elmer gas chromatograph (154-C) was used.

The silver nitrate phase was packed into a 12 ft. length of $^1/_4$ in. O.D. aluminium tubing and coiled, while the silica gel was contained in a 3.3 ft. Pyrex glass column;

TABLE I

Column used	*Retention times (min)*		
	C_2H_4	*CF_2CH_2*	*C_2F_4*
Silver nitrate–ethylene glycol	12.5	7.0	7.0
Silica gel	14.2	19.0	14.2
Silver nitrate–ethylene glycol plus silica gel	30.8	25.6	21.6

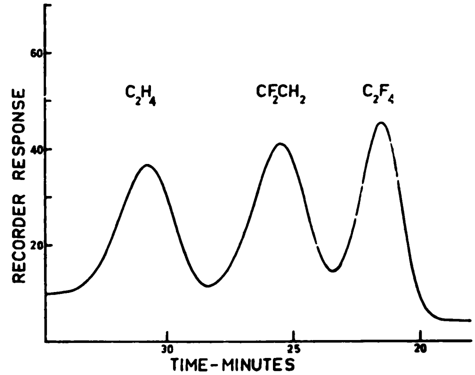

Fig. 1. Chromatogram of olefin mixture (25°, flow rate 36 ml/min).

the latter column was pretreated with nitrogen at 100° before use. Hydrogen was used as a carrier gas at a flow rate of 36 ml/min column temperature was 25°. The olefin mixtures were approximately equimolar and sample size was 0.06 ml.

The rasults of the separation are given in terms of retention times and are recorded in Table I; the recorded chromatograph using the combined columns is shown in Fig. 1.

Retention times may be decreased with some loss in separation by increasing the carrier flow and column temperature. A chromatogram at 45° and flow rate of 70 ml/min is shown in Fig. 2.

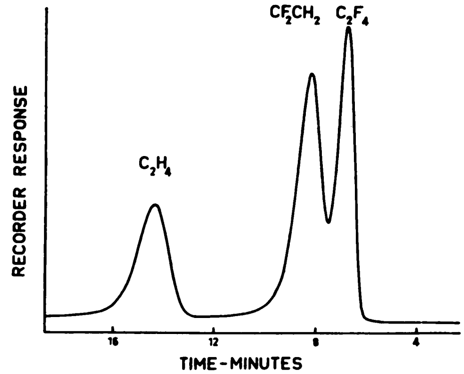

Fig. 2. Chromatogram of olefin mixture (45°, flow rate 70 ml/min).

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