THE REACTIONS OF BROMOTRICHLOROMETHANE AND BROMINE WITH HALOGENATED METHANES

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OF
BROMOTRICHLOROMETHANE
AND BROMINE
WITH
HALOGENATED METHANES

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DAVID E. COPP, B.Sc.

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RESEARCH TRAINING

The candidate entered Queen's College, University of St. Andrews (latterly the University of Dundee), in October 1964 and graduated from the Faculty of Pure Science with First Class Honours in Chemistry in July 1968.

The work described in this thesis was performed in the Chemistry Department, The University of Dundee between September 1968 and September 1969, and in the Chemistry Department, The University of St. Andrews between September 1969 and May 1971 under the supervision of Professor Lord Tedder.

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CERTIFICATE

I certify that DAVID EDWARD COPP, B.Sc., has spent eleven terms at research work under my direction and that he has fulfilled the conditions of Ordinance No. 12 and Resolution of the University Court, 1967, No. 1 so that he is qualified to submit the following Thesis for the Degree of Doctor of Philosophy.

Professor Lord Tedder

DECLARATION

I hereby declare that the following Thesis is a record of the results of experiments performed by me, and further that the Thesis is my own composition and has not previously been presented for a higher degree.

In memory

of

my late father

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INTRODUCTION

Chemical reactions involve the breaking and reforming of chemical bonds. The heterolytic fission of a chemical bond leads to charged entities or ions and their subsequent reactions have been exhaustively studied for many years. Besides heterolytic fission of a chemical bond, another mode of bond breaking is possible[1]. The entities produced by this homolytic fission of a bond are generally non-ionic and they can be either polyatomic or monoatomic. The reactions of these free radicals, with organic molecules, can be broadly divided into two main groups.

1) Addition reactions 2) Transfer reactions

Further reaction pathways for free radicals are radical-radical reactions, radical decomposition reactions and finally there is the possibility of electron transfer processes to yield ions and/or neutral molecules. Many of the chemical reactions used in the chemical industry and, for that matter, by nature, have been shown to involve free radicals as intermediates, and in recent years studies into the whole field of radical behaviour have been undertaken. The radical reactions which have received the greatest attention are the first two groups.

Radical additions of the type

$$X\cdot + E \longrightarrow XE\cdot$$

have received the greatest attention. The additions of simple radicals to olefinic[2], acetylenic[3] and aromatic[4] systems have been well investigated as have the commercially important radical induced polymerisations[5] of unsaturated molecules. Radical transfer reactions involve the abstraction of an atom from a molecule by the free radical, thereby producing a new radical species:

$$X\cdot + A{:}B \longrightarrow X{:}A + B\cdot$$

The radical transfer of hydrogen in the aliphatic hydrocarbon series has been well investigated[6,7]. The transfer of halogen atoms which in the main are chlorine, bromine and iodine[8,9] have also been subject to intensive investigation.

Until recently, a major problem in the kinetic study of the reactions of free radicals, has been the rigorous identification and quantitative analysis of all the reaction products. With the development of vapour phase chromatography, mass spectroscopy and nuclear magnetic resonance spectroscopy, the accurate analysis of a complex reaction system has become a relatively simple task. These product identification techniques enable a representative mechanism to be proposed and substantiated.

By performing the reactions in the gas phase, where intermolecular forces are relatively small, the experimentally derived properties can be compared with the theoretically derived properties of isolated molecules. It is much easier to develop quantitative theories, such as Transition State Theory, for molecules in gas phase reactions than for reactions in solution. For radicals of reasonable size, their partition functions can be calculated, and hence theoretical predictions can be made about radical reactions which can be compared with the experimental results. The majority of radical kinetic studies have been performed with atoms or small radicals such as methyl, trifluoromethyl and simple alkyl radicals. The comparison, between the radical reactions of atoms and small radicals, is particularly interesting in that atoms do not have any rotational or vibrational degrees of freedom, in contrast to alkyl radicals.

The halogenation of alkanes and substituted alkanes has been extensively studied, partly because of the tremendous utility of chlorination in the chemical industry[10]. The quantitative chlorination studies of Hass and co-workers[10,11] led to the conclusion that the ease of hydrogen abstraction, within a series of unsubstituted alkanes, was in the order tertiary > secondary > primary. This ordering has been found to be general for the hydrogen abstraction reactions of all free radicals, although there is a considerable variation in the selectivity displayed by different radicals[6,7]. The nature of the substituent in a substituted alkane can have a marked effect in that, depending on the attacking radical, it may accelerate attack of one radical but retard that of another.

Over recent years Tedder and co-workers have studied the chlorination[12,13] and bromination[14,15] of substituted alkanes in the gas phase. They have shown that the differences in selectivity between chlorination and bromination can be accounted for by the decrease in the importance of polarity and the increasing importance of the relative bond strength. In all cases the substituent was shown to have little effect beyond the β carbon atom, which was in contrast to the solution phase halogenation results of Walling and Mayahi[16].

The results obtained by Tedder confirmed and extended the results of Henne and co-workers[17,18] who initially observed that chlorination was directed away from highly fluorinated groups. Apart from the above work, which has utilized an internal competitive method of study, the fluorination[19,20], chlorination[21,22] and bromination[23,24] of many compounds have been undertaken using an 'external' competitive method. For these studies, pairs of molecules were halogenated together, to give relative rate constants for the hydrogen abstraction step from both substrates. The relative rate constants, so obtained can be put on an absolute basis by performing competitive experiments with substrates for which the abstraction rate is known absolutely. This technique can be used for chlorination and bromination, but not for fluorination, as no absolute rate measuremont for the abstraction of hydrogen by fluorine has so far been determined.

Absolute rate constants have been measured for:

$Cl\cdot + H_2 \longrightarrow H\cdot + HCl$ (ref. 25)

$Br\cdot + CH_3Br \longrightarrow CH_2Br\cdot + HBr$ (ref. 26)

$Br\cdot + CHF_3 \longrightarrow CF_3\cdot + HBr$ (ref. 27)

$Br\cdot + C_2H_6 \longrightarrow C_2H_5\cdot + HBr$ (ref. 28)

In general the reactivity order of the halogen atoms is $F > Cl > Br$, with the reverse as their order of selectivity.

Of recent years the competitive fluorination[19], chlorination[29] and bromination[23,27] of most of the fluoro and chloro halomethanes have been studied. The results can be explained by considering the relative magnitudes of the transition state polar forces between the incipient products and the bond energies, D(R-H), of the halomethanes.

Tedder[30], after the manner of Evans and Polanyi[31], has summarised the factors involved in free radical hydrogen abstractions in terms of potential energy surfaces. The ideas developed here have been found to be of great utility in explaining the trends observed in the halogenation of halomethanes and haloethanes.

Besides obtaining information on the effects of substituents on halogenation reactions, the observed activation energies have been made further use of in the calculation of the bond dissociation energies D(R-H) of the substituted alkanes[26,32,33]

The simple alkyl radicals, methyl and trifluoromethyl, have been extensively studied as their production is relatively easy, and convenient. Direct photolysis of acetone,

$$(CH_3)_2CO \xrightarrow[3130^{o}A]{} 2CH_3\cdot + CO$$

yields two methyl radicals and one molecule of carbon monoxide, which can act as a useful monitor on the rate of radical formation. The subsequent reactions of the methyl radical have been studied by numerous workers. Steacie and Raal[34,35] obtained results for the hydrogen abstraction by methyl radicals from halogenated methanes but later work[36,37] has thrown doubt on the validity of these experiments. More acceptable values of the rate constants for hydrogen abstraction from fluoromethanes by methyl radicals were obtained by Pritchard et.al.[38]. Recently, Whittle and co-workers have studied the reactions of trifluoromethyl radicals with fluoromethanes[39], chloromethanes[40], methyl halides[41] and fluoroethanes[39]. From these results, it appears that the ideas developed by Tedder[30], are also of use in discussing the results of hydrogen abstraction by alkyl radicals. Arrhenius rate parameters were also obtained by Whittle for the abstraction of chlorine from the chloromethane series[40]. The results were comparable with those obtained by Szwarc and co-workers[8,9], who studied reactions of the type:- $CH_3\cdot + RX \longrightarrow CH_3X + R\cdot$ X = Br or I.

The abstraction reaction rates of these alkyl radicals were measured relative to the recombination rate of the alkyl radicals, and the results can be set on an absolute basis if the recombination rate is known absolutely. The recombination rates for many simple radicals[e.g. $CH_3\cdot$[42], $CClF_2\cdot$[43], $CF_3\cdot$[44], $CCl_3\cdot$[45,46]] have now been measured with a good degree of accuracy, and thus absolute rate constants for hydrogen abstraction with these radicals can be obtained.

Over the past few years, the abstraction and addition reactions of trichloromethyl radicals, produced by the photolysis of bromotrichloromethane, have been studied in this laboratory. The addition reactions of the trichloromethyl radical have thrown considerable light onto the factors influencing the direction of addition to substituted olefins. The hydrogen abstraction reactions from substituted alkanes have indicated that the trichloromethyl radical is comparable in selectivity to the bromine atom.

The purpose of this work was to obtain absolute Arrhenius parameters for the abstraction of hydrogen from a representative selection of polychlorofluoromethanes. The results obtained are compared with the results obtained for similar reactions with methyl radicals and trifluoromethyl radicals. In order to reduce the unknown rate constants in the computer analysis of the proposed reaction mechanism, the brominations of all the halomethanes, for which literature data did not exist, were carried out. The thesis is divided into two parts:- Part I deals with the reaction of trichloromethyl radicals with difluoromethane (section I); chlorofluoromethane (section II), dichloromethane (section III) and dichlorofluoromethane (section IV) and Part II deals with the competitive brominations of chlorofluoromethane, dichloromethane and dichlorofluoromethane.

PART I

THE PHOTOCHEMICAL REACTIONS
OF
BROMOTRICHLOROMETHANE
WITH
HALOMETHANES

PART I

THE TRICHLOROMETHYL RADICAL; ITS PRODUCTION AND REACTIONS

The abstraction and addition reactions of the trichloromethyl radical have received some attention in recent years, though less than that paid to other radical systems such as the methyl and the trifluoromethyl radicals. This has been due to the lack of a good source of trichloromethyl radicals. The problems associated with the photolysis of potential radical sources are that, in most cases, the second species produced is invariably more reactive than the trichloromethyl radical itself.

Hautcloque[47] and Tomkinson, Galvin and Pritchard[48] have studied the photolysis of hexachloroacetone. They have demonstrated that trichloromethyl radicals are produced in an entirely analogous manner to the production of trifluoromethyl radicals from hexafluoroacetone[41]. The complicating feature of the photolysis of hexachloroacetone is the following reaction:-

$$CCl_3COCCl_3 \xrightarrow{hv} Cl^{\bullet} + {}^{\bullet}CCl_2COCCl_3$$

The chlorine atoms produced in this manner are much more reactive than the trichloromethyl radicals. This is a serious complicating feature of the kinetic studies which are based on the production of trichloromethyl radicals from the photolysis of hexachloroacetone.

The photolysis of carbon tetrachloride, studied initially by Pfordte[49], produced trichloromethyl radicals and chlorine atoms, the latter being more reactive. Wijnen and co-workers[50,51,52] have, however, used the gas phase photolysis of carbon tetrachloride, in the presence of ethylene and in ethylene-ethane mixtures, to obtain the combination and disproportionation ratios for three haloalkyl radicals. The primary step was the production of trichloromethyl radicals and chlorine atoms.

$CCl_4 + h\nu \longrightarrow CCl_3\cdot + Cl\cdot$

The chlorine atom could then either add to ethylene, or abstract hydrogen from ethane.

$Cl\cdot + C_2H_4 \longrightarrow C_2H_4Cl\cdot$

$Cl\cdot + C_2H_6 \longrightarrow C_2H_5\cdot + HCl$

Trichloromethyl radicals have been produced either by the γ radiolysis of carbon tetrachloride[53] or by the γ radiolysis of chloroform[54]. In either case the radiolysis was a means to studying the telomerisation of ethylene initiated by the radicals. Recently, Firestone and Dickey[55] have studied the radiolysis of chloroform vapour. Analysis of their results gave Arrhenius parameters relative to the recombination rate for dichloromethyl radicals for the reaction

$CHCl_2\cdot + CHCl_3 \longrightarrow CH_2Cl_2 + CCl_3\cdot$

They were further able to obtain the cross combination ratio for dichloromethyl and trichloromethyl radicals. Pritchard[48] reported that hexachloroethane did not give trichloromethyl radicals on photolysis, but Errede and Cassidy[56] found that $C_2Cl_6 + h\nu \longrightarrow 2CCl_3\cdot$ was the principal initiation step. Chlorine atoms were again produced in this system by the disproportionation of pentachloroethyl radicals:

$CCl_3\cdot + C_2Cl_6 \longrightarrow CCl_4 + C_2Cl_5\cdot$

$C_2Cl_5\cdot \longrightarrow C_2Cl_4 + Cl\cdot$

The addition, by a free radical mechanism, of polyhalomethanes to olefins, was first demonstrated by Kharasch, Jensen and Urry[57]. Later, these workers[58,59] studied the relative reactivities of different olefins towards the trichloromethyl radical, produced in the peroxide initiated or U.V. light induced decomposition of bromotrichloromethane. The formation of the products was explained by a chain process involving trichloromethyl radicals as the chain carriers.

The first kinetic study of the trichloromethyl radical was undertaken by Melville, Robb and Tutton[60], who measured the absolute Arrhenius parameters for the addition of trichloromethyl radicals to cyclohexene and vinyl acetate. As with most of these early studies, the reactions were carried out in the liquid phase, using dilatometry to measure the reaction rates. The addition rate was put on an absolute scale, by using the recombination rate of trichloromethyl radicals obtained by the rotating sector method. The solution phase work of Bengough and Thomson[61], confirmed the values for the addition and recombination rates, as long as there was excess bromotrichloromethane. The mechanism became more complicated when excess olefin was used, in that additional termination steps had to be postulated to explain the observed reaction orders. An identical effect was observed by Tedder and Walton[62] in the gas phase photolysis of bromotrichloromethane with ethylene. Martin and Gleicher[63] have studied the photochemical addition of bromotrichloromethane to aryl olefins and substituted alkenes. Beside obtaining a good correlation between the logarithms of the rate constants with the Hammett σ values for the aryl substituents, they obtained the allylic hydrogen abstraction rate by the trichloromethyl radical from the allylic position in the olefin molecule. Huyser[64] and Kooyman, Van Helden and Bichel[65] have studied the hydrogen abstraction reactions of trichloromethyl radicals from the saturated moiety of alkyl benzenes.

Relatively few gas phase studies of the reactions of trichloromethyl radicals have been published. Tedder and McGrath[66] photolysed, in the gas phase, bromotrichloromethane with propane, n-butane and iso-butane. This work differed from the previous studies in that the reaction products were identified and quantitatively analysed. The reaction scheme they proposed was as follows:-

$$CCl_3Br + h\nu \longrightarrow CCl_3\cdot + Br\cdot$$

$$CCl_3\cdot + RH \longrightarrow CHCl_3 + R\cdot$$

$$R\cdot + CCl_3Br \longrightarrow RBr + CCl_3\cdot$$

$$Br\cdot + RH \longrightarrow HBr + R\cdot$$

$$CCl_3\cdot + HBr \longrightarrow CCl_3H + Br\cdot$$

$$2CCl_3\cdot \longrightarrow C_2Cl_6$$

They showed that hydrogen abstraction by trichloromethyl radicals rather than bromine atoms was the major chain process, and thus the rate of formation of the alkyl bromides was equal to the rate of hydrogen abstraction from the different positions in the alkanes. The experiments gave activation energy differences between the abstraction of primary, secondary and tertiary hydrogens by trichloromethyl radicals.

The work was later extended by Tedder and Watson[67] to include substituted butanes. They also set the results on an absolute basis by using the recominbation rate constant for $2CCl_3\cdot \rightarrow C_2Cl_6$ obtained by Goldfinger et.al.[68]. The absolute values were later modified by using the recombination rate obtained by Tedder and Walton[69].

The addition reactions of bromotrichloromethane with olefins, in the gas phase, have been studied in a similar manner[70,71,72] in that all the reaction products were identified and quantitatively analysed. The importance of these addition reactions lies in the fact that they provide the basis of a new theory of radical addition to olefins. In contrast to the theory of Mayo and Walling[73], which is based on the relative stability of the initial addend radicals, Tedder and Walton propose that attention should be focused on the strength of the bond formed and not on the site of the odd electron. Further refinements to their theory, come from the postulation that, in the transition state, polar forces must be invoked.

The kinetic study of the reactions of the trichloromethyl radical has been of value in developing general theories of radical reactions. The purpose of the work described in this Thesis was to determine reliable kinetic data for the hydrogen abstraction from halomethanes by trichloromethyl radicals. It appears that the most satisfactory source of trichlormethyl radicals is from the photolysis, at 3660 Å, of bromotrichloromethane which gives trichloromethyl radicals and bromine atoms. With hydrogen abstraction reactions, there is the possibility of the bromine atoms competing with the trichloromethyl radicals for the halomethane substrate. This feature would complicate the reaction kinetics but would be less serious than in the photolysis of carbon tetrachloride which, beside producing trichloromethyl radicals, gives the highly reactive chlorine atom. The participation of bromine atoms in the reaction mechanism had been shown to be unimportant in the reaction of bromotrichloromethane with substituted alkanes[67]. It was also hoped that, in this study, the reactions of bromine atoms would be negligible in comparison with the abstraction reactions of the trichloromethyl radical.

Regardless of which primary radical attacks the halomethane substrate, the most likely reaction of the secondary radicals produced, is the bromine atom abstraction from bromotrichloromethane because of the weak C-Br bond ($D(CCl_3-Br) = 49$ Kcal/mole).

With the present system, the abstraction rate constants are obtained relative to the rate of dimerisation of the trichloromethyl radicals. These relative rate constants can then be set on an absolute basis by using the literature value[69] for the recombination rate constant. The absolute rates so obtained, can then be compared with similar absolute rates obtained for the hydrogen abstraction reactions of trifluoromethyl radicals and methyl radicals with halomethanes.

A comparison of the behaviour of these three radicals would be particularly interesting as the halomethyl radicals are polar in nature, whereas the methyl radical is non-polar. Furthermore, the trifluoromethyl and methyl radicals are comparable in size, whereas the trichloromethyl radical is considerably larger.

Comparison between the rate parameters obtained for hydrogen abstraction by the halomethyl radicals and those obtained for the analogous halogen atom reactions ($X = F$, Cl, Br) would also be of interest, as abstraction reactions have been shown to be dependent, to some degree, on the size and polarity of the attacking radical.

In an attempt to determine a representative reaction mechanism for the reaction of bromotrichloromethane with a halomethane, several experimental series were carried out at different temperatures, different reactant pressures and at different light intensity. The studies involving difluoromethane as the halomethane are described in Part I, section I. The work was extended to include chlorofluoromethane, dichloromethane and dichlorofluoromethane. The results for each of these halomethanes are described in Part I, Sections II, III and IV respectively. For each of these halomethanes, similar experiments to those performed in section I, were carried out to see if the 'peculiarities' observed with difluoromethane were general within the series. Each section describes the determination of possible absolute Arrhenius parameters for the hydrogen abstraction reaction of the trichloromethyl radical. No previous gas phase reactions of the trichloromethyl radical with these halomethanes have been reported in the literature.

PART I

SECTION I

THE PHOTOCHEMICAL REACTIONS
OF
BROMOTRICHLOROMETHANE
WITH
DIFLUOROMETHANE

EXPERIMENTAL

REACTANTS

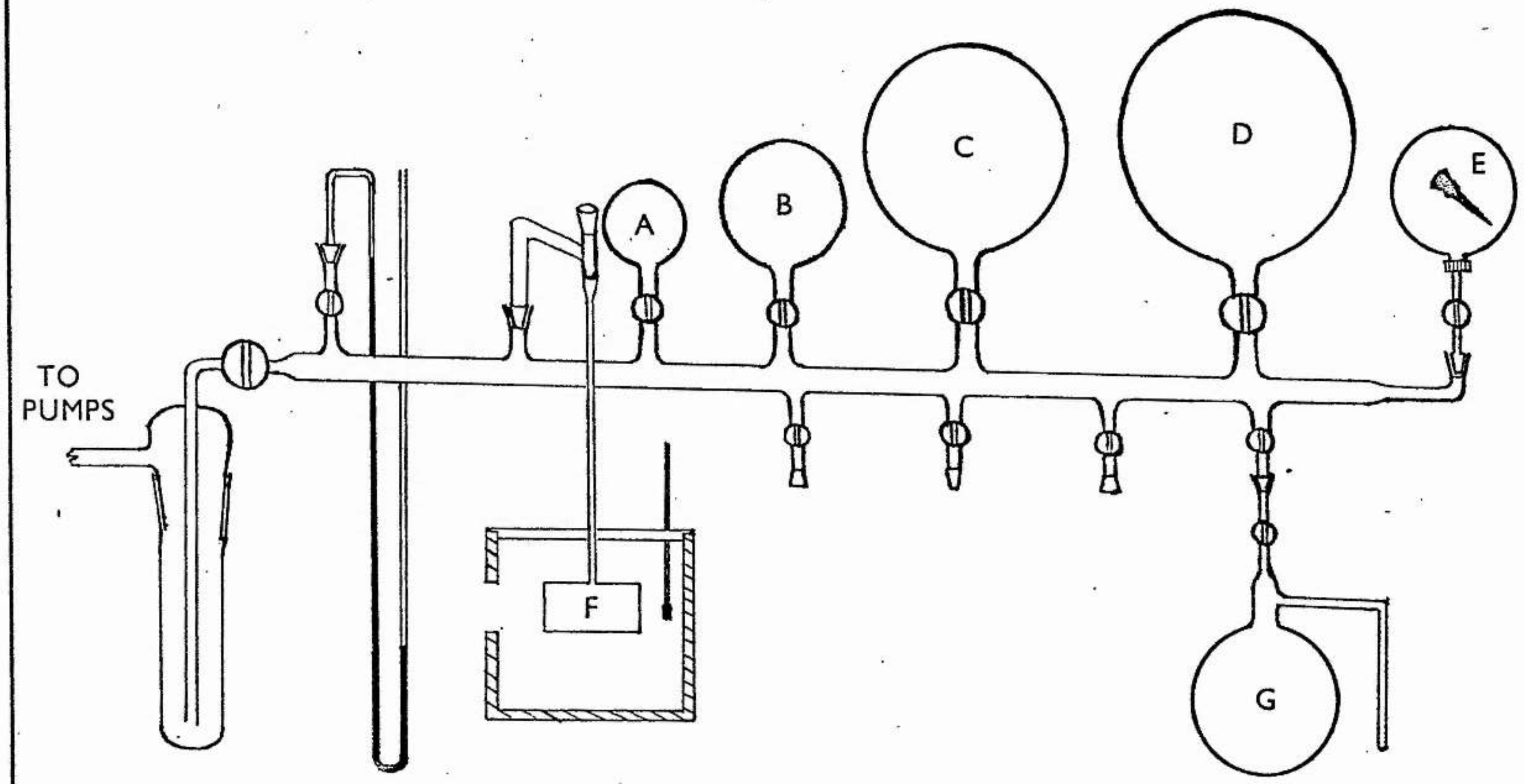
1) DIFLUOROMETHANE:- was 'Peninsular Chemical Research' material and being better than 99.5% pure, as shown by analytical gas chromatography, it was used without further purification.

2) BROMOTRICHLOROMETHANE:- was 'Schuchardt' material and, prior to use, it was purified on a Pye 105 preparative chromatograph using a 30 ft. glass column packed with 20% Siliçon gum on 60-100 mesh Embacel. With a nitrogen flow rate of 200 ml./min., obtained by setting the column temperature to 98°C, the injector nitrogen pressure to 60 lb./sq.in. and the column pressure to 35 lb./sq.in. the resolution was such that better than 99.9% pure bromotrichloromethane was collected in the high efficiency trap which was cooled in liquid nitrogen. Repetitive injections of 250 μl samples finally gave about 10 ml. of pure bromotrichloromethane which was then stored in the dark in a deep freeze. It was found, by analytical gas chromatography, that the frozen bromotrichloromethane maintained its purity for at least six months. The above procedure was repeated whenever fresh amounts of bromotrichloromethane were required.

APPARATUS

The apparatus, shown in Fig. 1, consisted of a conventional high vacuum line made of 'Pyrex' glass. The vacuum was maintained by a 'Speedivac' oil vapour diffusion pump, model 102A, backed by a 'Speedivac' single stage rotary pump, model 1SC 50B. The line

APPARATUS FIG I



had four storage bulbs (A,B,C and D) of volume 62 ml., 149 ml.,2458 ml., and 5226 ml. respectively. The latter bulb was painted black to avoid photochemical decomposition of any material stored in it. Originally the reactant pressures were measured by a mercury manometer connected to the main vacuum line but later a barometrically compensated 'Speedivac' capsule dial gauge (model CG3) was used. The range of the gauge was 0-100 torr (E). The cylindrical 'Pyrex' reaction vessel (F) of volume 142 ml. was connected to the main vacuum line by blackened 2 mm. capillary tubing which minimised the amount of reaction occurring outside the reaction vessel. The reaction vessel was heated by a furnace whose temperature was controlled by a 0-250 volt 'Variac' transformer. The temperature, as measured by a mercury in glass thermometer, was found to be invariant throughout the furnace volume and constant to within ± 2°C for any one experiment. Illumination of all kinetic experiments was with a 'Hanovia' U.V.S. 220 medium pressure arc lamp, which was held 8 in. from the front face of the cylindrical reaction cell for a few experiments. The remainder were carried out with the lamp 6 in. away from the cell. The experiment, performed for mass spectral analysis of the reaction products in the system, was illuminated by an 'Osram'ME/D high pressure, compact source, mercury arc.

Variable incident light intensity was achieved by placing gauzes of different mesh sizes between the lamp and reaction vessel. The gauze transmissions were calibrated on a 'Unicam' SP 800 ultraviolet spectrometer at 3650 Å.

EXPERIMENTAL PROCEDURE

Difluoromethane, which has a very low boiling point (- 52°C), was stored in a large bulb (G) fitted with a side arm which could be cooled with liquid nitrogen. Bromotrichloromethane was stored in a small tube attached to the main line. This tube was also surrounded by liquid nitrogen. Each component was individually 'degassed' by allowing the frozen compound to warm until liquid. It was then frozen again and the tap to the tube or storage bulb opened to the main line and the pumps. This procedure was repeated several times for each compound.

Finally, the 'degassed' difluoromethane was allowed to expand into the main line and bulb B. When a suitable pressure was registered, the bulb tap was closed and the difluoromethane in the line was redistilled back into the storage bulb arm by cooling in liquid nitrogen. The measured amount was then distilled from bulb B into the evacuated reaction vessel by cooling the reaction vessel with liquid nitrogen. After sufficient time for complete distillation, a measured amount of bromotrichloromethane was added in a similar manner to the reaction vessel. The pre-heated furnace was then raised around the reaction vessel and the temperature allowed to stabilize. During this time the mercury arc lamp was struck and allowed to reach its normal working range before the shutter was removed from the illumination aperture in the furnace wall. Because of the highly volatile nature of the difluoromethane more consistent injections into the analytical gas chromatograph were obtained by adding a ballast liquid to the final reaction mixture. The ballast liquid must be well resolved in the final chromatogram and must not interact with any of the reaction products. A few series were carried out with trichloroethylene as ballast. This was well separated from reaction components but in the liquid phase, in the sample tube, the bromine formed in the reaction probably added to the trichloroethylene. This would account for the appearance of a peak in the chromatogram with a longer retention time than hexachloroethane. With successive injections this unidentified peak enlarged. The use of trichloroethylene as ballast was therefore abandoned in favour of tetrachloromethane (carbon tetrachloride) which was adequately resolved from the reaction products and unlikely to take part in any solution phase reactions.

During the reaction a measured amount, generally 10 mm. pressure in bulb B, of 'degassed' ballast was taken. At the end of the reaction the reaction mixture was distilled into a small tube attached to the main line. After about five minutes the tap of bulb B was also opened and the ballast compound allowed to distil into the sample tube. Samples could then be taken from the tube and injected into the chromatographic apparatus.

ANALYSIS

A Griffin and George D6 gas chromatograph was used for all quantitative analytical work. The instrument employs a Martin and James gas density balance for which the relationship $q = KAM/M-m$ holds for all compounds (q = weight of compound with molecular weight M, A = peak area on chromatogram, K = constant and m = molecular weight of the carrier gas which was nitrogen). Hence the concentration of any material is given by $q/M = KA/M-m$ and thus from a chromatogram where all the peaks are identified, relative concentrations are readily obtained. The most suitable stationary phase for the separation of halomethanes was found to be silicone oil which was used in 20% proportions supported on 60-100 mesh 'Embacel'. The stainless steel columns used were 6' x 3/16". By a suitable choice of column temperature and nitrogen flow rates a well resolved chromatogram was obtained from the 4 µl injections made onto the column with the stainless steel capillary needle.

The chromatogram peak areas were, for a few experiments, measured by a fixed arm planimeter. Later the peak areas were measured using a Honeywell Precision Integrator with a threshold of 2% full scale deflection. A Du Pont 310 Curve resolver was also employed to measure the area of the hexachloroethane and bromotrichloromethane peaks.

Identification of Products

A typical analytical chromatogram showed five peaks (fig 11), but the mass spectra chromatogram showed nine peaks. By comparing the retention times of these peaks with those for authentic difluoromethane, chloroform, bromotrichloromethane and hexachloroethane, the peaks corresponding to these compounds could be assigned in the analytical chromatogram. Retention time comparisons for dichloromethane, carbon tetrachloride and tetrachloroethylene further identified three of the extra peaks occurring in the mass spectra chromatogram. The fourth unknown peak in this chromatogram had a retention time which was comparable with that for the known dibromodichloromethane impurity in authentic bromotrichloromethane.

The experiment carried out for mass spectral analysis consisted of 60 mm. of CH_2F_2 in 149 ml. with 22 mm., of CCl_3Br in 62 ml. This mixture was photolysed for 25 hours at 176°C with a high pressure mercury arc lamp. Approximately 2 µl. of the final reaction mixture was injected into a Perkin-Elmer F11 chromatograph fitted with a 150 metre silicon oil capillary column held at 70°C with a helium pressure of 11 lb./sq.in. The separated mixture was led to the ionization chamber of an A.E.I. M.S.12 mass spectrometer, where the spectra were recorded with the following settings:- magnet range 5; decrease 9; ionization current 22 ev; acceleration potential 8 Kv; band width 500 c/s and chart speed 1.5 in./s.

Peak 1

This was shown to be difluoromethane by comparison of retention time with that of an authentic sample.

Peak 2 Multiplier 4.50

m/e	Relative Intensity	Assignment
51	100	CHF_2^+
111, 113	26, 24	$CHFBr^+$
130, 132	50, 56	CHF_2Br^+
79, 81	11, 12	Br^+

Peak identified as bromodifluoromethane (CHF_2Br)

Peak 3

This was shown to be dichloromethane by comparison of retention time with an authentic sample.

Peak 4 Multiplier 4.50

m/e	Relative Intensity	Assignment
35, 37	5, 2.3	Cl^+
36, 38	12, 6	HCl^+
47, 49	89, 34	CCl^+
48, 50	66, 17	$CHCl^+$
82, 84, 86	34, 31, 14	CCl_2^+
83, 85, 87	100, 98, 65	$CHCl_2^+$
117, 119, 121, 123	17, 15, 8, 2.3	CCl_3^+
118, 120, 122, 124	20, 20, 8, 2.3	$CHCl_3^+$

Peak identified as chloroform ($CHCl_3$) and was confirmed by comparison of retention time with an authentic sample.

Peak 5

Peak probably carbon tetrachloride from comparison of retention time with that for an authentic sample.

Peak 6 Multiplier 4.00

m/e	Relative Intensity	Assignment
35, 37	4, 2	Cl^+
36, 38	11, 4	HCl^+
47, 49	58, 23	CCl^+
79, 81	6.5, 5.6	Br^+
82, 84, 86	60, 58, 11	CCl_2^+
91, 93	5.6, 5.6	CBr^+
117, 119, 121, 123	100,100,58,13	CCl_3^+
126, 128, 130	12, 14, 4.6	$CClBr^+$
161, 163, 165, 167	41, 58, 37, 9	CCl_2Br^+

Peak identified as bromotrichloromethane (CCl_3Br) and was confirmed by comparison of retention time with that for authentic CCl_3Br.

Peak 7 Multiplier 5.50

m/e	Relative Intensity	Assignment
36, 38	84, 38	HCl^+
47, 49	25, 16	CCl^+
82, 84, 86	33, 25, 13	CCl_2^+
94, 96, 98	42, 42, 16	$C_2Cl_2^+$
117, 119, 121, 123	66, 66, 29, 13	CCl_3^+
129, 131, 133, 135	75, 75, 33, 13	$C_2Cl_3^+$
161, 163, 165, 167	42, 54, 33, 16	CCl_2Br^+
164, 166, 168, 170, 172	92, 100, 58, 29, 8	$C_2Cl_4^+$

Peak identified as tetrachloroethylene (C_2Cl_4) with traces of bromotrichloromethane (CCl_3Br). This was confirmed by comparison of retention time with an authentic sample of C_2Cl_4.

Peak 8 Multiplier 5.50

m/e	Relative Intensity	Assignment
36, 38	39, 13	HCl^+
47, 49	17, 11	CCl^+
79, 81	6.5, 6.5	Br^+
82, 84, 86	22, 15, 9	CCl_2^+
91, 93	6.5, 6.5	CBr^+
117, 119, 121, 123	17, 15, 9	CCl_3^+
126, 128, 130	20, 20, 6.5	$CClBr^+$
161, 163, 165, 167	70, 100, 52, 15	CCl_2Br^+
170, 172, 174	4, 4, 4	CBr_2^+
205, 207, 209, 211	15, 35, 22, 9	$CClBr_2^+$

Peak identified as dibromodichloromethane (CCl_2Br_2) and the retention time was that of the known CCl_2Br_2 impurity in authentic bromotrichloromethane.

Peak 9 Multiplier 4.50

m/e	Relative Intensity	Assignment
35, 37	97, 33	Cl^+
36, 38	24, 10	HCl^+
47, 49	100, 60	CCl^+
59, 61	86, 29	C_2Cl^+
82, 84, 86	83, 56, 11	CCl_2^+
94, 96, 98	100, 95, 21	$C_2Cl_2^+$
117, 119, 121, 123	100, 100, 59, 8	CCl_3^+
129, 131, 133, 135	92, 92, 33, 6	$C_2Cl_3^+$
164, 166, 168, 170, 172	100, 98, 68, 19, 3	$C_2Cl_4^+$
199, 201, 203, 205, 207, 209	75, 98, 78, 27, 13, 3	$C_2Cl_5^+$

Peak identified as hexachloroethane (C_2Cl_6), confirmed by comparison of the retention time with an authentic sample.

The elution order of the peaks from an analytical mixture was as follows:- CH_2F_2; CHF_2Br; $CHCl_3$; CCl_3Br and C_2Cl_6. (fig. 11)

The ballast compound was eluted between $CHCl_3$ and CCl_3Br regardless of whether it was carbon tetrachloride or trichloroethylene.

RESULTS

THE REACTIONS OF BROMOTRICHLOROMETHANE WITH DIFLUOROMETHANE

The products of photolysis of bromotrichloromethane with difluoromethane were found to be bromodifluoromethane, chloroform and hexachloroethane. Because of the high volatility of bromodifluoromethane it was impossible, with the sampling method used here, to obtain a valid estimate for its concentration. With this limitation, series of experiments were carried out with a view to establishing the reaction mechanism. Within a given series one initial condition was varied while all others were kept constant. The bromine formed in the reaction was not detected by gas chromatography.

1) Variation of Reaction Time

A series of experiments was carried out at a constant temperature, with fixed amounts of reactants and constant incident light intensity but for various lengths of time. The results are shown in Table I.1, 1

TABLE I.1,1

$[CH_2F_2]_i = 3.73 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction temperature 163 ± 2°C; lamp to cell distance = 6 in.

Reaction time Sec.	$\frac{[CHCl_3]_f}{[CCl_3Br]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
3600	0.73×10^{-2}	3.19×10^{-2}
5400	1.05×10^{-2}	4.23×10^{-2}
7200	1.38×10^{-2}	5.63×10^{-2}
9600	2.33×10^{-2}	6.71×10^{-2}

FIG 2

SCALE A for CH_2F_2

SCALE B for CH_2FCl; $CHCl_2F$; CH_2Cl_2

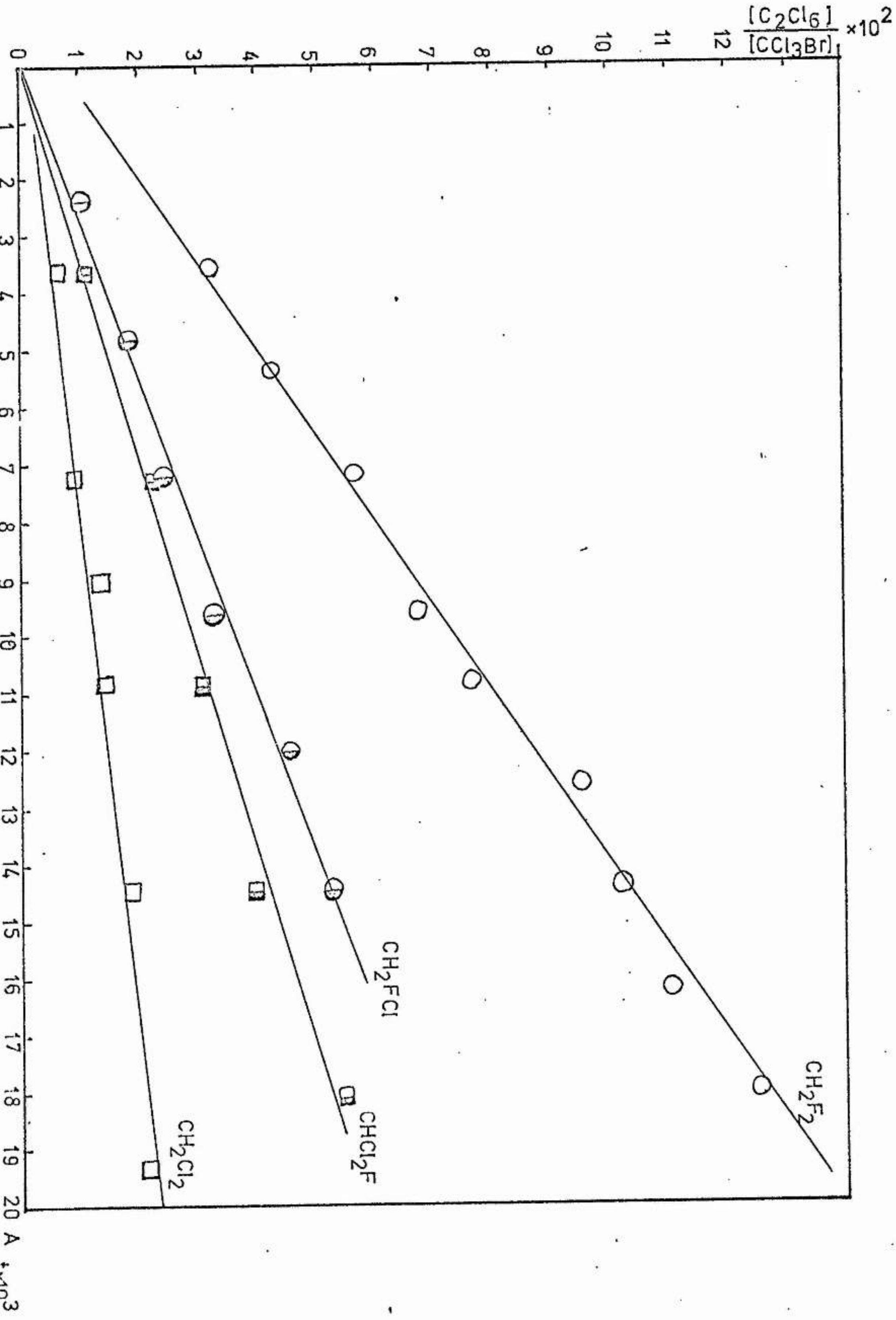


TABLE I.1, 1 (cont)

Reaction time Sec.	$\frac{[CHCl_3]_f}{[CCl_3Br]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
10,800	3.04×10^{-2}	7.62×10^{-2}
12,600	3.81×10^{-2}	9.46×10^{-2}
14,400	4.10×10^{-2}	10.14×10^{-2}
16,200	6.53×10^{-2}	10.99×10^{-2}
18,000	7.08×10^{-2}	12.99×10^{-2}

The ratio $[C_2Cl_6]_f/[CCl_3Br]_f$ was plotted against time and gave a straight line passing close to the origin (fig 2). All the data were combined in a 'least squares' calculation and gave the time intercept - 1060 secs and the slope $\phi I_a/2[CCl_3Br]_i = 6.6 \times 10^{-6}$ sec^{-1}.

2) Variation of Reaction Temperature

A series of experiments was carried out, with fixed reactant concentrations, reaction time and constant light illumination , but variable reaction temperature. The results are shown in Table I.1, 2.

FIG 3

The halomethanes are

○ = CH_2F_2 □ = CH_2Cl_2

◐ = CH_2ClF ▨ = $CHCl_2F$

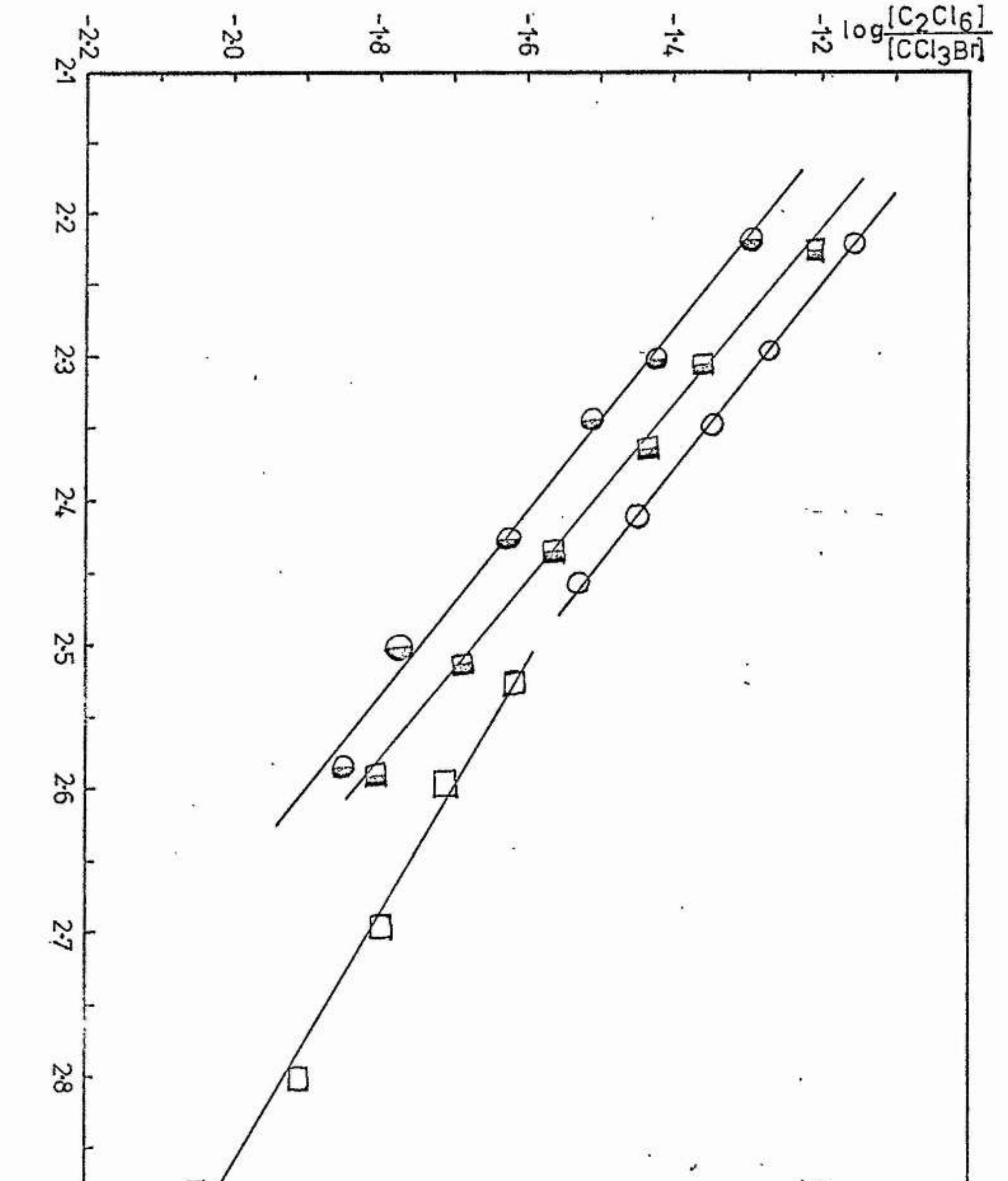


FIG 4

The halomethanes are

○ = CH_2F_2 □ = CH_2Cl_2

⦶ = $CH_2Cl F$ ▥ = $CHCl_2F$

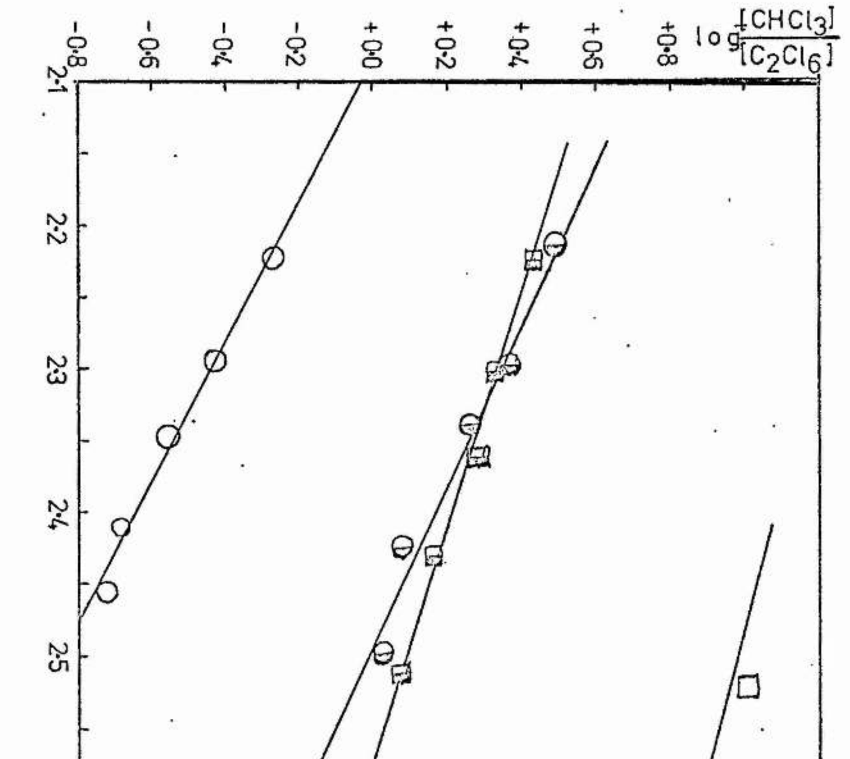


TABLE I.1, 2

$[CH_2F_2]_i = 3.73 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l;

Reaction time 14,400 secs; lamp to cell distance = 8 in.

Temp. °C	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
177	0.538	6.90×10^{-2}
163	0.370	5.31×10^{-2}
153	0.276	4.46×10^{-2}
142	0.204	3.52×10^{-2}
134	0.187	2.94×10^{-2}

Assuming the simple mechanism holds, a plot of $\log [CHCl_3]/[C_2Cl_6]$ v $10^3/T$ gave a straight line of slope $(E_2-\frac{1}{2}E_6)/2.303R = +2.01 \pm 0.20$ and intercept $\log \frac{\sqrt{2}[CH_2F_2]A_2}{(\phi I_a A_6)^{\frac{1}{2}}} = 4.18 \pm 0.09$. (fig 4)

Similarly a plot of $\log [C_2Cl_6]_f/[CCl_3Br]_f$ v $10^3/T$ gave a straight line of slope $= -1.57 \pm 0.12$ and intercept $= 2.32 \pm 0.05$ (fig.3) The errors quoted throughout this thesis are the root mean deviations from the protracted straight line.

3) Variation of Incident Light Intensity

A series of experiments was carried out with constant reaction temperature, fixed amounts of reactants and constant reaction time. The incident light intensity was varied by placing calibrated wire gauzes between the lamp and the reaction cell which was 8 in. distant from the lamp. The results are shown in the following table:

FIG 5

The halomethanes are

○ = CH_2F_2 □ = CH_2Cl_2

◐ = CH_2FCl ▨ = $CHCl_2F$

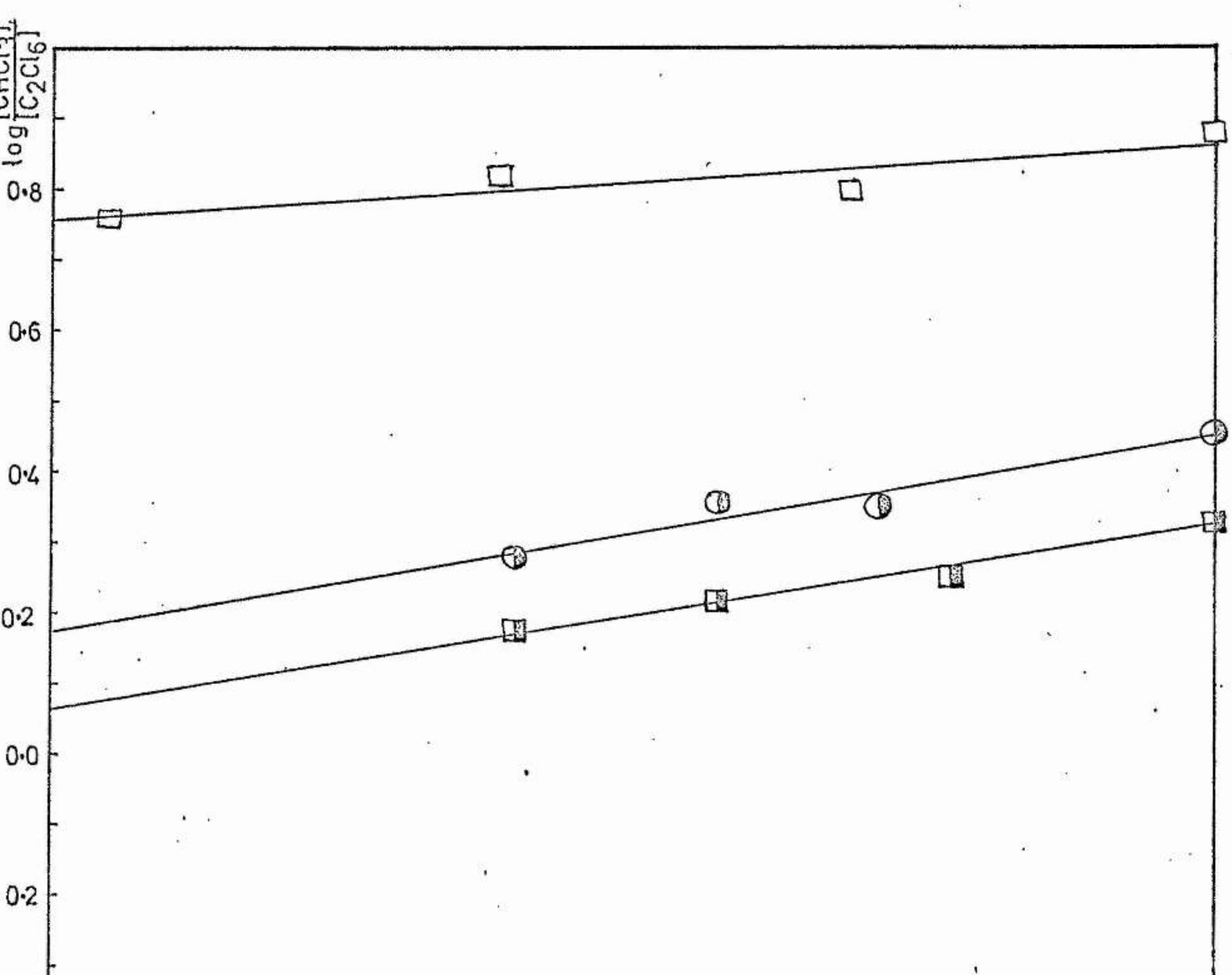


FIG 6

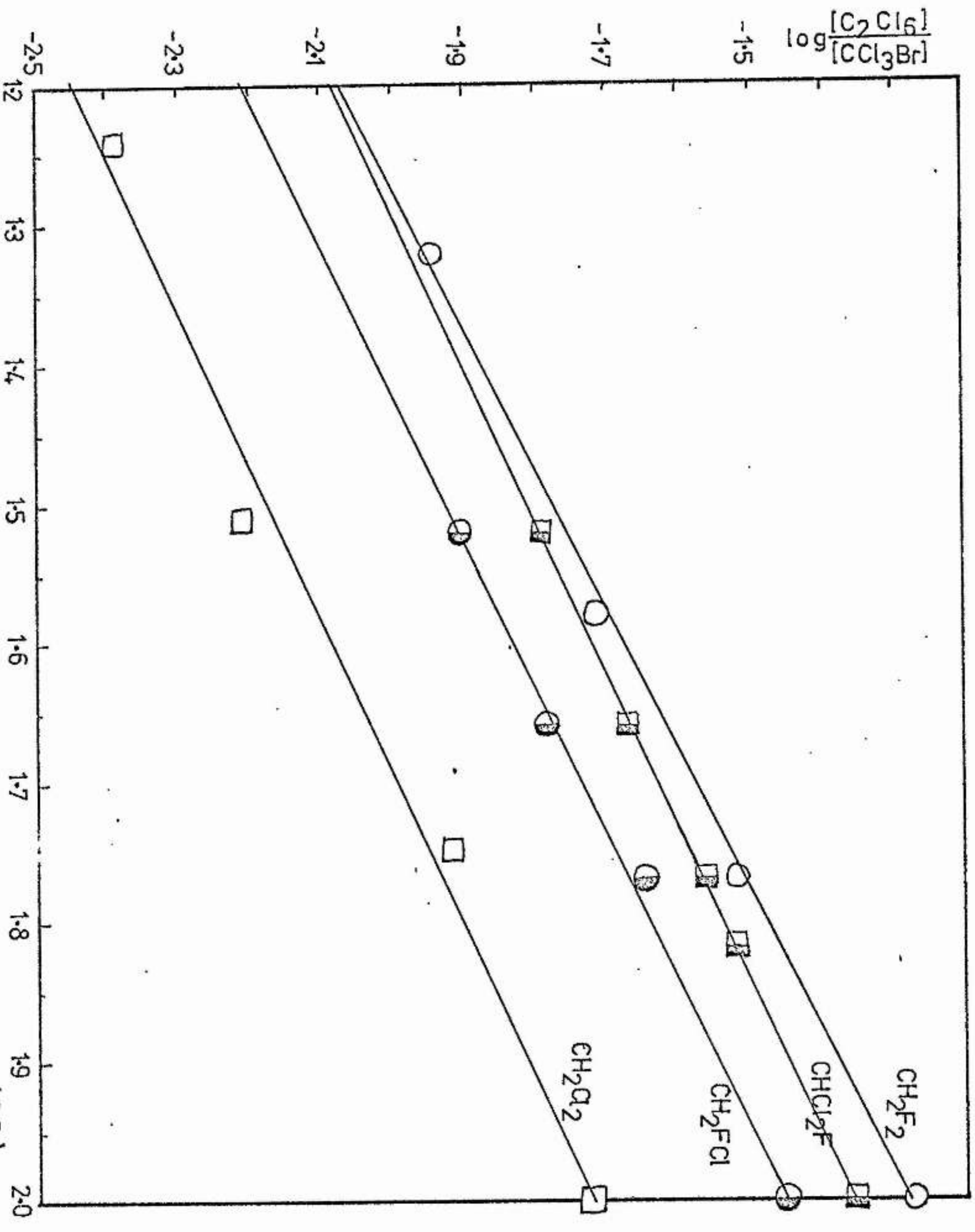

$\log\frac{[C_2Cl_6]}{[CCl_3Br]}$
-1·5
-1·7
-1·9
-2·1
-2·3
-2·5
1·2
1·3
1·4
1·5
1·6
1·7
1·8
1·9
2·0
log(R.I.)
CH_2F_2
$CHCl_2F$
CH_2FCl
CH_2Cl_2

TABLE I.1, 3

$[CH_2F_2]_i = 3.73 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l;
Reaction time = 14,400 secs; Reaction temperature = 163 ± 2°C

Relative Intensity %	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
100	0.370	5.31×10^{-2}
59	0.357	3.05×10^{-2}
38	0.337	1.93×10^{-2}
21	0.378	1.13×10^{-2}

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs. log (Relative Intensity) gave (fig.5) a straight line of slope = -0.006 ± 0.05 and intercept = -0.43 ± 0.03.

Similarly a plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs. log (R.I.) gave a straight line and the least squares method gave the slope = 0.99 ± 0.04 and intercept = -3.27 ± 0.02. (fig. 6)

4) Variation of concentration of bromotrichloromethane

A series of experiments was performed in which the reaction time, reaction temperature, concentration of difluoromethane and incident light intensity were all held constant while the bromotrichloromethane concentration was varied.

The initial experiment in this set was analysed to determine the amount of bromine present. The analysis was performed by measuring the % transmission of the reaction cell with reactants both before and after photolysis. From the difference of % transmission at 420 nm. (the absorption maximum for bromine in range 320-700 nm.) the concentration of bromine finally present was calculated to be 6.02 x 10^{-5} moles/l.

The ratio $[C_2Cl_6]_f/[CCl_3Br]_f$ for this experiment was found to be 4.42 x 10^{-2}. Assuming $[CCl_3Br]_f = [CCl_3Br]_i$ the concentration of hexachloroethane was calculated to be 6.50 x 10^{-5} moles/l. The % difference between these values is approximately 8%. If corrections are made for the change in the bromotrichloromethane concentration, the ratio $[Br_2]_f/[CCl_3Br]_i = 4.10 \times 10^{-2}$ and $[C_2Cl_6]_f/[CCl_3Br]_i = 3.97 \times 10^{-2}$. The percentage difference between these two ratios is now approximately 3%. With this single experiment it was reasonable to suppose that with these systems the amount of bromine formed equalled the amount of hexachloroethane. The results are shown below:-

TABLE I.1, 4

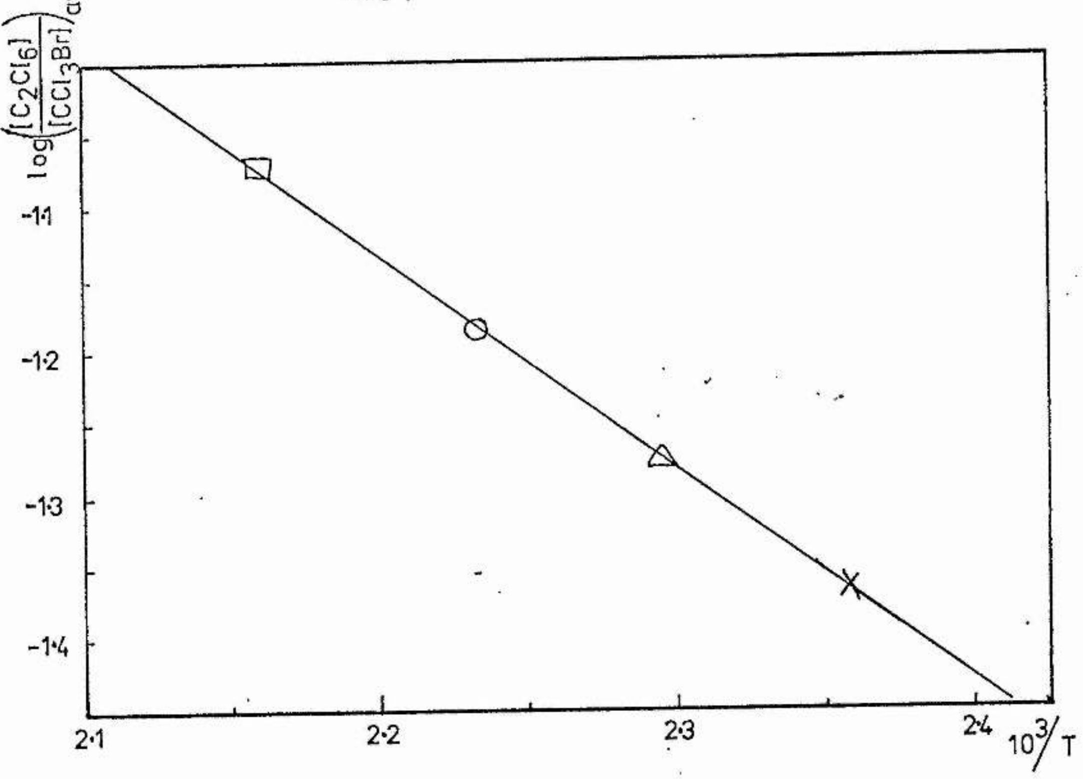
$[CH_2F_2]_i = 3.73 \times 10^{-3}$ moles/l; Reaction time = 14,400 secs.; Reaction temperature = 163 ± 2°C; lamp to cell distance 8 in.

$[CCl_3Br]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
1.47 x 10^{-3}	0.559	4.42 x 10^{-2}
1.13 x 10^{-3}	0.606	4.34 x 10^{-2}
0.85 x 10^{-3}	0.668	4.46 x 10^{-2}
0.57 x 10^{-3}	0.791	3.99 x 10^{-2}
0.34 x 10^{-3}	0.878	4.30 x 10^{-2}

A least squares plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CCl_3Br]_i$ gave a straight line of slope = -0.32 ± 0.09 and extrapolated intercept of -1.16 ± 0.03.

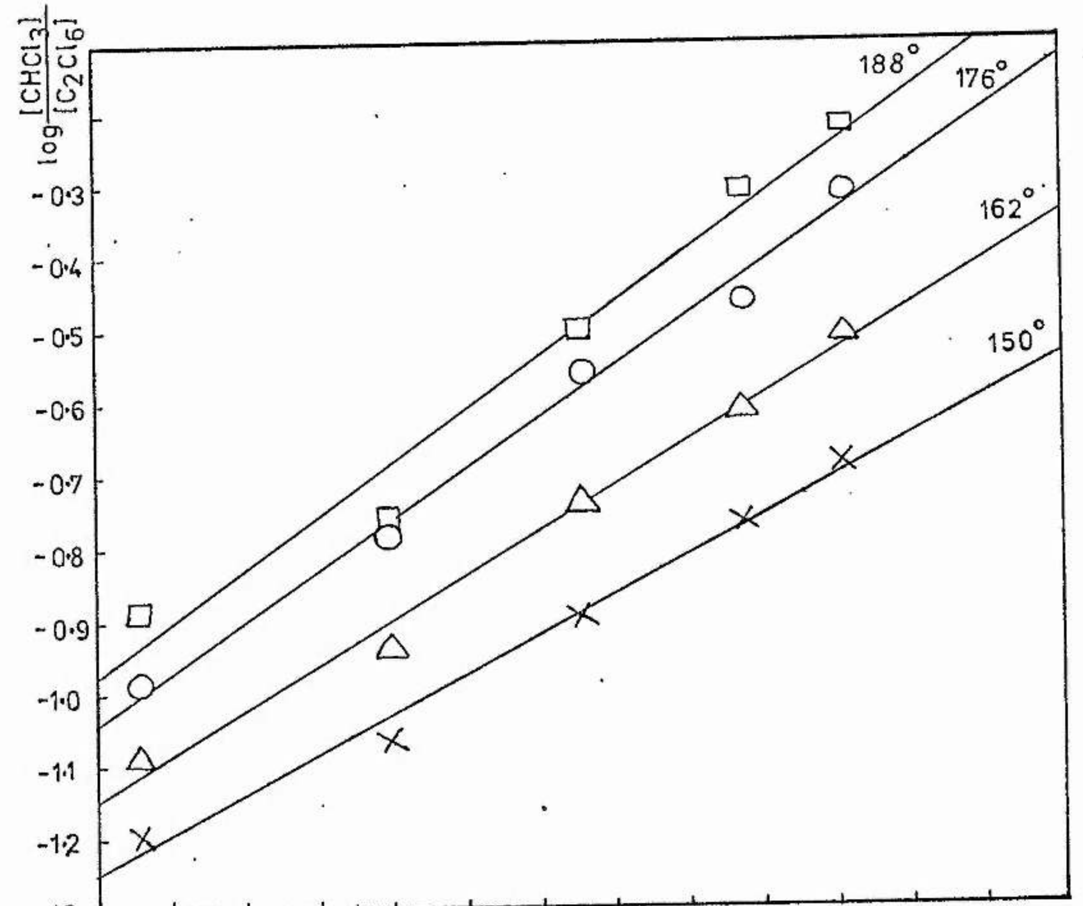
A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs. log $[CCl_3Br]_i$ gave a straight line with a least squares slope of 0.03 ± 0.08 and intercept = -1.26 ± 0.03.

FIG 7'



log([C2Cl6]/[CCl3Br])av
-1·1
-1·2
-1·3
-1·4
2·1
2·2
2·3
2·4
10³/T

FIG 7



log [CHCl3]/[C2Cl6]
-0·3
-0·4
-0·5
-0·6
-0·7
-0·8
-0·9
-1·0
-1·1
-1·2
-1·3
-3·3
-3·1
-2·9
-2·7
-2·5
-2·3
-2·1
log[CH2F2]i
188°
176°
162°
150°

5) Variation of Concentration of Difluoromethane at T = 188°C

A series of experiments was performed in which the concentration of difluoromethane was varied at a fixed temperature. The other variables were held constant.

TABLE I.1, 5

$[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction time = 7200 secs., Reaction temperature = 188 ± 2°C; lamp to cell distance = 6 in.

$[CH_2F_2]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
0.57×10^{-3}	0.130	9.13×10^{-2}
1.24×10^{-3}	0.175	10.59×10^{-2}
2.26×10^{-3}	0.316	9.33×10^{-2}
3.73×10^{-3}	0.491	9.08×10^{-2}
5.09×10^{-3}	0.603	9.54×10^{-2}

A least squares plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs. log $[CH_2F_2]_i$ gave a good straight line of slope = 0.74 ± 0.09 and intercept = -1.46 ± 0.03. (fig. 7)

A similar plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs. log $[CH_2F_2]_i$ gave a straight line of slope = -0.009 ± 0.05 and intercept = -1.05 ± 0.02.

6) Variation of Concentration of Difluoromethane at T = 176°C

This set of experiments was a repeat of those in the previous section except for the lower reaction temperature. The results are given below:-

TABLE I.1, 6

$[CCl_3Br]_i$ = 1.24 x 10^{-3} moles/l; Reaction time = 7200 secs.,
Reaction temperature = 176 ± 2°C; lamp to cell distance = 6 in.

$[CH_2F_2]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
0.57 x 10^{-3}	0.104	7.94 x 10^{-2}
1.24 x 10^{-3}	0.165	7.25 x 10^{-2}
2.26 x 10^{-3}	0.278	7.38 x 10^{-2}
3.73 x 10^{-3}	0.347	6.98 x 10^{-2}
5.09 x 10^{-3}	0.491	6.92 x 10^{-2}

A least squares plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs. log $[CH_2F_2]_i$ gave a straight line of slope = 0.70 ± 0.08 and intercept = -1.27 ± 0.03. (fig. 7)

Similarly a plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs. log $[CH_2F_2]_i$ gave a straight line of slope = -0.06 ± 0.04 and intercept = -1.30 ± 0.02.

7) Variation of Concentration of Difluoromethane at T = 162°C

The same experiments as performed in 6) were repeated here but at a lower temperature.

The results are tabulated below.

TABLE I.1, 7

$[CCl_3Br]$ =1.24 x 10^{-3} moles/l; Reaction time = 7200 secs.; Reaction temperature = 162 ± 2°C; lamp to cell distance = 6 in.

$[CH_2F_2]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
0.57×10^{-3}	0.081	5.77×10^{-2}
1.24×10^{-3}	0.116	6.56×10^{-2}
2.26×10^{-3}	0.182	5.99×10^{-2}
3.73×10^{-3}	0.245	5.63×10^{-2}
5.09×10^{-3}	0.310	5.64×10^{-2}

A least squares plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs. log $[CH_2F_2]_i$ gave a straight line of slope = 0.63 ± 0.10 and intercept = 0.90 ± 0.04. (fig. 7)

Also a least squares plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs. log $[CH_2F_2]_i$ gave a line of slope = -0.03 ± 0.05 and intercept = -1.31 ± 0.02.

8) Variation of Concentration of Difluoromethane at T = 150°C

The experiments were repeats of the previous section 7) except that the reaction temperature was lower.

TABLE I.1, 8

$[CCl_3Br]_i$ = 1.24 x 10^{-3} moles/l; Reaction time = 7200 secs.; Reaction temperature = 150 ± 2°C; lamp to cell distance = 6 in.

$[CH_2F_2]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
0.57×10^{-3}	0.064	4.41×10^{-2}
1.24×10^{-3}	0.086	4.56×10^{-2}
2.26×10^{-3}	0.127	5.14×10^{-2}
3.73×10^{-3}	0.172	5.07×10^{-2}
5.09×10^{-3}	0.207	4.94×10^{-2}

A least squares plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs. log $[CH_2F_2]_i$ gave a straight line of slope = 0.57 ± 0.06 and intercept = 0.60 ± 0.02. (fig. 7)

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs. log $[CH_2F_2]_i$ gave a straight line and the least squares method gave the slope = -0.07 ± 0.04 and the intercept = -1.14 ± 0.01.

DETAILS OF REACTIONS

Chromatographic Analysis:-

Column 20% Silicone Oil on 60-100 mesh Embacel

Temperature = 110°C

Nitrogen flow rate 120 ml./min.

Chart speed 48 in./hr.

1) Variation of Reaction Time

Temp. 163°C, Reactant pressures, CH_2F_2 66 mm., CCl_3Br 22 mm.,

Relative final concentrations of products:-

a) Time = 3600 secs.

$[CCl_3Br]$	$[CHCl_3] \times 10^3$	$[C_2Cl_6] \times 10^2$	
1.0	6.99	3.17	
1.0	7.53	3.36	
1.0	6.93	3.06	
1.0	7.74	3.28	
1.0	7.35	3.09	
1.0	7.31	3.19	Mean

b) Time = 5400 secs.

$[CCl_3Br]$	$[CHCl_3] \times 10^3$	$[C_2Cl_6] \times 10^2$	
1.0	9.25	4.24	
1.0	10.64	4.06	
1.0	11.64	4.50	
1.0	10.26	4.15	
1.0	10.46	4.21	
1.0	10.46	4.23	Mean

c) Time = 7200 secs.

$[CCl_3Br]$	$[CHCl_3] \times 10^2$	$[C_2Cl_6] \times 10^2$	
1.0	1.45	5.46	
1.0	1.38	5.80	
1.0	1.44	5.75	
1.0	1.33	5.65	
1.0	1.28	5.50	
1.0	1.38	5.63	Mean

d) Time = 9600 secs.

$[CCl_3Br]$	$[CHCl_3] \times 10^2$	$[C_2Cl_6] \times 10^2$	
1.0	2.52	6.12	
1.0	2.27	6.02	
1.0	2.31	6.07	
1.0	2.28	7.14	
1.0	2.29	7.61	
1.0	2.33	6.71	Mean

e) Time = 10,800 secs.

$[CCl_3Br]$	$\left([CHCl_3] \times 10^2\right)$	$\left([C_2Cl_6] \times 10^2\right)$	
1.0	2.65	7.94	
1.0	3.60	7.28	
1.0	3.07	7.52	
1.0	2.85	7.74	
1.0	3.04	7.62	Mean

f) Time = 12,600 secs.

$[CCl_3Br]$	$\left([CHCl_3] \times 10^2\right)$	$\left([C_2Cl_6] \times 10^2\right)$	
1.0	3.77	8.67	
1.0	3.68	9.45	
1.0	3.80	9.84	
1.0	3.99	9.88	
1.0	3.81	9.46	Mean

g) Time = 14,400 secs.

$[CCl_3Br]$	$\left([CHCl_3] \times 10^2\right)$	$\left([C_2Cl_6] \times 10\right)$	
1.0	4.13	0.93	
1.0	3.60	0.97	
1.0	4.34	1.09	
1.0	4.01	1.03	
1.0	4.43	1.05	
1.0	4.10	1.01	Mean

h) Time = 16,200 secs.

$[CCl_3Br]$	$\left([CHCl_3] \times 10^2\right)$	$\left([C_2Cl_6] \times 10\right)$	
1.0	7.00	1.05	
1.0	7.06	1.07	
1.0	6.05	1.14	
1.0	6.00	1.14	
1.0	6.53	1.10	Mean

i) Time = 18,000 secs.

$[CCl_3Br]$	$\left([CHCl_3] \times 10^2\right)$	$\left([C_2Cl_6] \times 10\right)$	
1.0	6.92	1.25	
1.0	7.06	1.29	
1.0	7.34	1.26	
1.0	6.99	1.40	
1.0	7.08	1.30	Mean

2) Variation of Reaction Temperature

Time = 14,400 secs.; Reactant pressures CH_2F_2 66 mm., CCl_3Br 22 mm.. Relative final concentrations of products:-

a) Temp. 177°C

$[CCl_3Br]$	$([CHCl_3] \times 10^2)$	$([C_2Cl_6] \times 10^2)$	
1.0	3.63	6.87	
1.0	3.66	6.73	
1.0	3.88	6.84	
1.0	3.48	6.82	
1.0	3.89	7.23	
1.0	3.71	6.90	Mean

b) Temp. 163°C

$[CCl_3Br]$	$([CHCl_3] \times 10^2)$	$([C_2Cl_6] \times 10^2)$	
1.0	1.86	5.15	
1.0	2.15	5.44	
1.0	1.91	5.29	
1.0	2.07	5.49	
1.0	1.82	5.18	
1.0	1.96	5.31	Mean

c) Temp. 153°C

$[CCl_3Br]$	$([CHCl_3] \times 10^2)$	$([C_2Cl_6] \times 10^2)$	
1.0	1.21	3.82	
1.0	1.23	4.61	
1.0	1.31	4.57	
1.0	1.17	4.52	
1.0	1.20	4.76	
1.0	1.22	4.46	Mean

d) Temp. 142°C

$[CCl_3Br]$	$([CHCl_3] \times 10^3)$	$([C_2Cl_6] \times 10^2)$	
1.0	7.40	3.42	
1.0	7.97	3.73	
1.0	6.63	3.45	
1.0	6.65	3.46	
1.0	7.16	3.52	Mean

e) Temp. 134°C

$[CCl_3Br]$	$([CHCl_3] \times 10^3)$	$([C_2Cl_6] \times 10^2)$	
1.0	5.45	2.86	
1.0	5.41	2.84	
1.0	5.74	2.79	
1.0	5.56	3.11	
1.0	5.18	3.09	
1.0	5.47	2.94	Mean

3) Variation of Incident Light Intensity

Time 14,400 secs.; Temp. 163°C; Reactant pressures, CH_2F_2 66 mm., CCl_3Br 22 mm.

Relative final concentration of products:-

a) 100%

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	5.15	0.361	
1.0	5.44	0.396	
1.0	5.29	0.361	
1.0	5.49	0.378	
1.0	5.18	0.352	
1.0	5.31	0.370	Mean

b) 59%

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	2.89	0.370	
1.0	3.13	0.371	
1.0	3.05	0.367	
1.0	3.09	0.324	
1.0	3.06	0.352	
1.0	3.05	0.357	Mean

c) 38%

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	1.80	0.376	
1.0	1.86	0.362	
1.0	2.00	0.312	
1.0	1.83	0.330	
1.0	2.17	0.306	
1.0	1.93	0.337	Mean

d) 21%

$[CCl_2Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	1.15	0.378	
1.0	1.15	0.387	
1.0	1.08	0.424	
1.0	1.20	0.359	
1.0	1.06	0.343	
1.0	1.13	0.378	Mean

4) Variation of Concentration of Bromotrichloromethane

Temp. 163°C, Reaction time 14,400 secs., Reactant pressures, CH_2F_2 66 mm. Relative final concentration of products:-

CCl_3Br pressures

a) 26 mm.

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	3.80	0.579	
1.0	4.40	0.599	
1.0	4.42	0.593	
1.0	4.70	0.536	
1.0	4.79	0.487	
1.0	4.42	0.559	Mean

b) 20 mm.

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	3.90	0.676	
1.0	4.34	0.613	
1.0	4.50	0.628	
1.0	4.24	0.542	
1.0	4.71	0.570	
1.0	4.34	0.606	Mean

c) 15mm.

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	4.25	0.593	
1.0	4.42	0.711	
1.0	4.40	0.664	
1.0	4.74	0.702	
1.0	4.48	0.672	
1.0	4.46	0.668	Mean

d) 10 mm.

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	4.09	0.793	
1.0	3.97	0.822	
1.0	4.01	0.831	
1.0	3.91	0.719	
1.0	3.99	0.791	Mean

e) 6 mm.

$[CCl_3Br]$	$\left(\begin{matrix}[C_2Cl_6] \\ \times 10^2\end{matrix}\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	4.44	0.867	
1.0	4.33	0.846	
1.0	4.19	0.853	
1.0	4.25	0.945	
1.0	4.30	0.878	Mean

5) Variation of Concentration of Difluoromethane at $T = 188^\circ C$

Time 7200 secs.; Reactant pressure: CCl_3Br 22 mm.

Relative final concentrations of products:-

CH_2F_2 pressures

a) 10 mm.

$[CCl_3Br]$	$\left(\begin{matrix}[C_2Cl_6] \\ \times 10^2\end{matrix}\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	9.68	0.132	
1.0	8.56	0.137	
1.0	9.04	0.142	
1.0	9.14	0.118	
1.0	9.23	0.122	
1.0	9.13	0.130	Mean

b) 22 mm.

$[CCl_3Br]$	$\left(\begin{matrix}[C_2Cl_6] \\ \times 10^2\end{matrix}\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	10.77	0.188	
1.0	10.60	0.182	
1.0	10.18	0.175	
1.0	10.71	0.159	
1.0	10.67	0.173	
1.0	10.59	0.175	Mean

c) 40 mm.

$[\mathrm{CCl_3Br}]$	$\left(\begin{matrix}[\mathrm{C_2Cl_6}] \\ \times 10^2\end{matrix}\right)$	$\frac{[\mathrm{CHCl_3}]}{[\mathrm{C_2Cl_6}]}$	
1.0	8.76	0.385	
1.0	9.61	0.311	
1.0	9.68	0.292	
1.0	9.11	0.296	
1.0	9.52	0.294	
1.0	9.33	0.316	Mean

d) 66 mm.

$[\mathrm{CCl_3Br}]$	$\left(\begin{matrix}[\mathrm{C_2Cl_6}] \\ \times 10^2\end{matrix}\right)$	$\frac{[\mathrm{CHCl_3}]}{[\mathrm{C_2Cl_6}]}$	
1.0	9.17	0.530	
1.0	9.17	0.517	
1.0	8.96	0.488	
1.0	9.04	0.477	
1.0	9.08	0.443	
1.0	9.08	0.491	Mean

e) 90 mm.

$[\mathrm{CCl\ Br}]$	$\left(\begin{matrix}[\mathrm{C_2Cl_6}] \\ \times 10^2\end{matrix}\right)$	$\frac{[\mathrm{CHCl_3}]}{[\mathrm{C_2Cl_6}]}$	
1.0	8.67	0.691	
1.0	9.68	0.597	
1.0	8.70	0.617	
1.0	10.18	0.552	
1.0	10.49	0.558	
1.0	9.54	0.603	Mean

6) Variation of Concentration of Difluoromethane at T = 176°C

Time 7200 secs.; Reactant pressure: $\mathrm{CCl_3Br}$ 22 mm.

Relative final concentrations of product:-

$\mathrm{CH_2F_2}$ pressures

a) 10 mm.

$[\mathrm{CCl_3Br}]$	$\left(\begin{matrix}[\mathrm{C_2Cl_6}] \\ \times 10^2\end{matrix}\right)$	$\frac{[\mathrm{CHCl_3}]}{[\mathrm{C_2Cl_6}]}$
1.0	7.93	0.114
1.0	8.11	0.110
1.0	8.04	0.095
1.0	8.47	0.089

b) 22 mm.

$[\mathrm{CCl\ Br}]$	$\left(\begin{matrix}[\mathrm{C_2Cl_6}] \\ \times 10^2\end{matrix}\right)$	$\frac{[\mathrm{CHCl_3}]}{[\mathrm{C_2Cl_6}]}$
1.0	7.42	0.202
1.0	7.26	0.169
1.0	6.83	0.161
1.0	7.51	0.159

a) 10 mm.

$[CCl_3Br]$	$\begin{pmatrix}[C_2Cl_6]\\ \times 10^2\end{pmatrix}$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	7.16	0.113	
1.0	7.94	0.104	Mean

b) 22 mm.

$[CCl\ Br]$	$\begin{pmatrix}[C_2Cl_6]\\ \times 10^2\end{pmatrix}$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	7.22	0.132	
1.0	7.25	0.165	Mean

c) 40 mm.

$[CCl_3Br]$	$\begin{pmatrix}[C_2Cl_6]\\ \times 10^2\end{pmatrix}$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	6.59	0.325	
1.0	7.16	0.287	
1.0	7.02	0.270	
1.0	7.59	0.272	
1.0	8.52	0.238	
1.0	7.38	0.278	Mean

d) 66 mm.

$[CCl\ Br]$	$\begin{pmatrix}[C_2Cl_6]\\ \times 10^2\end{pmatrix}$	$\frac{[CHCl_3]}{[C_2Cl_7]}$	
1.0	7.12	0.369	
1.0	6.74	0.357	
1.0	6.78	0.344	
1.0	7.12	0.333	
1.0	7.13	0.331	
1.0	6.98	0.347	Mean

e) 90 mm.

$[CCl_3Br]$	$\begin{pmatrix}[C_2Cl_6]\\ \times 10^2\end{pmatrix}$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	6.59	0.543	
1.0	6.20	0.515	
1.0	7.18	0.481	
1.0	7.10	0.480	
1.0	7.51	0.436	
1.0	6.92	0.491	Mean

7) Variation of Concentration of Difluoromethane at T = 162°C

Time 7200 secs.; Reactant pressure: CCl_3Br 22 mm.

Relative final concentrations of products:-

a) 10 mm.

$[CCl_3Br]$	$\left(\begin{matrix}[C_2Cl_6]\\ \times 10^2\end{matrix}\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$
1.0	5.32	0.104
1.0	5.54	0.097
1.0	5.77	0.065
1.0	5.84	0.075
1.0	6.39	0.066
1.0	5.77	0.081 Mean

b) 22 mm.

$[CCl_3Br]$	$\left(\begin{matrix}[C_2Cl_6]\\ \times 10^2\end{matrix}\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$
1.0	6.39	0.148
1.0	6.51	0.122
1.0	6.51	0.117
1.0	6.80	0.097
1.0	6.59	0.096
1.0	6.56	0.116 Mean

c) 40 mm.

$[CCl_3Br]$	$\left(\begin{matrix}[C_2Cl_6]\\ \times 10^2\end{matrix}\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$
1.0	6.26	0.183
1.0	5.58	0.216
1.0	5.86	0.182
1.0	5.68	0.179
1.0	6.59	0.151
1.0	5.99	0.182 Mean

d) 66 mm.

$[CCl_3Br]$	$\left(\begin{matrix}[C_2Cl_6]\\ \times 10^2\end{matrix}\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$
1.0	5.46	0.266
1.0	5.80	0.238
1.0	5.75	0.250
1.0	5.65	0.236
1.0	5.50	0.233
1.0	5.63	0.245 Mean

e) 90 mm.

$[CCl_3Br]$	$\left(\begin{matrix}[C_2Cl_6]\\ \times 10^2\end{matrix}\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$
1.0	5.58	0.312
1.0	6.16	0.318
1.0	5.32	0.288
1.0	5.91	0.300
1.0	5.22	0.332
1.0	5.64	0.310 Mean

8) Variation of Concentration of Difluoromethane at T = 150°C

Time 7200 secs.; Reactant pressure: CCl_3Br 22 mm.

Relative final concentrations of products:-

CH_2F_2 pressures

a) 10 mm.

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	4.55	0.076	
1.0	4.18	0.070	
1.0	4.42	0.056	
1.0	4.59	0.058	
1.0	4.28	0.058	
1.0	4.41	0.064	Mean

b) 22 mm.

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	4.43	0.088	
1.0	4.49	0.085	
1.0	4.46	0.092	
1.0	4.94	0.086	
1.0	4.50	0.079	
1.0	4.56	0.086	Mean

c) 40 mm.

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	5.08	0.136	
1.0	5.20	0.126	
1.0	5.16	0.130	
1.0	5.08	0.122	
1.0	5.16	0.120	
1.0	5.14	0.127	Mean

d) 66 mm.

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	5.06	0.183	
1.0	5.11	0.170	
1.0	5.06	0.180	
1.0	5.00	0.172	
1.0	5.13	0.158	
1.0	5.07	0.172	Mean

e) 90 mm.

$[CCl_3Br]$	$\left([C_2Cl_6] \times 10^2\right)$	$\frac{[CHCl_3]}{[C_2Cl_6]}$	
1.0	4.50	0.218	
1.0	4.67	0.213	
1.0	5.08	0.202	
1.0	5.08	0.209	
1.0	5.36	0.194	
1.0	4.94	0.207	Mean

PART I

SECTION II

THE PHOTOCHEMICAL REACTIONS
OF
BROMOTRICHLOROMETHANE
WITH
CHLOROFLUOROMETHANE

EXPERIMENTAL

REACTANTS

1) CHLOROFLUOROMETHANE:- was Du Pont's 'Freon 31' and was found to be better than 99.9% pure by analytical gas chromatography and as such was used without further purification.

2) BROMOTRICHLOROMETHANE:- was 'Schuchardt' material which was purified in the manner described in Section I.

APPARATUS

The apparatus was essentially the same as described in Section I. For all experiments the reactant pressures were measured with the capsule dial gauge and the mercury arc lamp was held 6 in. from the front face of the reaction cell.

Again the chlorofluoromethane (CH_2FCl) was stored in a bulb fitted with a side arm as the boiling point of $CH_2FCl = - 9^oC$.

EXPERIMENTAL PROCEDURE

The same procedure as described in Section I was adopted. A minor difference was that the addition of ballast liquid was not required to achieve consistent analytical chromatograms.

ANALYSIS

A Griffin and George D6 gas density balance was used for all quantitative analyses.

The chromatogram peak areas were measured using a combination of the Honeywell Precision Integrator for the initial peaks and the Du Pont Curve Resolver for the long retention time hexachloroethane peak.

IDENTIFICATION OF PRODUCTS

An analytical chromatogram gave five peaks (Fig 12) of which the last three could be assigned on the basis of retention time comparisons with authentic material.

Mass spectral analysis was carried out on a mixture of CH_2FCl (120 mm. in 149 ml.) and CCl_3Br (22 mm. in 149 ml.) photolysed for 90 mins. at 163°C with light from a Hanovia U.V.S. 220 medium pressure arc lamp. The elution order of the peaks did not change in going from a silicone oil column to a tritolylphosphate column. This was checked as the mass spectra were run using a 50 metre Tritolyl Phosphate capillary column in the Perkin Elmer F11.

Mass spectral analysis:-

Perkin Elmer F11, Helium pressure = 1.0 lb./sq.in., Column temperature = 40°C until elution of bromotrichloromethane. Thereafter the column temperature was increased to 100°C with a helium pressure of 10 lb./sq.in.

A.E.I. M.S.12; magnet setting 5; decrease 9; ionization current 22 ev; accelerating potential 8 Kv; band width 500 c/s and chart speed 1.5 in./s..

Peak 1 Multiplier 2.50

m/e	Relative Intensity	Assignment
31	3	CF^+
33	100	CH_2F^+
47, 49	4, 12	CCl^+
48, 50	1.5, 0.5	$CHCl^+$
49, 51	12, 4	CH_2^+Cl
67, 69	2, 1.5	$CHFCl^+$
68, 70	80, 25	CH_2FCl^+

Peak identified as chlorofluoromethane (CH_2FCl).

Confirmed by comparison of retention time with an authentic sample.

Peak 2 Multiplier 3.50

m/e	Relative Intensity	Assignment
31	4.5	CF^+
33	11	CH_2F
47, 49	3, 3	CCl^+
48, 50	3, 1	$CHCl^+$
49, 51	3, 1	CH_2Cl^+
67, 69	100, 31	$CHClF^+$
68, 70	8, 2.3	CH_2ClF^+
79, 81	0.4, 0.4	Br^+
110, 112	8, 8	$CFBr^+$
126, 128, 130	1.5, 2, 0.4	$CClBr^+$
146, 148, 150	1.2, 1.5, 0.3	$CHClFBr^+$

Peak identified as bromochlorofluoromethane (CHClFBr) with traces of chlorofluoromethane (CH_2FCl)

Peak 3 Mutliplier 4.00

m/e	Relative Intensity	Assignment
35, 37	Trace	Cl^+
47, 49	20, 6	CCl^+
48, 50	14, 4.5	$CHCl^+$
82, 84, 86	4.5, 4.5, 0.8	CCl_2^+
83, 85, 87	100, 92, 14	$CHCl_2^+$
117, 119, 121, 123	Trace	CCl_3^+
118, 120, 122, 124	Trace	$CHCl_3^+$
146, 148, 150	3, 3, 0.8	$CHClFBr^+$

Peak identified as chloroform ($CHCl_3$) with a trace of CHClFBr. Confirmed by comparison of retention time with an authentic sample.

Peak 4 Multiplier 2.50

m/e	Relative Intensity	Assignment
47, 49	11, 4	CCl^+
79, 81	0.5, 0.5	Br^+
82, 84, 86	28, 17, 3	CCl_2^+
91, 93	0.5, 0.5	CBr^+
117, 119, 121, 123	100, 100, 42, 5	CCl_3^+
126, 128, 130	2, 3, 0.5	$CClBr^+$
161, 163, 165, 167	23, 39, 15, 1.5	CCl_2Br^+

Peak identified as bromotrichloromethane (CCl_3Br). Confirmed by comparison of retention time with an authentic sample.

Peak 5 Multiplier 6.00

m/e	Relative Intensity	Assignment
94, 96, 98	18, 12, 2	$C_2Cl_2^+$
117, 119, 121, 123	100, 94, 30, 4	CCl_3^+
129, 131, 133, 135	23, 20, 6, 1	$C_2Cl_3^+$
164, 166, 170, 172, 174	32, 40, 20, 4, ?	$C_2Cl_4^+$
199, 201, 203, 205, 207, 209	35, 60, 35,12, 3, ?	$C_2Cl_5^+$

Peak identified as hexachloroethane (C_2Cl_6). Comfirmed by comparison of retention time with an authentic sample.

The analytical chromatogram gave in order of elution,

CH_2FCl, $CHClFBr$, $CHCl_3$, CCl_3Br, C_2Cl_6

RESULTS

THE REACTIONS OF BROMOTRICHLOROMETHANE WITH CHLOROFLUOROMETHANE

In order of elution, the peaks of an analytical chromatogram were found to correspond to chlorofluoromethane, bromochlorofluoromethane, chloroform, bromotrichloromethane and finally hexachloroethane. The bromine produced in the reaction was not detected by analytical gas chromatography, but was assumed to be equal to the concentration of hexachloroethane. As in section I, a series of experiments were carried out in which one variable at a time was varied while the others were held constant. In all cases the lamp to reaction cell distance was 6 in.

1) Variation of Reaction Time.

A series of experiments was performed at a constant temperature with fixed amounts of reactants and constant incident light intensity but for various time intervals. The results are shown in the following table.

TABLE I.2, 1

$[CH_2FCl]_i = 3.73 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l;
Reaction temperature = 163 ± 3°C

Reaction time Sec.	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHClFBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
7200	3.23	3.03	5.27×10^{-2}
6000	2.60	2.71	4.54×10^{-2}
4800	2.44	2.61	3.24×10^{-2}
3600	1.75	1.85	2.42×10^{-2}
2400	1.13	1.34	1.79×10^{-2}
1200	0.49	0.66	0.98×10^{-2}

The ratio $[C_2Cl_6]_f/[CCl_3Br]_f$ was plotted against time, and gave a straight line passing close to the origin. A least squares calculation on all the data gave for the time intercept 15 secs. and slope $\phi I_a/2[CCl_3Br]_i = 0.73 \times 10^{-5}$ sec.$^{-1}$. (fig. 2)

2) Variation of Reaction Temperature

A series of experiments was performed in which the only variable was the reaction temperature. The results are shown in table I.2, 2.

TABLE I.2, 2

$[CH_2FCl]_i = 3.73 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l;
Reaction time = 5400 secs.

Temp. °C	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHClFBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
178	3.05	2.97	5.00×10^{-2}
162	2.29	2.51	3.75×10^{-2}
151	1.82	1.94	3.07×10^{-2}
139	1.19	1.34	2.36×10^{-2}
127	1.06	1.27	1.68×10^{-2}
114	0.68	0.62	1.42×10^{-2}

A least squares plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs $10^3/T$ gave a straight line of slope $(E_2-\frac{1}{2}E_6)/2.303R = 1.77 \pm 0.25$ and extrapolated intercept

$$\log \frac{\sqrt{2}[CH_2FCl]A_2}{(\phi I_a A_6)^{\frac{1}{2}}} = 4.40 \pm 0.11. \text{ (fig. 4)}$$

Similarly, a plot of log $[CHClFBr]_f/[C_2Cl_6]_f$ vs. $10^3/T$ gave a slope $(E_2-\frac{1}{2}E_6)/2.303R = 1.78 \pm 0.41$, and intercept $\log \frac{\sqrt{2}[CH_2FCl]A_2}{(\phi I_a A_6)^{\frac{1}{2}}}$

$= 4.45 \pm 0.17$.

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs $10^3/T$ gave, by the least squares method, a slope = -1.54 ± 0.12 and an extrapolated intercept of 2.10 ± 0.05. (fig. 3)

3) Variation of Incident Light Intensity

A series of light variation experiments was carried out by interposing calibrated wire gauzes between the light source and the reaction vessel. The results are tabulated below.

TABLE I.2, 3

$[CH_2FCl]_i = 3.73 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l;
Reaction temperature = 163 ± 2°C; Reaction time = 5400 secs.

Relative Intensity %	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHClFBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
100	2.83	2.77	3.46×10^{-2}
59	2.25	2.31	2.26×10^{-2}
46	2.27	2.17	1.65×10^{-2}
33	1.89	1.97	1.23×10^{-2}

The least squares method gave for a plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log (R.I.) a slope = 0.36 ± 0.12 and intercept = -0.27 ± 0.07.(fig.5) When applied to a plot of log $[CHClFBr]_f/[C_2Cl_6]_f$ vs log (R.I.), the method gave a slope = 0.33 ± 0.15 and intercept = -0.22 ± 0.09. A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log (R.I.) gave a slope = 0.94 ± 0.06 and intercept = -3.34 ± 0.03. (fig. 6)

4) Variation of Concentration of Bromotrichloromethane

A series of experiments was performed in which the reaction time, reaction temperature, concentration of chlorofluoromethane and incident light intensity were all held constant while the bromotrichloromethane concentration was varied. The results are tabulated below.

TABLE I.2, 4

$[CH_2ClF]_i = 3.73 \times 10^{-3}$ moles/l; Reaction time = 5400 secs., Reaction temperature = 163 ± 2°C.

$[CCl_3Br]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHClFBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
1.24×10^{-3}	2.29	2.51	3.75×10^{-2}
1.02×10^{-3}	2.50	2.71	3.60×10^{-2}
0.79×10^{-3}	2.32	2.48	3.81×10^{-2}
0.57×10^{-3}	2.29	2.30	3.89×10^{-2}
0.34×10^{-3}	2.32	2.23	3.57×10^{-2}

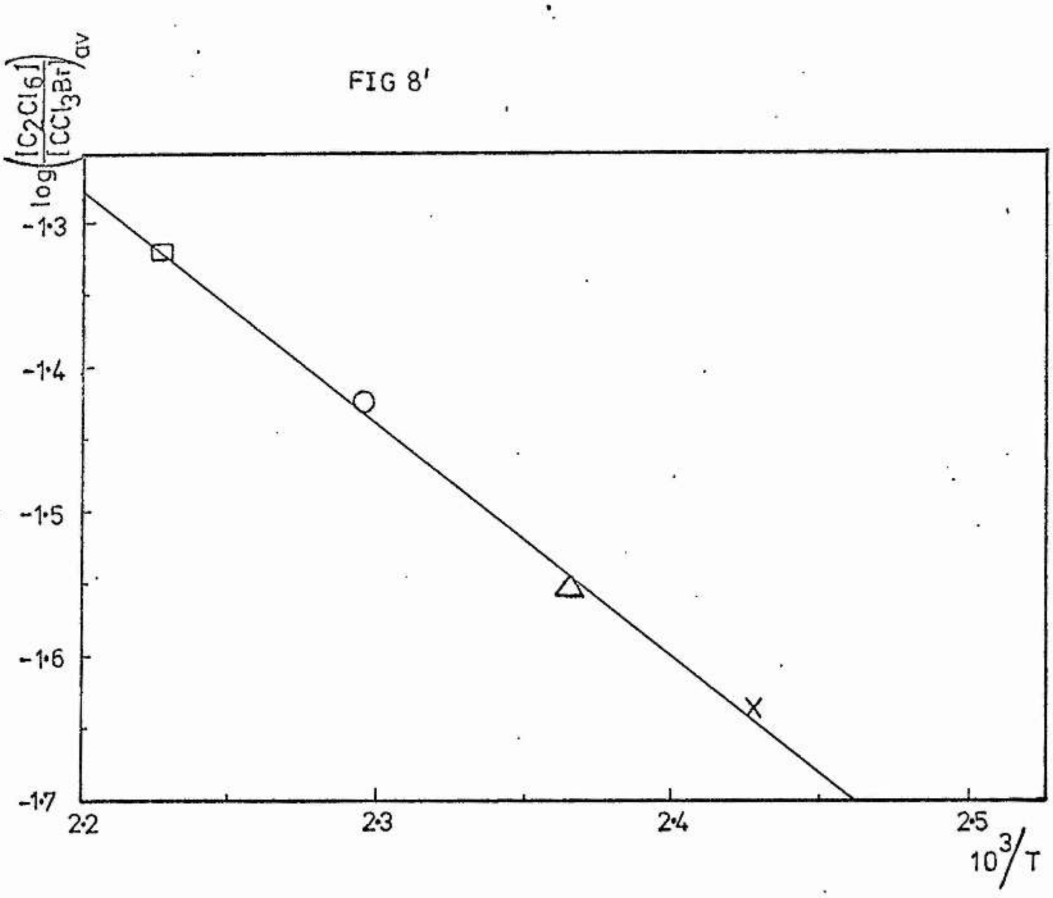
The least squares method applied to the above data gave for a plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CCl_3Br]_i$ a slope = 0.03 ± 0.22 and intercept = 0.45 ± 0.07. For a plot of log $[CHClFBr]_f/[C_2Cl_6]_f$ vs log $[CCl_3Br]_i$ the straight line had a slope = 0.14 ± 0.38 and an extrapolated intercept = 0.81 ± 0.12.

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CCl_3Br]_i$ was a straight line with a 'least squares' slope = 0.01 ± 0.11 and intercept = -1.40 ± 0.03.

5) Variation of Concentration of Chlorofluoromethane at T = 177°C

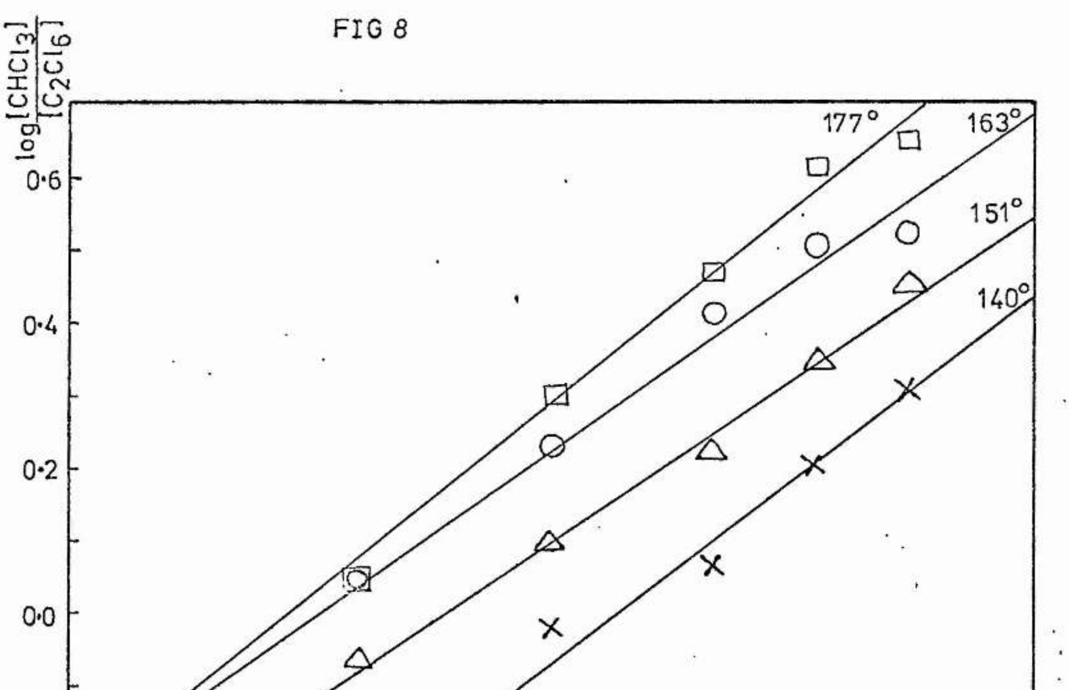
This set of experiments formed part of a set in which the concentration of chlorofluoromethane was varied at various set reaction temperatures. The results are listed in the following table.

FIG 8'



$\log\left(\frac{[C_2Cl_6]}{[CCl_3Br]}\right)_{av}$
-1·3
-1·4
-1·5
-1·6
-1·7
2·2
2·3
2·4
2·5
$10^3/T$

FIG 8



$\log\frac{[CHCl_3]}{[C_2Cl_6]}$
177°
163°
151°
140°
0·6
0·4
0·2
0·0
-0·2
-0·4
-0·6
-3·3
-3·1
-2·9
-2·7
-2·5
-2·3
-2·1
$\log[CH_2FCl]$

TABLE I.2, 5

$[CCl_3Br]$ = 1.24 x 10^{-3} moles/l; Reaction time = 5400 secs.

Reaction temperature = 177 ± 2°C

$[CH_2FCl]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHClFBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
0.57 x 10^{-3}	0.63	0.68	5.07 x 10^{-2}
1.24 x 10^{-3}	1.10	1.13	4.95 x 10^{-2}
2.26 x 10^{-3}	1.97	2.02	4.80 x 10^{-2}
3.73 x 10^{-3}	2.92	2.99	4.43 x 10^{-2}
5.09 x 10^{-3}	4.08	4.07	4.61 x 10^{-2}
6.78 x 10^{-3}	4.44	4.47	4.83 x 10^{-2}

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CH_2FCl]_i$ gave a straight line and the least squares method led to a slope = 0.83 ± 0.08 and to an intercept = 2.47 ± 0.03. For a plot of log $[CHClFBr]_f/[C_2Cl_6]_f$ vs log $[CH_2FCl]_i$ the least squares method led to a slope = 0.79 ± 0.09 and an intercept = 2.39 ± 0.03. (fig. 8)

The straight line plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CH_2FCl]_i$ had a 'least squares' slope = -0.04 ± 0.03 and an intercept = -1.42 ± 0.01.

6) Variation of Concentration of Chlorofluoromethane at T = 163°C

The concentration of chlorofluoromethane was varied while all other variables were held constant. The results are tabulated below.

TABLE I.2, 6

$[CCl_3Br]$ = 1.24 x 10^{-3} moles/l; Reaction time = 5400 secs., Reaction temperature = 163 ± 3°C

$[CH_2FCl]_i$ moles/l	$[CHCl_3]_f$ / $[C_2Cl_6]_f$	$[CHClFBr]_f$ / $[C_2Cl_6]_f$	$[C_2Cl_6]_f$ / $[CCl_3Br]_f$
0.57 x 10^{-3}	0.62	0.58	3.91 x 10^{-2}
1.24 x 10^{-3}	1.10	1.11	3.81 x 10^{-2}
2.26 x 10^{-3}	1.68	1.78	3.65 x 10^{-2}
3.73 x 10^{-3}	2.55	2.72	3.59 x 10^{-2}
5.09 x 10^{-3}	3.18	3.46	3.58 x 10^{-2}
6.78 x 10^{-3}	3.28	3.58	4.16 x 10^{-2}

The least squares method was applied to the following straight line plots to obtain slope and intercept values. A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs. log $[CH_2FCl]_i$ had a slope = 0.70 ± 0.06 and an intercept = 2.08 ± 0.02. (fig. 8)

A plot of log $[CHClFBr]_f/[C_2Cl_6]_f$ vs log $[CH_2FCl]_i$ had a slope = 0.77 ± 0.10 and an intercept = 2.26 ± 0.04. A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CH_2FCl]_i$ had a slope = -0.002 ± 0.05 and an intercept = -1.43 ± 0.02.

7) Variation of Concentration of Chlorofluoromethane at T = 151°C

Within this series the concentration of chlorofluoromethane was varied while all the other variables were held constant. The results are tabulated below.

TABLE I.2, 7

$[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction time = 5400 secs.,
Reaction temperature = 151 ±2°C

$[CH_2FCl]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHClFBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
0.57×10^{-3}	0.48	0.34	2.82×10^{-2}
1.24×10^{-3}	0.85	0.70	3.04×10^{-2}
2.26×10^{-3}	1.23	1.16	2.68×10^{-2}
3.73×10^{-3}	1.65	1.78	2.85×10^{-2}
5.09×10^{-3}	2.19	2.32	2.48×10^{-2}
6.78×10^{-3}	2.81	2.68	2.87×10^{-2}

The least squares method applied to the straight line plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CH_2FCl]_i$ gave the slope = 0.69 ± 0.08 and the intercept = 1.93 ± 0.03. Similar application to the straight line plot of log $[CHClFBr]_f/[C_2Cl_6]_f$ vs log $[CH_2FCl]_i$ led to a slope = 0.84 ± 0.14 and an intercept = 2.27 ± 0.05. (fig. 8)

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CH_2FCl]_i$ gave a straight line of slope = -0.03 ± 0.06 and intercept = -1.64 ± 0.02.

8) Variation of Concentration of Chlorofluoromethane at T = 140°C

A series of experiments was performed in which the concentration of chlorofluoromethane was varied while the other variables were held constant. The results are listed below.

TABLE I.2, 8

$[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction time = 5400 secs., Reaction temperature = $140 \pm 2^{\circ}C$

$[CH_2FCl]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHClFBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
0.57×10^{-3}	0.29	0.33	2.49×10^{-2}
1.24×10^{-3}	0.50	0.48	2.43×10^{-2}
2.26×10^{-3}	0.94	0.86	2.11×10^{-2}
3.73×10^{-3}	1.15	1.14	2.45×10^{-2}
5.09×10^{-3}	1.58	1.60	2.08×10^{-2}
6.78×10^{-3}	2.02	2.01	2.29×10^{-2}

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CH_2FCl]_i$ was a straight line with slope = 0.78 ± 0.10 and intercept = 1.98 ± 0.05. (fig. 8)

Similarly, the least squares method gave 0.74 ± 0.13 for the slope and 1.88 ± 0.05 for the intercept of a plot of log $[CHClFBr]_f/[C_2Cl_6]_f$ vs log $[CH_2FCl]_i$. Finally, the least squares method gave, for a plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CH_2FCl]_i$, a slope = -0.05 ± 0.05 and an intercept of -1.76 ± 0.02.

DETAILS OF REACTION

Chromatographic Analysis:-

Column 20% Silicone Oil on 60-100 mesh Embacel.

Temperature 90°C

Nitrogen flow rate 120 ml./min.,

Chart speed 48 in./hr.

1) Variation of Reaction Time

Temp. 163°C, Reactant pressures, CH_2FCl 66 mm., CCl_3Br 22 mm.

Relative final concentrations of products.

a) Time 7200 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.41	3.44	5.12×10^{-2}	
1.0	3.26	2.80	5.23×10^{-2}	
1.0	3.30	3.53	6.03×10^{-2}	
1.0	3.13	2.70	4.92×10^{-2}	
1.0	3.03	2.69	5.06×10^{-2}	
1.0	3.23	3.03	5.27×10^{-2}	Mean

b) Time 6000 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.65	3.12	4.67×10^{-2}	
1.0	2.62	2.79	4.55×10^{-2}	
1.0	2.72	2.73	4.55×10^{-2}	
1.0	2.76	2.55	4.39×10^{-2}	
1.0	2.27	2.36	4.56×10^{-2}	
1.0	2.60	2.71	4.54×10^{-2}	Mean

c) Time 4800 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.68	3.02	3.08×10^{-2}	
1.0	2.17	2.28	3.36×10^{-2}	
1.0	2.51	2.79	3.25×10^{-2}	
1.0	2.64	2.76	3.12×10^{-2}	
1.0	2.20	2.20	3.41×10^{-2}	
1.0	2.44	2.61	3.24×10^{-2}	Mean

d) Time 3600 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.09	2.43	2.27×10^{-2}	
1.0	1.90	2.04	2.28×10^{-2}	
1.0	1.55	1.61	2.60×10^{-2}	
1.0	1.69	1.71	2.36×10^{-2}	
1.0	1.50	1.47	2.58×10^{-2}	
1.0	1.75	1.85	2.42×10^{-2}	Mean

e) Time 2400 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.30	1.41	1.60×10^{-2}	
1.0	1.01	1.25	1.91×10^{-2}	
1.0	1.20	1.36	1.91×10^{-2}	
1.0	1.13	1.54	1.76×10^{-2}	
1.0	0.99	1.14	1.78×10^{-2}	
1.0	1.13	1.34	1.79×10^{-2}	Mean

f) Time 1200 secs..

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.01	*	9.07×10^{-3}	
1.0	0.55	0.80	9.68×10^{-3}	
1.0	0.31	0.59	10.19×10^{-3}	
1.0	0.31	0.75	9.73×10^{-3}	
1.0	0.24	0.49	10.53×10^{-3}	
1.0	0.49	0.66	9.84×10^{-3}	Mean

*Analysis failure

2) Variation of Reaction Temperature

Time 5400 secs., Reactant pressures, CH_2FCl 66 mm., CCl_3Br 22 mm.

Relative final concentrations of products:-

a) Temp. 178°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.49	3.44	4.94×10^{-2}	
1.0	2.99	3.11	4.98×10^{-2}	
1.0	3.04	2.88	4.98×10^{-2}	
1.0	2.81	2.72	5.05×10^{-2}	
1.0	2.92	2.69	5.06×10^{-2}	
1.0	3.05	2.97	5.00×10^{-2}	Mean

b) Temp. 162°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.30	2.58	3.74×10^{-2}	
1.0	2.33	2.54	3.74×10^{-2}	
1.0	2.34	2.67	3.87×10^{-2}	
1.0	2.20	2.24	3.67×10^{-2}	
1.0	2.29	2.51	3.75×10^{-2}	Mean

c) Temp. 151°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.97	2.15	2.89×10^{-2}	
1.0	2.20	2.55	2.98×10^{-2}	
1.0	1.63	1.62	3.16×10^{-2}	
1.0	1.91	2.12	2.98×10^{-2}	
1.0	1.37	1.27	3.38×10^{-2}	
1.0	1.82	1.94	3.07×10^{-2}	Mean

d) Temp. 139°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.46	1.98	2.20×10^{-2}	
1.0	1.08	1.02	2.61×10^{-2}	
1.0	1.40	1.81	2.14×10^{-2}	
1.0	1.11	1.03	2.29×10^{-2}	
1.0	0.91	0.84	2.59×10^{-2}	
1.0	1.19	1.34	2.36×10^{-2}	Mean

e) Temp. 127°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.43	1.81	1.47×10^{-2}	
1.0	0.99	1.14	1.75×10^{-2}	
1.0	1.18	1.48	1.63×10^{-2}	
1.0	0.92	0.94	1.78×10^{-2}	
1.0	0.77	0.98	1.79×10^{-2}	
1.0	1.06	1.27	1.68×10^{-2}	Mean

f) Temp. 114°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_2Br]}$	
1.0	0.55	0.47	1.62×10^{-2}	
1.0	0.73	0.72	1.35×10^{-2}	
1.0	0.71	0.65	1.35×10^{-2}	
1.0	0.79	0.78	1.35×10^{-2}	
1.0	0.62	0.51	1.43×10^{-2}	
1.0	0.68	0.62	1.42×10^{-2}	Mean

3) Variation of Incident Light Intensity

Time 5400 secs., Reactant pressures, CH_2FCl 66 mm., CCl_3Br 22 mm. Temp. 163°C

Relative final concentrations of products:-

Transmissions

a) 100%

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.05	3.13	3.27×10^{-2}	
1.0	2.96	3.22	3.47×10^{-2}	
1.0	2.75	2.46	3.49×10^{-2}	
1.0	2.74	2.60	3.58×10^{-2}	
1.0	2.67	2.45	3.48×10^{-2}	
1.0	2.83	2.77	3.46×10^{-2}	Mean

b) 59%

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.27	2.44	2.27×10^{-2}	
1.0	2.31	2.54	2.17×10^{-2}	
1.0	2.37	2.33	2.29×10^{-2}	
1.0	2.20	2.08	2.28×10^{-2}	
1.0	2.08	2.14	2.31×10^{-2}	
1.0	2.25	2.31	2.26×10^{-2}	Mean

c) 46%

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.56	2.54	1.49×10^{-2}	
1.0	2.14	1.95	1.70×10^{-2}	
1.0	2.55	2.47	1.54×10^{-2}	
1.0	2.25	2.30	1.65×10^{-2}	
1.0	1.85	1.58	1.84×10^{-2}	
1.0	2.27	2.17	1.65×10^{-2}	Mean .

d) 33%

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.00	2.35	1.18×10^{-2}	
1.0	1.94	2.02	1.16×10^{-2}	
1.0	2.45	2.31	1.22×10^{-2}	
1.0	1.67	1.82	1.29×10^{-2}	
1.0	1.40	1.38	1.32×10^{-2}	
1.0	1.89	1.97	1.23×10^{-2}	Mean

4) Variation of Concentration of Bromotrichloromethane

Time 5400 secs., Reactant pressure: CH_2FCl 66 mm., Temp. 163°C

Relative final concentrations of products:-

CCl_3Br pressures

a) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.30	2.58	3.74×10^{-2}	
1.0	2.33	2.54	3.74×10^{-2}	
1.0	2.34	2.67	3.87×10^{-2}	
1.0	2.20	2.24	3.67×10^{-2}	
1.0	2.29	2.51	3.75×10^{-2}	Mean

b) 18 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.07	3.77	3.30×10^{-2}	
1.0	2.35	2.72	3.67×10^{-2}	
1.0	2.54	2.66	3.53×10^{-2}	
1.0	2.34	2.37	3.67×10^{-2}	
1.0	2.19	2.00	3.84×10^{-2}	
1.0	2.50	2.71	3.60×10^{-2}	Mean

c) 14 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.27	3.82	3.17×10^{-2}	
1.0	1.85	1.85	4.39×10^{-2}	
1.0	2.42	2.81	3.68×10^{-2}	
1.0	2.30	2.33	3.63×10^{-2}	
1.0	1.78	1.58	4.15×10^{-2}	
1.0	2.32	2.48	3.81×10^{-2}	Mean

d) 10 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.82	3.83	3.96×10^{-2}	
1.0	1.91	1.39	3.99×10^{-2}	
1.0	2.16	2.15	3.75×10^{-2}	
1.0	2.03	1.95	3.94×10^{-2}	
1.0	2.52	2.17	3.83×10^{-2}	
1.0	2.29	2.30	3.89×10^{-2}	Mean

e) 6 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.27	1.95	3.46×10^{-2}	
1.0	2.34	2.50	3.69×10^{-2}	
1.0	2.21	2.09	3.63×10^{-2}	
1.0	2.45	2.39	3.51×10^{-2}	
1.0	2.32	2.23	3.57×10^{-2}	Mean

5) Variation of Concentration of Chlorofluoromethane at T = 177°C

Time 5400 secs., Reactant pressure:- CCl_3Br 22 mm.,

Relative final concentrations of products:-

CH_2FCl pressures

a) 10 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	0.76	0.75	5.14×10^{-2}	
1.0	0.66	0.66	5.06×10^{-2}	
1.0	0.60	0.71	4.98×10^{-2}	
1.0	0.50	0.61	5.11×10^{-2}	
1.0	0.63	0.68	5.07×10^{-2}	Mean

b) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.17	1.18	5.23×10^{-2}	
1.0	1.03	1.10	4.86×10^{-2}	
1.0	0.91	1.04	5.06×10^{-2}	
1.0	1.29	1.19	4.67×10^{-2}	
1.0	1.10	1.13	4.95×10^{-2}	Mean

c) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.18	2.29	4.94×10^{-2}	
1.0	2.07	2.17	4.67×10^{-2}	
1.0	1.92	2.21	4.60×10^{-2}	
1.0	1.88	1.79	4.75×10^{-2}	
1.0	1.79	1.64	5.06×10^{-2}	
1.0	1.97	2.02	4.80×10^{-2}	Mean

d) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	[CHClFBr]	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.37	3.41	4.41×10^{-2}	
1.0	2.76	3.01	4.60×10^{-2}	
1.0	2.62	2.72	4.32×10^{-2}	
1.0	3.32	3.34	4.13×10^{-2}	
1.0	2.52	2.49	4.71×10^{-2}	
1.0	2.92	2.99	4.43×10^{-2}	Mean

e) 90 mm.

$[C_2Cl_6]$	$[CHCl_3]$	[CHClFBr]	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	4.98	5.18	4.18×10^{-2}	
1.0	4.30	4.20	4.49×10^{-2}	
1.0	4.29	4.63	4.64×10^{-2}	
1.0	3.71	3.46	4.78×10^{-2}	
1.0	3.12	2.89	4.94×10^{-2}	
1.0	4.08	4.07	4.61×10^{-2}	Mean

f) 120 mm.

$[C_2Cl_6]$	$[CHCl_3]$	[CHClFBr]	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	5.14	5.20	4.45×10^{-2}	
1.0	4.08	4.08	5.10×10^{-2}	
1.0	4.59	4.80	4.85×10^{-2}	
1.0	4.54	4.59	4.74×10^{-2}	
1.0	3.83	3.67	5.02×10^{-2}	
1.0	4.44	4.67	4.83×10^{-2}	Mean

6) Variation of Concentration of Chlorofluoromethane at T = 163°C

Time 5400 secs. Reactant pressure:- CCl_3Br 22 mm.

Relative final concentrations of products:-

CH_2FCl pressures

a) 10 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	0.71	0.73	4.48×10^{-2}	
1.0	0.58	0.58	3.61×10^{-2}	
1.0	0.57	0.54	4.15×10^{-2}	
1.0	0.63	0.56	3.38×10^{-2}	
1.0	0.64	0.50	3.95×10^{-2}	
1.0	0.62	0.58	3.91×10^{-2}	Mean

b) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.20	1.18	3.40×10^{-2}	
1.0	1.18	1.33	3.86×10^{-2}	
1.0	1.07	1.09	3.75×10^{-2}	
1.0	1.04	0.98	3.75×10^{-2}	
1.0	1.00	0.96	4.26×10^{-2}	
1.0	1.10	1.11	3.81×10^{-2}	Mean

c) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.94	2.26	3.40×10^{-2}	
1.0	1.64	1.99	3.56×10^{-2}	
1.0	1.82	1.99	3.80×10^{-2}	
1.0	1.52	1.37	3.64×10^{-2}	
1.0	1.48	1.27	3.80×10^{-2}	
1.0	1.68	1.78	3.64×10^{-2}	Mean

d) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.83	3.05	3.58×10^{-2}	
1.0	2.52	2.87	3.51×10^{-2}	
1.0	2.59	2.99	3.51×10^{-2}	
1.0	2.52	2.77	3.63×10^{-2}	
1.0	2.27	1.92	3.74×10^{-2}	
1.0	2.55	2.72	3.59×10^{-2}	Mean

e) 90 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.40	3.75	3.50×10^{-2}	
1.0	3.66	4.42	3.53×10^{-2}	
1.0	3.21	3.50	3.45×10^{-2}	
1.0	2.88	3.01	3.69×10^{-2}	
1.0	2.73	2.59	3.74×10^{-2}	
1.0	3.18	3.46	3.58×10^{-2}	Mean

f) 120 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.35	3.59	4.19×10^{-2}	
1.0	3.56	3.30	4.23×10^{-2}	
1.0	2.81	3.27	4.59×10^{-2}	
1.0	3.47	4.11	3.94×10^{-2}	
1.0	3.20	3.64	3.87×10^{-2}	
1.0	3.28	3.58	4.16×10^{-2}	Mean

7) Variation of Concentration of Chlorofluoromethane at T = 151°C

Time 5400 secs., Reactant pressure:- CCl_3Br 22 mm.,

Relative final concentrations of products:-

CH_2FCl pressures

a) 10 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	0.49	0.28	2.71×10^{-2}	
1.0	0.55	0.35	2.97×10^{-2}	
1.0	0.50	0.36	2.92×10^{-2}	
1.0	0.43	0.36	2.76×10^{-2}	
1.0	0.42	0.33	2.76×10^{-2}	
1.0	0.48	0.34	2.82×10^{-2}	Mean

b) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.14	1.01	2.76×10^{-2}	
1.0	0.84	0.63	3.01×10^{-2}	
1.0	0.86	0.68	3.06×10^{-2}	
1.0	0.79	0.62	3.07×10^{-2}	
1.0	0.65	0.54	3.30×10^{-2}	
1.0	0.85	0.70	3.04×10^{-2}	Mean

c) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.15	1.43	2.61×10^{-2}	
1.0	1.32	1.25	2.54×10^{-2}	
1.0	1.37	1.14	2.62×10^{-2}	
1.0	1.10	0.82	2.95×10^{-2}	
1.0	1.23	1.16	2.68×10^{-2}	Mean

d) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.60	1.63	2.82×10^{-2}	
1.0	1.87	2.10	2.79×10^{-2}	
1.0	1.73	1.71	2.85×10^{-2}	
1.0	1.62	2.22	2.69×10^{-2}	
1.0	1.42	1.22	3.10×10^{-2}	
1.0	1.65	1.78	2.85×10^{-2}	Mean

e) 90 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.40	3.29	2.24×10^{-2}	
1.0	2.37	2.75	2.06×10^{-2}	
1.0	2.05	2.20	2.56×10^{-2}	
1.0	2.14	1.98	2.76×10^{-2}	
1.0	1.98	1.36	2.77×10^{-2}	
1.0	2.19	2.32	2.48×10^{-2}	Mean

f) 120 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.38	3.39	2.49×10^{-2}	
1.0	3.02	3.35	2.75×10^{-2}	
1.0	2.32	1.91	2.93×10^{-2}	
1.0	2.50	2.05	3.31×10^{-2}	
1.0	2.81	2.68	2.87×10^{-2}	Mean

8) Variation of Concentration of Chlorofluoromethane at T = 140°C

Time 5400 secs., Reactant pressure:- CCl_3Br 22 mm.

Relative final concentrations of products:-

CH_2FCl pressures

a) 10 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	0.40	0.51	2.31×10^{-2}	
1.0	0.25	0.28	2.88×10^{-2}	
1.0	0.28	0.30	2.63×10^{-2}	
1.0	0.27	0.26	2.45×10^{-2}	
1.0	0.25	0.29	2.20×10^{-2}	
1.0	0.29	0.33	2.49×10^{-2}	Mean

b) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	0.53	0.48	2.39×10^{-2}	
1.0	0.52	0.49	2.47×10^{-2}	
1.0	0.50	0.45	2.47×10^{-2}	
1.0	0.52	0.47	2.45×10^{-2}	
1.0	0.42	0.52	2.35×10^{-2}	
1.0	0.50	0.48	2.43×10^{-2}	Mean

c) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.25	1.16	1.83×10^{-2}	
1.0	0.96	0.90	2.25×10^{-2}	
1.0	0.73	0.65	2.10×10^{-2}	
1.0	0.83	0.73	2.25×10^{-2}	
1.0	0.94	0.86	2.11×10^{-2}	Mean

d) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.22	1.09	2.42×10^{-2}	
1.0	1.37	1.43	2.35×10^{-2}	
1.0	1.22	1.17	2.52×10^{-2}	
1.0	1.07	1.30	2.36×10^{-2}	
1.0	0.86	0.69	2.61×10^{-2}	
1.0	1.15	1.14	2.45×10^{-2}	Mean

e) 90 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.16	2.55	1.83×10^{-2}	
1.0	1.51	1.42	2.06×10^{-2}	
1.0	1.35	1.22	2.29×10^{-2}	
1.0	1.61	1.81	2.02×10^{-2}	
1.0	1.28	1.03	2.19×10^{-2}	
1.0	1.58	1.60	2.08×10^{-2}	Mean

f) 120 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHClFBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.21	2.01	2.04×10^{-2}	
1.0	1.98	2.22	2.40×10^{-2}	
1.0	2.18	2.06	2.34×10^{-2}	
1.0	2.09	2.04	2.28×10^{-2}	
1.0	1.65	1.72	2.37×10^{-2}	
1.0	2.02	2.01	2.29×10^{-2}	Mean

PART I

SECTION III

THE PHOTOCHEMICAL REACTIONS
OF
BROMOTRICHLOROMETHANE
WITH
DICHLOROMETHANE

EXPERIMENTAL

REACTANTS

1) DICHLOROMETHANE:- was 'British Drug Houses' material and, as analytical gas chromatography showed it to be better than 99.7% pure, it was used without further purification.

2) BROMOTRICHLOROMETHANE:- as described in Section I.

APPARATUS

The apparatus has been described in Section I. As in Section II the reactant pressures were measured with a capsule dial gauge. With this system both reactants were stored in small tubes surrounded by liquid nitrogen, as the boiling point of dichloromethane was sufficiently high (40°C) to obviate the risk of blowing the storage tube off the vacuum line should it have warmed up.

EXPERIMENTAL PROCEDURE

The procedure was as described in Section I except that no ballast liquid was required.

ANALYSIS

A Griffin and George D6 gas density balance was used for all quantitative analysis.

The chromatogram peak areas were originally measured by a Honeywell Precision Integrator. With later experiments a combination of the precision integrator with the Du Pont Curve Resolver was used as it was found that the curve resolver gave a more consistent range of values for the peak area of hexachloroethane which has a long retention time. The percentage difference between the ratio C_2Cl_6/CCl_3Br as determined by the precision integrator and the curve resolver was insignificant as long as there was a reasonable amount of the termination product, hexachloroethane.

Identification of Products

The reaction products of the photolysis of dichloromethane (22 mm. in 62 ml.) with bromotrichloromethane (22 mm. in 149 ml.) for four hours at 212°C with a high pressure mercury arc lamp as light source gave eight peaks whereas the analytical chromatograms gave five significant peaks. In all cases it was possible to assign the peaks produced by comparison of retention times of authentic materials.

In order of elution the peaks were

CH_2Cl_2, $CHCl_3$, CCl_4, $CHCl_2Br$, CCl_3Br, C_2Cl_4, CCl_2Br_2 and C_2Cl_6

These assignments were confirmed by mass spectral analysis of the reaction mixture produced above.

Analysis was as follows:-

Perkin-Elmer F11, Helium Pressure 20 lb./sq.in. Column temperature 120°C, 150 metre siliconeoil capillary column. Injection $\approx$ 2μl.

A.E.I. M.S. 12; magnet setting 5; decrease 9; ionization current 60 ev; accelerating potential 8 Kv; band width 500 c/s and chart speed 1.5 in./s..

Peak 1 Multiplier 5.00

m/e	Relative Intensity	Assignment
35, 37	18, 6	Cl^+
36, 38	25, 11	HCl^+
48, 50	18, 5	$CHCl^+$
49, 51	100, 38	CH_2Cl^+
84, 86, 88	58, 47, 13	$CH_2Cl_2^+$

Peak identified as dichloromethane (CH_2Cl_2). Confirmed by comparison of retention time with an authentic sample.

Peak 2 Multiplier 5.00

m/e	Relative Intensity	Assignment
35, 37	11, 5	Cl^+
36, 38	8, 3	HCl^+
47, 49	33, 11	CCl^+
48, 50	14, 4	$CHCl^+$
83, 85, 87	5, 5, 1	CCl_2^+
84, 86, 88	100, 67, 11	$CHCl_2^+$
117, 119, 121, 123	3, 3, 3, 1	CCl_3^+
118, 120, 122, 124	3, 3, 3, 1	$CHCl_3^+$

Peak identified as chloroform ($CHCl_3$). Confirmed by comparison of retention time with an authentic sample.

Peak 3 Multiplier 6.00

m/e	Relative Intensity	Assignment
35, 37	25, 13	Cl^+
47, 49	40, 16	CCl^+
82, 84, 86	40, 25, 6	CCl_2^+
117, 119, 121, 131	100, 99, 45, 12	CCl_3^+

Peak assigned to carbon tetrachloride (CCl_4). Confirmed by comparison of retention time with an authentic sample.

Peak 4   Multiplier 6.00

m/e	Relative Intensity	Assignment
35, 37	9, 3	Cl^+
36, 38	10, 3	HCl^+
47, 49	24, 9	CCl^+
48, 50	24, 6	$CHCl^+$
79, 81	8, 8	Br^+
82, 84, 86	4, 4, 3.5	CCl_2^+
83, 85, 87	100, 72, 11	$CHCl_2^+$
91, 93	3, 3	CBr^+
127, 129, 131	11, 17, 3	$CHClBr^+$

Peak assigned to bromodichloromethane ($CHCl_2Br$). Confirmed by comparison of retention time with an authentic sample.

Peak 5   Multiplier 4.00

m/e	Relative Intensity	Assignment
35, 37	16, 6	Cl^+
47, 49	31, 12	CCl^+
79, 81	12, 12	Br^+
82, 84, 86	32, 21, 5	CCl_2^+
91, 93	6, 6	CBr^+
117, 119, 121, 123	100, 94, 9	CCl_3^+
126, 128, 130	6, 8, 3	$CClBr^+$
161, 163, 165, 167	27, 40, 20, 5	CCl_2Br^+

Peak identified as bromotrichloromethane (CCl_3Br). Confirmation was by comparison of retention time with an authentic sample.

Peak 6 Multiplier 6.00

m/e	Relative Intensity	Assignment
35, 37	38, 23	Cl^+
47, 49	63, 25	CCl^+
59, 61	43, 18	C_2Cl^+
82, 84, 86	30, 23, 10	CCl_2^+
94, 96, 98	61, 53, 20	$C_2Cl_2^+$
117, 119, 121, 123	38, 38, 18, 7	CCl_3^+
129, 131, 133, 135	100, 100, 54, 14	$C_2Cl_3^+$
164, 166, 168, 170, 172	99, 100, 63, 30, 10	$C_2Cl_4^+$

Peak identified as tetrachloroethylene (C_2Cl_4). Confirmation was by comparison of retention time with an authentic sample.

Peak 7 Multiplier 5.50

m/e	Relative Intensity	Assignment
35, 37	14, 6	Cl^+
47, 49	26, 10	CCl^+
79, 81	19, 21	Br^+
82, 84, 86	19, 14, 4	CCl_2^+
91, 93	10, 10	CBr^+
126, 128, 130	14, 18, 7	$CClBr^+$
161, 163, 165, 167	70, 100, 60, 12	CCl_2Br^+
205, 207, 209, 211	10, 34, 19, 5	$CClBr_2^+$

Peak assigned to dibromodichloromethane (CCl_2Br_2). Confirmation was by comparison of retention time with the known dibromodichloromethane impurity in authentic bromotrichloromethane.

Peak 8

Peak was assigned to hexachloroethane (C_2Cl_6) by comparison of retention time with authentic material.

The analytical chromatogram gave in order of elution, CH_2Cl_2, $CHCl_3$, $CHCl_2Br$, CCl_3Br, traces CCl_2Br_2, and C_2Cl_6. (fig. 13)

RESULTS

THE REACTIONS OF BROMOTRICHLOROMETHANE WITH DICHLOROMETHANE

The elution order of the six peaks found in an analytical chromatogram was dichloromethane, chloroform, bromodichloromethane, bromotrichloromethane, traces of dibromodichloromethane, and hexachloroethane. The bromine produced in the reaction was undetected by analytical gas chromatography and was assumed to be equal to the concentration of hexachloroethane. Under some conditions a detectable trace amount of a seventh material was noticed in the analytical chromatograms. This peak was eluted prior to the hexachloroethane peak and by comparison with the retention time of authentic pentachloroethane in carbon tetrachloride as solvent, it could reasonably be assumed that this seventh peak was due to pentachloroethane.

As in section 1, a series of experiments were carried out in which one variable at a time was varied while the others were held constant. In all cases the lamp to reaction cell distance was 6 in.

1) Variation of Reaction Time.

A series of experiments was performed at a constant temperature with fixed amounts of reactants and constant incident light intensity. The reaction time was varied and the results are shown in the following table.

TABLE I.3, 1

$[CH_2Cl_2]_i$ = 3.73 x 10^{-3} moles/l; $[CCl_3Br]_i$ = 1.24 x 10^{-3} moles/l;

Reaction temperature = 108 ± 2°C

Reaction time Secs.	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHCl_2Br]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
1800	2.60	2.00	6.23 x 10^{-3}
3600	4.67	3.89	9.32 x 10^{-3}
4500	4.42	4.04	1.33 x 10^{-2}
5400	6.22	5.44	1.39 x 10^{-2}
7200	7.46	6.74	1.87 x 10^{-2}
9660	8.73	7.84	2.14 x 10^{-2}

The ratio $[C_2Cl_6]_f/[CCl_3Br]_f$ was plotted against time and gave a straight line passing close to the origin. A least squares calculation on the data gave for the time intercept - 1500 secs. and slope $\phi I_a/2[CCl_3Br]_i$ = 0.20 x 10^{-5} sec.$^{-1}$ (fig. 2)

2) Variation of Reaction Temperature

A series was carried out in which the reaction temperature was varied while the other variables were held constant.

TABLE I.3, 2

$[CH_2Cl_2]_i$ = 3.73 x 10^{-3} moles/l; $[CCl_3Br]_i$ = 1.24 x 10^{-3} moles/l;

Reaction time = 7200 secs.

Temp. °C	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHCl_2Br]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
63	3.43	2.40	7.27 x 10^{-3}
74	3.81	2.84	9.01 x 10^{-3}
84	4.74	3.96	1.23 x 10^{-2}

TABLE I.3, 2 (cont.)

Temp. $^{\circ}C$	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHCl_2Br]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
98	6.67	5.63	1.59×10^{-2}
112	6.82	6.47	1.96×10^{-2}
123	10.07	9.04	2.42×10^{-2}

A least squares plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs $10^3/T$ gave a straight line of slope $(E_2-\frac{1}{2}E_6)/2.303R = 1.02 \pm 0.15$ and intercept

$$\log \frac{\sqrt{2}A_2(CH_2Cl_2]}{(A_6\phi I_a)^{\frac{1}{2}}} = 3.53 \pm 0.06. \text{ (fig. 4)}$$

Similarly a plot of log $[CHCl_2Br]_f/[C_2Cl_6]_f$ vs $10^3/T$ gave a straight line of slope $(E_2-\frac{1}{2}E_6)/2.303R = 1.27 \pm 0.13$ and intercept

$$\log \frac{\sqrt{2}A_2[CH_2Cl_2]}{(A_6\emptyset I_a)^{\frac{1}{2}}} = 4.16 \pm 0.05.$$

Also a least squares plot of log $[C_2Cl_6]_f/[CCl_3Br]$ vs $10^3/T$ gave a straight line of slope = -1.16 ± 0.11 and intercept = 1.31 ± 0.04. (fig. 3).

2') Variation of Reaction Temperature

A series of experiments, identical to those performed in 2) except for the higher initial concentration of CH_2Cl_2, was carried out. The results are tabulated below.

TABLE I.3, 2'

$[CH_2Cl_2]_i = 8.48 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l;

Reaction time = 7200 secs.

Temp. °C	$[CHCl_3]_f$ / $[C_2Cl_6]_f$	$[CHCl_2Br]_f$ / $[C_2Cl_6]_f$	$[C_2Cl_6]_f$ / $[CCl_3Br]_f$
65	7.34	4.98	6.04×10^{-3}
76	7.84	5.42	8.88×10^{-3}
85	8.86	6.60	1.21×10^{-2}
97	12.16	9.49	1.34×10^{-2}
112	15.20	12.54	1.91×10^{-2}
127	17.69	15.15	2.54×10^{-2}

A least squares plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs $10^3/T$ gave a straight line of slope = -0.91 ± 0.16 and intercept = 3.53 ± 0.05. Similarly a plot of log $[CHCl_2Br]_f/[C_2Cl_6]_f$ vs $10^3/T$ gave a straight line of slope = -1.14 ± 0.14 and intercept = 4.16 ± 0.05.

Finally, a least squares plot of log $[C_2Cl_6]_f/[CCl_3Br]$ vs $10^3/T$ gave a straight line of slope = -1.29 ± 0.10 and intercept = 1.63 ± 0.04.

3) Variation of Incident Light Intensity

A series of light variation experiments was carried out by placing calibrated wire gauzes between the light source and the reaction vessel. The results are tabulated below.

TABLE I.3, 3

$[CH_2Cl_2]_i = 3.73 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction temperature = 108 ± 2°C; Reaction time = 7200 secs.

Relative Intensity %	$[CHCl_3]_f$ / $[C_2Cl_6]_f$	$[CHCl_2Br]_f$ / $[C_2Cl_6]_f$	$[C_2Cl_6]_f$ / $[CCl_3Br]_f$
100	7.46	6.74	1.87×10^{-2}
56	6.28	5.27	1.22×10^{-2}
33	6.54	4.97	6.18×10^{-3}
17.5	5.73	4.00	4.08×10^{-3}

The least squares method gave, for a plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log (R.I.), a slope = 0.13 ± 0.09 and an intercept = 0.60 ± 0.05 (fig. 5). For a plot of log $[CHCl_2Br]_f/[C_2Cl_6]_f$ vs log (R.I.) the least squares method gave for the slope 0.28 ± 0.09, and for the intercept 0.26 ± 0.05.

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log (R.I.) had a slope = 0.90 ± 0.10 and an intercept = -3.58 ± 0.06. (fig. 6).

4) Variation of Concentration of Bromotrichloromethane

The experimental results are tabulated below.

TABLE I.3, 4

$[CH_2Cl_2]_i = 3.73 \times 10^{-3}$ moles/l; Reaction temperature = 113 ± 2°C
Reaction time = 7200 secs.

$[CCl_3Br]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHCl_2Br]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
1.24×10^{-3}	9.52	7.84	1.67×10^{-2}
1.02×10^{-3}	9.62	7.66	1.62×10^{-2}
0.79×10^{-3}	8.96	7.46	1.75×10^{-2}
0.57×10^{-3}	8.73	7.02	1.71×10^{-2}
0.34×10^{-3}	7.47	5.61	1.84×10^{-2}

The least squares method gave the slope and intercept values for the following plots.

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CCl_3Br]_i$ gave a straight line of slope = 0.19 ± 0.09 and intercept = 1.54 ± 0.03.

A plot of log $[CHCl_2Br]_f/[C_2Cl_6]_f$ vs log $[CCl_3Br]_i$ gave a straight line of slope = 0.25 ± 0.09 and intercept = 1.65 ± 0.03.

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CCl_3Br]_i$ gave a straight line of slope = -0.08 ± 0.08 and intercept = -2.01 ± 0.03.

FIG 9'

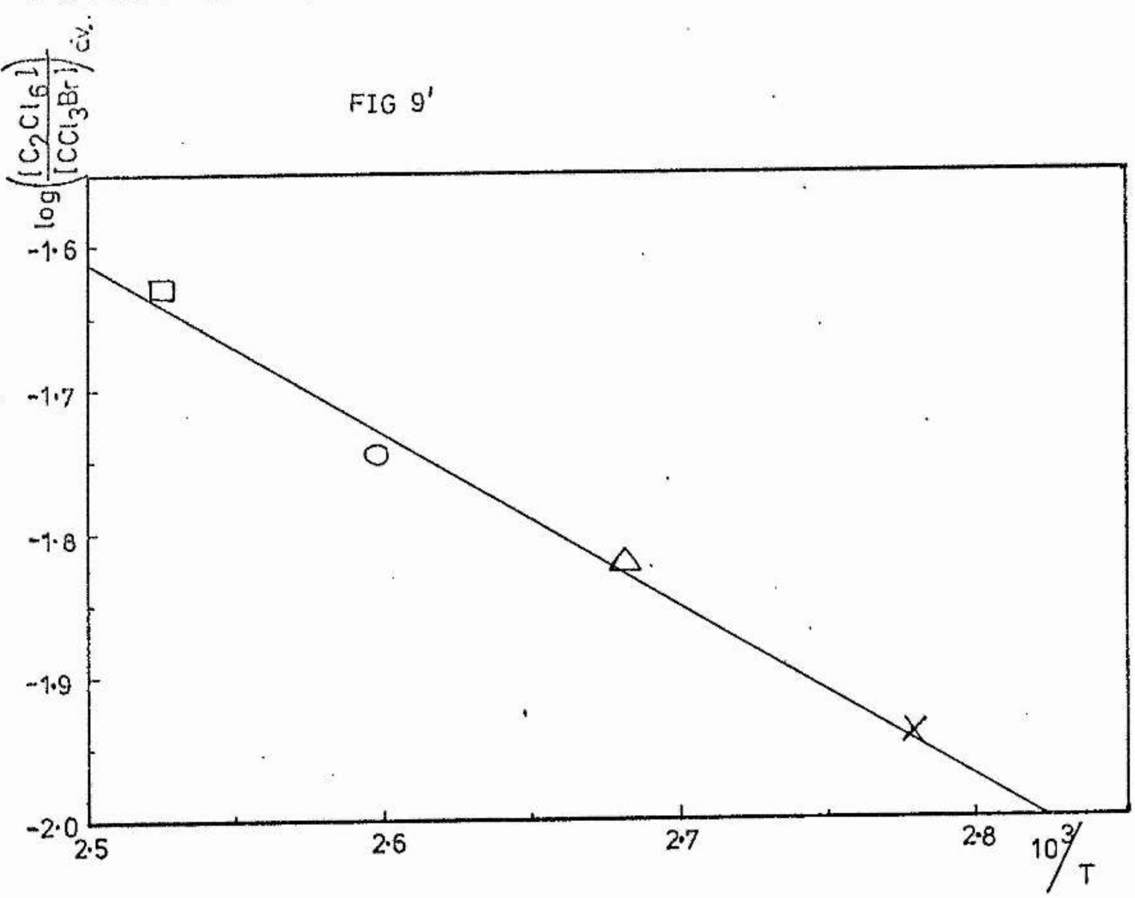
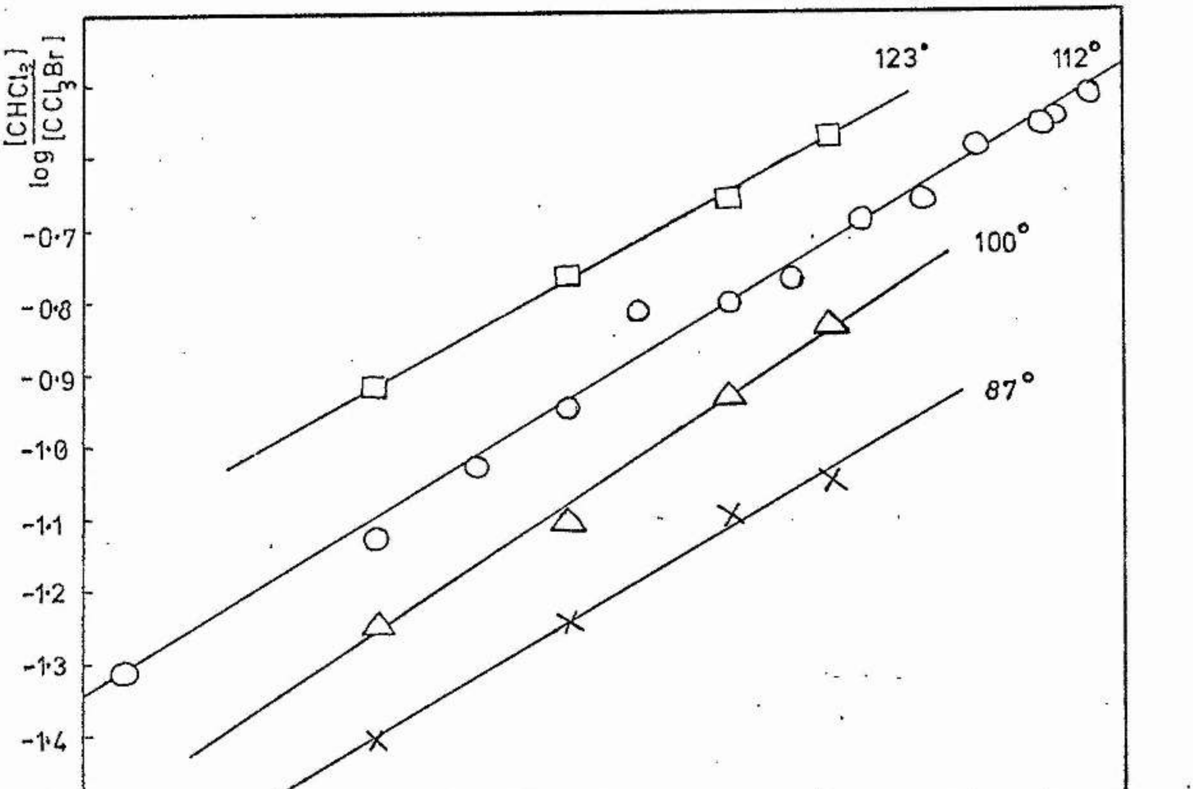

log([C2Cl6]/[CCl3Br])cv.
-1·6
-1·7
-1·8
-1·9
-2·0
2·5
2·6
2·7
2·8
10³/T

FIG 9


log [CHCl3]/[CCl3Br]
-0·7
-0·8
-0·9
-1·0
-1·1
-1·2
-1·3
-1·4
-1·5
-3·3
-3·1
-2·9
-2·7
-2·5
-2·3
-2·2
log[CH2Cl2]
123°
112°
100°
87°

5) Variation of Concentration of Dichloromethane at T = 123°C

The experimental results are tabulated below.

TABLE I.3, 5

$[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction temperature = 123 ± 2°C

Reaction time = 7200 secs.

$[CH_2Cl_2]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHCl_2Br]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
5.09×10^{-3}	11.68	10.07	2.28×10^{-2}
3.73×10^{-3}	9.93	8.44	2.23×10^{-2}
2.26×10^{-3}	7.06	5.97	2.45×10^{-2}
1.24×10^{-3}	4.92	3.97	2.46×10^{-2}

The least squares method applied to the above data gave, for a plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CH_2Cl_2]_i$, a slope = 0.62 ± 0.06 and an intercept = 2.50 ± 0.02. (fig. 9)

For a plot of log $[CHCl_2Br]_f/[C_2Cl_6]_f$ vs log $[CH_2Cl_2]_i$ the slope = 0.67 ± 0.06 and the intercept = 2.54 ± 0.02. A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CH_2Cl_2]_i$ was a straight line of slope = -0.06 ± 0.06 and intercept = -1.79 ± 0.02.

6) Variation of Concentration of Dichloromethane at T = 112°C

The experimental results are tabulated below.

TABLE I.3, 6

$[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction temperature = 112 ± 2°C

Reaction time = 7200 secs.

$[CH_2Cl_2]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHCl_2Br]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
0.57×10^{-3}	2.90	2.55	1.68×10^{-2}
1.24×10^{-3}	4.43	4.18	1.67×10^{-2}
1.70×10^{-3}	5.24	4.80	1.79×10^{-2}
2.26×10^{-3}	6.63	5.93	1.70×10^{-2}
2.83×10^{-3}	6.54	6.07	1.80×10^{-2}
3.73×10^{-3}	8.43	7.53	1.88×10^{-2}
4.50×10^{-3}	9.52	8.44	1.79×10^{-2}
5.65×10^{-3}	10.43	9.06	1.97×10^{-2}
6.78×10^{-3}	11.47	10.04	1.90×10^{-2}
8.02×10^{-3}	13.87	11.34	1.87×10^{-2}
9.04×10^{-3}	15.51	12.72	1.78×10^{-2}
10.17×10^{-3}	16.14	13.38	1.76×10^{-2}
11.30×10^{-3}	16.91	13.74	1.79×10^{-2}

Using all points, the least squares method gave for a plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CH_2Cl_2]_i$ a slope = 0.60 ± 0.03 and an intercept = 2.38 ± 0.01. (fig. 9)

For a plot of log $[CHCl_2Br]_f/[C_2Cl_6]_f$ vs log $[CH_2Cl_2]_i$ the slope = 0.56 ± 0.02 and the intercept = 2.23 ± 0.01.

A plot of log $[C_2Cl_6]_f/[CCl_2Br]_f$ vs log $[CH_2Cl_2]_i$ was a poor straight line of slope = 0.02 ± 0.02 and intercept = -1.67 ± 0.01.

7) Variation of Concentration of Dichloromethane at T = 100°C

The results of the variation of dichloromethane concentration at T = 100°C are shown in the following table.

TABLE I.3, 7

$[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction time = 7200 secs.;

Reaction temperature = $100 \pm 2^{\circ}C$

$[CH_2Cl_2]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHCl_2Br]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
5.09×10^{-3}	10.10	7.62	1.46×10^{-2}
3.73×10^{-3}	8.23	6.26	1.41×10^{-2}
2.26×10^{-3}	5.14	4.09	1.52×10^{-2}
1.24×10^{-3}	3.51	2.68	1.61×10^{-2}

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CH_2Cl_2]_i$ gave a straight line and the least squares method gave the slope = 0.77 ± 0.07 and the intercept = 2.76 ± 0.03. Similarly, a plot of log $[CHCl_2Br]_f/[C_2Cl_6]_f$ vs log $[CH_2Cl_2]_i$ had its slope = 0.74 ± 0.07 and its intercept = 2.59 ± 0.03. (fig. 9)

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CH_2Cl_2]_i$ had its slope = -0.09 ± 0.06 and its intercept = -2.05 ± 0.02 from the application of the least squares method.

8) Variation of Concentration of Dichloromethane at T = $87^{\circ}C$

The results of the dichloromethane concentration variation experiments at $87^{\circ}C$ are tabulated below.

TABLE I.3, 8

$[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction time = 7200 secs.,

Reaction temperature = $87 \pm 2^{\circ}C$

$[CH_2Cl_2]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CHCl_2Br]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
5.09×10^{-3}	7.44	5.13	1.19×10^{-2}
3.73×10^{-3}	7.29	4.86	1.10×10^{-2}
2.26×10^{-3}	5.11	3.77	1.12×10^{-2}
1.24×10^{-3}	3.33	2.50	1.18×10^{-2}

Application of the least squares method to the above experimental results leads to the slope and intercept values for the following straight line plots.

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CH_2Cl_2]_i$ has its slope = 0.60 ± 0.07 and its intercept = 2.28 ± 0.03.

A plot of log $[CHCl_2Br]_f/[C_2Cl_6]_f$ vs log $[CH_2Cl_2]_i$ has its slope = 0.52 ± 0.07 and its intercept = 1.92 ± 0.03.

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CH_2Cl_2]_i$ has its slope = -0.003 ± 0.05 and its intercept = -1.95 ± 0.02.

Details of Reaction

Chromatographic Analysis:-

Column 20% Silicone Oil on 60-100 mesh Embacel

Temperature 90°C

Nitrogen flow rate 120 ccs/min.

Chart speed 48 in./hr.

1) Variation of Reaction Time

Temp. 108°C, Reactant pressures, CH_2Cl_2 66 mm., CCl_3Br 22 mm.,

Relative final concentrations of products:-

a) Time 1800 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.18	1.71	7.30×10^{-3}	
1.0	2.63	2.10	5.98×10^{-3}	
1.0	2.85	2.20	5.59×10^{-3}	
1.0	2.75	2.04	6.06×10^{-3}	
1.0	2.57	1.96	6.25×10^{-3}	
1.0	2.60	2.00	6.23×10^{-3}	Mean

b) Time 3600 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	4.53	3.76	9.86×10^{-3}	
1.0	4.93	4.12	8.67×10^{-3}	
1.0	4.50	3.84	9.36×10^{-3}	
1.0	4.35	3.67	9.86×10^{-3}	
1.0	5.04	4.09	8.85×10^{-3}	
1.0	4.67	3.89	9.32×10^{-3}	Mean

c) Time 4500 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	4.41	4.04	1.32×10^{-2}	
1.0	4.82	4.31	1.26×10^{-2}	
1.0	4.29	3.79	1.44×10^{-2}	
1.0	4.33	4.10	1.27×10^{-2}	
1.0	4.26	3.98	1.33×10^{-2}	
1.0	4.42	4.04	1.33×10^{-2}	Mean

d) Time 5400 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	6.68	5.85	1.27×10^{-2}	
1.0	5.87	5.15	1.46×10^{-2}	
1.0	5.89	5.14	1.49×10^{-2}	
1.0	6.42	5.61	1.34×10^{-2}	
1.0	6.22	5.44	1.39×10^{-2}	Mean

e) Time 7200 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	7.40	6.72	1.86×10^{-2}	
1.0	7.12	6.40	1.98×10^{-2}	
1.0	7.80	7.11	1.75×10^{-2}	
1.0	7.14	6.55	1.93×10^{-2}	
1.0	7.81	6.93	1.85×10^{-2}	
1.0	7.46	6.74	1.87×10^{-2}	Mean

f) Time 9660 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	8.40	7.67	2.18×10^{-2}	
1.0	8.28	7.61	2.21×10^{-2}	
1.0	8.89	7.88	2.08×10^{-2}	
1.0	9.55	8.40	2.06×10^{-2}	
1.0	8.53	7.61	2.19×10^{-2}	
1.0	8.73	7.84	2.14×10^{-2}	Mean

2) Variation of Reaction Temperature

Time 7200 secs., Reactant pressures, CH_2Cl_6 66 mm., CCl_3Br 22 mm.

Relative final concentrations of products:-

a) 63°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.55	2.65	6.29×10^{-3}	
1.0	3.19	2.31	7.81×10^{-3}	
1.0	3.26	2.28	7.51×10^{-3}	
1.0	3.73	2.36	7.45×10^{-3}	
1.0	3.43	2.40	7.27×10^{-3}	Mean

b) 74°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.73	3.05	8.25×10^{-3}	
1.0	3.72	2.87	9.26×10^{-3}	
1.0	3.74	2.63	9.72×10^{-3}	
1.0	4.04	2.82	8.80×10^{-3}	
1.0	3.81	2.84	9.01×10^{-3}	Mean

c) 84°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	4.96	4.01	1.19×10^{-2}	
1.0	4.71	3.84	1.25×10^{-2}	
1.0	4.45	3.94	1.30×10^{-2}	
1.0	4.81	4.03	1.20×10^{-2}	
1.0	4.74	3.96	1.23×10^{-2}	Mean

d) 98°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	6.97	5.91	1.51×10^{-2}	
1.0	7.25	5.98	1.51×10^{-2}	
1.0	6.39	5.30	1.66×10^{-2}	
1.0	6.07	5.31	1.68×10^{-2}	
1.0	6.67	5.63	1.59×10^{-2}	Mean

e) 112°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	6.88	6.73	1.87×10^{-2}	
1.0	7.16	6.85	1.84×10^{-2}	
1.0	6.60	6.19	2.05×10^{-2}	
1.0	6.65	6.08	2.07×10^{-2}	
1.0	6.82	6.47	1.96×10^{-2}	Mean

f) 123°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$
1.0	9.06	7.87	2.62×10^{-2}
1.0	10.30	9.15	2.25×10^{-2}
1.0	11.10	9.77	2.14×10^{-2}
1.0	9.11	8.20	2.53×10^{-2}
1.0	10.78	10.21	2.55×10^{-2}
1.0	10.07	9.04	2.42×10^{-2}

2') Variation of Reaction Temperature

Time 7200 secs., Reactant pressures, CH_2Cl_2 150 mm., CCl_3Br 22 mm.,

Relative final concentrations of products:-

a) 65°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	8.06	5.80	5.09×10^{-3}	
1.0	7.66	4.71	6.68×10^{-3}	
1.0	7.73	5.20	5.78×10^{-3}	
1.0	6.94	4.86	6.07×10^{-3}	
1.0	6.33	4.34	6.59×10^{-3}	
1.0	7.34	4.98	6.04×10^{-3}	Mean

b) 76°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	7.94	5.35	8.98×10^{-3}	
1.0	7.72	5.33	9.37×10^{-3}	
1.0	8.00	5.45	9.01×10^{-3}	
1.0	7.00	5.30	8.62×10^{-3}	
1.0	8.52	5.66	8.40×10^{-3}	
1.0	7.84	5.42	8.88×10^{-3}	Mean

c) 85°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	9.25	6.96	1.14×10^{-2}	
1.0	8.80	6.48	1.25×10^{-2}	
1.0	8.71	6.58	1.22×10^{-2}	
1.0	8.35	6.19	1.29×10^{-2}	
1.0	9.20	6.79	1.16×10^{-2}	
1.0	8.86	6.60	1.21×10^{-2}	Mean

d) 97°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	11.66	9.13	1.38×10^{-2}	
1.0	13.36	10.21	1.24×10^{-2}	
1.0	13.03	10.03	1.27×10^{-2}	
1.0	11.30	9.05	1.38×10^{-2}	
1.0	11.43	9.03	1.42×10^{-2}	
1.0	12.16	9.49	1.34×10^{-2}	Mean

e) 112°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	15.06	12.53	1.90×10^{-2}	
1.0	16.78	13.62	1.74×10^{-2}	
1.0	15.80	13.05	1.85×10^{-2}	
1.0	12.57	10.54	2.22×10^{-2}	
1.0	15.78	12.96	1.84×10^{-2}	
1.0	15.20	12.54	1.91×10^{-2}	Mean

f) 127°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	21.03	17.36	2.18×10^{-2}	
1.0	17.67	15.20	2.48×10^{-2}	
1.0	14.59	13.05	2.97×10^{-2}	
1.0	18.52	15.58	2.42×10^{-2}	
1.0	16.65	14.57	2.64×10^{-2}	
1.0	17.69	15.15	2.54×10^{-2}	Mean

3) Variation of Incident Light Intensity

Time 7200 secs., Reactant pressures, CH_2Cl_2 66 mm., CCl_3Br 22 mm., Reaction temp. 108°C
Relative final concentrations of products:-

Transmissions

a) 100%

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	7.40	6.72	1.86×10^{-2}	
1.0	7.12	6.40	1.98×10^{-2}	
1.0	7.80	7.11	1.75×10^{-2}	
1.0	7.14	6.55	1.93×10^{-2}	
1.0	7.81	6.93	1.85×10^{-2}	
1.0	7.46	6.74	1.87×10^{-2}	Mean

b) 56%

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	5.86	5.02	1.29×10^{-2}	
1.0	6.63	5.41	1.19×10^{-2}	
1.0	6.11	5.17	1.21×10^{-2}	
1.0	6.68	5.64	1.15×10^{-2}	
1.0	6.14	5.12	1.25×10^{-2}	
1.0	6.28	5.27	1.22×10^{-2}	Mean

c) 32.5%

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	6.33	4.74	6.50×10^{-3}	
1.0	7.06	5.25	5.89×10^{-3}	
1.0	5.85	4.54	6.80×10^{-3}	
1.0	6.43	4.90	6.06×10^{-3}	
1.0	7.02	5.43	5.65×10^{-3}	
1.0	6.54	4.97	6.18×10^{-3}	Mean

d) 17.5%

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	5.39	3.79	4.23×10^{-3}	
1.0	6.31	4.43	3.71×10^{-3}	
1.0	5.49	3.79	4.30×10^{-3}	
1.0	5.73	4.00	4.08×10^{-3}	Mean

4) Variation in Concentration of Bromotrichloromethane

Time 7200 secs., Reactant pressure CH_2Cl_2 66 mm., Temp. 113°C

Relative final concentrations of products:-

CCl_3Br pressures

a) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	9.67	8.13	1.63×10^{-2}	
1.0	10.39	8.21	1.60×10^{-2}	
1.0	8.59	7.69	1.70×10^{-2}	
1.0	9.70	7.53	1.72×10^{-2}	
1.0	9.26	7.66	1.72×10^{-2}	
1.0	9.52	7.84	1.67×10^{-2}	Mean

b) 18 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	11.06	8.09	1.50×10^{-2}	
1.0	9.04	7.32	1.68×10^{-2}	
1.0	9.52	7.65	1.63×10^{-2}	
1.0	9.60	7.94	1.57×10^{-2}	
1.0	8.89	7.32	1.70×10^{-2}	
1.0	9.62	7.66	1.62×10^{-2}	Mean

c) 14 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	9.48	7.93	1.65×10^{-2}	
1.0	8.91	7.30	1.79×10^{-2}	
1.0	8.17	6.81	1.90×10^{-2}	
1.0	8.70	7.35	1.75×10^{-2}	
1.0	9.52	7.89	1.64×10^{-2}	
1.0	8.96	7.46	1.75×10^{-2}	Mean

d) 10 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	9.08	7.44	1.62×10^{-2}	
1.0	8.89	7.52	1.58×10^{-2}	
1.0	7.99	6.05	1.93×10^{-2}	
1.0	8.53	7.05	1.72×10^{-2}	
1.0	9.17	7.04	1.70×10^{-2}	
1.0	8.73	7.02	1.71×10^{-2}	Mean

e) 6 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	7.14	5.34	1.92×10^{-2}	
1.0	8.09	6.14	1.68×10^{-2}	
1.0	7.33	5.33	1.91×10^{-2}	
1.0	7.27	5.52	1.86×10^{-2}	
1.0	7.52	5.71	1.83×10^{-2}	
1.0	7.47	5.61	1.84×10^{-2}	Mean

5) Variation of Concentration of Dichloromethane at T = 123°C

Time 7200 secs., Reactant pressure, CCl_3Br 22 mm.

Relative final concentrations of products:-

CH_2Cl_2 pressures

a) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	5.60	4.56	2.23×10^{-2}	
1.0	4.82	3.92	2.53×10^{-2}	
1.0	4.97	3.62	2.38×10^{-2}	
1.0	4.85	4.08	2.48×10^{-2}	
1.0	4.36	3.64	2.68×10^{-2}	
1.0	4.92	3.97	2.46×10^{-2}	Mean

b) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	6.71	5.69	2.61×10^{-2}	
1.0	6.72	5.82	2.56×10^{-2}	
1.0	7.35	6.14	2.34×10^{-2}	
1.0	7.36	6.20	2.31×10^{-2}	
1.0	7.14	6.01	2.41×10^{-2}	
1.0	7.06	5.97	2.45×10^{-2}	Mean

c) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	9.69	8.34	2.28×10^{-2}	
1.0	10.31	8.42	2.23×10^{-2}	
1.0	10.22	8.60	2.17×10^{-2}	
1.0	9.59	8.37	2.25×10^{-2}	
1.0	9.83	8.49	2.23×10^{-2}	
1.0	9.93	8.44	2.23×10^{-2}	Mean

d) 90 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	12.57	10.70	2.18×10^{-2}	
1.0	11.74	9.90	2.33×10^{-2}	
1.0	11.86	10.06	2.24×10^{-2}	
1.0	10.85	9.67	2.31×10^{-2}	
1.0	11.38	10.01	2.35×10^{-2}	
1.0	11.68	10.07	2.28×10^{-2}	Mean

6) Variation of Concentration of Dichloromethane at $T = 112^{\circ}C$

Time 7200 secs., Reactant pressure CCl_3Br 22 mm.

Relative final concentrations of products:-

CH_2Cl_2 pressures

a) 10 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.90	2.61	1.61×10^{-2}	
1.0	2.87	2.56	1.65×10^{-2}	
1.0	2.87	2.49	1.69×10^{-2}	
1.0	2.85	2.50	1.78×10^{-2}	
1.0	2.99	2.59	1.68×10^{-2}	
1.0	2.90	2.55	1.68×10^{-2}	Mean

b) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	4.07	4.45	1.63×10^{-2}	
1.0	4.01	3.69	1.87×10^{-2}	
1.0	5.06	4.54	1.54×10^{-2}	
1.0	4.73	4.28	1.61×10^{-2}	
1.0	4.31	3.94	1.72×10^{-2}	
1.0	4.43	4.18	1.67×10^{-2}	Mean

c) 30 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	4.59	4.14	2.01×10^{-2}	
1.0	5.40	4.87	1.72×10^{-2}	
1.0	5.36	4.91	1.70×10^{-2}	
1.0	5.17	4.76	1.87×10^{-2}	
1.0	5.68	5.33	1.64×10^{-2}	
1.0	5.24	4.80	1.79×10^{-2}	Mean

d) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	6.02	5.54	1.86×10^{-2}	
1.0	6.94	6.15	1.64×10^{-2}	
1.0	6.45	5.78	1.73×10^{-2}	
1.0	6.98	6.10	1.63×10^{-2}	
1.0	6.76	6.08	1.63×10^{-2}	
1.0	6.63	5.93	1.70×10^{-2}	Mean

e) 50 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	6.17	5.92	1.82×10^{-2}	
1.0	6.70	6.18	1.78×10^{-2}	
1.0	6.42	5.89	1.86×10^{-2}	
1.0	6.58	6.08	1.79×10^{-2}	
1.0	6.86	6.31	1.75×10^{-2}	
1.0	6.54	6.07	1.80×10^{-2}	Mean

f) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	8.34	7.50	1.87×10^{-2}	
1.0	8.62	7.63	1.83×10^{-2}	
1.0	8.24	7.37	1.89×10^{-2}	
1.0	9.69	8.74	1.75×10^{-2}	
1.0	7.24	6.41	2.04×10^{-2}	
1.0	8.43	7.53	1.88×10^{-2}	Mean

g) 80 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	9.89	8.74	1.65×10^{-2}	
1.0	9.03	8.01	1.94×10^{-2}	
1.0	9.64	8.58	1.78×10^{-2}	
1.0	9.52	8.44	1.79×10^{-2}	Mean

h) 100 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	9.74	8.51	2.11×10^{-2}	
1.0	10.59	9.24	1.93×10^{-2}	
1.0	9.87	8.87	2.01×10^{-2}	
1.0	11.42	9.49	1.87×10^{-2}	
1.0	10.51	9.20	1.93×10^{-2}	
1.0	10.43	9.06	1.97×10^{-2}	Mean

i) 120 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	12.12	10.72	1.78×10^{-2}	
1.0	10.36	9.12	2.10×10^{-2}	
1.0	12.09	10.56	1.80×10^{-2}	
1.0	10.87	9.58	1.98×10^{-2}	
1.0	11.90	10.20	1.87×10^{-2}	
1.0	11.47	10.04	1.90×10^{-2}	Mean

j) 142 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	13.89	11.22	1.87×10^{-2}	
1.0	15.62	12.57	1.70×10^{-2}	
1.0	12.95	10.63	1.99×10^{-2}	
1.0	13.09	10.82	1.93×10^{-2}	
1.0	13.80	11.47	1.84×10^{-2}	
1.0	13.87	11.34	1.87×10^{-2}	Mean

k) 160 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	16.17	13.19	1.74×10^{-2}	
1.0	16.09	13.08	1.73×10^{-2}	
1.0	15.35	12.54	1.81×10^{-2}	
1.0	15.33	12.33	1.83×10^{-2}	
1.0	14.60	12.47	1.79×10^{-2}	
1.0	15.51	12.72	1.78×10^{-2}	Mean

l) 180 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	16.50	13.37	1.79×10^{-2}	
1.0	16.91	14.06	1.65×10^{-2}	
1.0	14.90	12.56	1.84×10^{-2}	
1.0	16.28	13.17	1.77×10^{-2}	
1.0	16.10	13.72	1.73×10^{-2}	
1.0	16.14	13.38	1.76×10^{-2}	Mean

m) 200 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	16.80	14.09	1.70×10^{-2}	
1.0	16.93	13.57	1.81×10^{-2}	
1.0	16.96	14.10	1.75×10^{-2}	
1.0	16.97	13.19	1.88×10^{-2}	
1.0	16.91	13.74	1.79×10^{-2}	Mean

7) Variation of Concentration of Dichloromethane at T = 100°C

Time 7200 secs., Reactant pressure, CCl_3Br 22 mm.

Relative final concentrations of products:-

CH_2Cl_2 pressures

a) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.49	2.78	1.62×10^{-2}	
1.0	3.68	2.70	1.59×10^{-2}	
1.0	3.26	2.65	1.64×10^{-2}	
1.0	3.40	2.58	1.62×10^{-2}	
1.0	3.70	2.71	1.60×10^{-2}	
1.0	3.51	2.68	1.61×10^{-2}	Mean

b) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	5.28	4.31	1.49×10^{-2}	
1.0	5.49	4.17	1.46×10^{-2}	
1.0	4.93	4.02	1.57×10^{-2}	
1.0	4.92	3.90	1.60×10^{-2}	
1.0	5.08	4.05	1.51×10^{-2}	
1.0	5.14	4.09	1.52×10^{-2}	Mean

c) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	7.99	6.02	1.45×10^{-2}	
1.0	7.82	6.37	1.42×10^{-2}	
1.0	8.23	6.34	1.41×10^{-2}	
1.0	8.92	6.54	1.39×10^{-2}	
1.0	8.20	6.02	1.40×10^{-2}	
1.0	8.23	6.26	1.41×10^{-2}	Mean

d) 90 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	9.97	6.92	1.73×10^{-2}	
1.0	10.14	7.77	1.39×10^{-2}	
1.0	11.25	8.43	1.29×10^{-2}	
1.0	9.50	7.29	1.46×10^{-2}	
1.0	9.65	7.70	1.41×10^{-2}	
1.0	10.10	7.62	1.46×10^{-2}	Mean

8) Variation of Concentration of Dichloromethane at $T = 87^{\circ}C$

Time 7200 secs., Reactant pressure, CCl_3Br 22 mm.,
Relative final concentrations of products:-

CH_2Cl_2 pressures

a) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.23	2.45	1.19×10^{-2}	
1.0	3.11	2.37	1.23×10^{-2}	
1.0	3.56	2.66	1.09×10^{-2}	
1.0	3.42	2.53	1.19×10^{-2}	
1.0	3.31	2.49	1.19×10^{-2}	
1.0	3.33	2.50	1.18×10^{-2}	Mean

b) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	5.29	3.85	1.09×10^{-2}	
1.0	5.02	3.73	1.14×10^{-2}	
1.0	5.13	3.73	1.13×10^{-2}	
1.0	4.94	3.74	1.12×10^{-2}	
1.0	5.20	3.82	1.11×10^{-2}	
1.0	5.11	3.77	1.12×10^{-2}	Mean

c) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	7.43	5.19	1.05×10^{-2}	
1.0	7.59	4.67	1.13×10^{-2}	
1.0	7.49	4.91	1.07×10^{-2}	
1.0	7.01	4.80	1.11×10^{-2}	
1.0	6.92	4.75	1.14×10^{-2}	
1.0	7.29	4.86	1.10×10^{-2}	Mean

d) 90 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CHCl_2Br]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	7.52	5.51	1.16×10^{-2}	
1.0	8.31	5.33	1.14×10^{-2}	
1.0	7.79	5.07	1.21×10^{-2}	
1.0	7.06	4.85	1.23×10^{-2}	
1.0	6.53	4.87	1.22×10^{-2}	
1.0	7.44	5.13	1.19×10^{-2}	Mean

PART I

SECTION IV

THE PHOTOCHEMICAL REACTIONS

OF

BROMOTRICHLOROMETHANE

WITH

DICHLOROFLUOROMETHANE

EXPERIMENTAL

REACTANTS

1) DICHLOROFLUOROMETHANE:- was 'Cambrian Chemicals Ltd' material and as analytical gas chromatography showed it to be better than 99.5% pure it was used without further purification.

2) BROMOTRICHLOROMETHANE:- as described in Section I.

3) CHLOROFORM:- was Fisons 'Analar' material and, prior to use, was purified on a Pye 105 preparative chromatograph to remove the ethanol stabilizer and the traces of dichloromethane and carbon tetrachloride which were the only impurities detected. Pure chloroform was obtained by repeatedly passing 0.3 ml samples onto a 15 ft preparative column packed with 20% D.N.P. on 40-60 mesh Embacel. The column temperature was 65°C, the injector pressure was 60 lb./sq.in. of nitrogen and the column pressure was 34 lb./sq.in. of nitrogen. The purified material was stored in a deep freeze until required.

APPARATUS

The apparatus was as described in Section I. As in Section II the reactant pressures were measured with a capsule dial gauge. The dichlorofluoromethane was again stored in a 2 l. bulb with a side arm, because of its low boiling point (9°C).

EXPERIMENTAL PROCEDURE.

The procedure was as described in Section I. Again no ballast liquid was required to obtain consistent injections.

ANALYSIS

A Griffin and George D6 gas density balance was used for all quantitative analysis. The chromatogram peak areas were measured using a combination of the Honeywell precision integrator with the Du Pont curve resolver.

Identification of Products

Mass spectral analysis was carried out on a mixture of dichlorofluoromethane (62 mm. in 149 ml.) and bromotrichloromethane (22 mm. in 149 ml.) which was photolysed for 36 hours at 177°C with a high pressure mercury arc lamp. Analytical gas chromatography gave eight peaks of which the five predominant peaks were identified from their mass spectra. The unidentified trace peaks were not found in the analytical chromatograms.

Mass spectral analysis was as follows:-

Perkin-Elmer F11 with a 150 metre silicone oil capillary column held at 70°C with a Helium pressure of 10 lb./sq.in.

A.E.I. M.S.12; magnet setting 5; decrease 9; ionization current 22 ev; accelerating potential 8 Kv; band width 500 c/s; and chart speed 1.5 in./s..

Peak 1

Peak unidentified, but was insignificant even in the over-reacted mixture used for analysis.

Peak 2 Multiplier 4.00

m/e	Relative Intensity	Assignment
31	4.6	CF^+
36, 38	4.6, 1.2	HCl^+
47, 49	4.6, 2.3	CCl^+
48, 50	3, 0.7	$CHCl^+$
66, 68	5.4, 5.4	$CFCl^+$
67, 69	100, 68	$CHFCl^+$
82, 84, 86	3, 2.3, 0.7	CCl_2^+
83, 85, 87	18, 11, 2.3	$CHCl_2^+$
101, 103, 105	3.8, 2.3, 0.7	$CFCl_2^+$
102, 104, 106	9, 6, 1.2	$CHFCl_2^+$

Peak identifed as dichlorofluoromethane ($CHFCl_2$)

Peak 3 Multiplier 4.00

m/e	Relative Intensity	Assignment
31	5	CF^+
36, 38	4, 1.6	HCl^+
47, 49	1, 0.3	CCl^+
66, 68	15, 5	$CFCl^+$
79, 81	0.6, 0.6	Br^+
82, 84, 86	2.3, 1.6, 0.3	CCl_2^+
101, 103, 105	100, 84, 24	$CFCl_2^+$
110, 112	1.6, 2.4	$CFBr^+$
126, 128, 130	trace	$CBrCl^+$
145, 147, 149	42, 55, 13	$CFBrCl^+$
161, 163, 165, 167	2.4, 3.2, 2.4, 0.3	$CBrCl_2^+$

Peak identified as bromodichlorofluoromethane ($CFCl_2Br$)

Peak 4 Multiplier 4.50

m/e	Relative Intensity	Assignment
36, 38	6.5, 2.4	HCl^+
47, 49	16, 5	CCl^+
48, 50	15, 5	$CHCl^+$
82, 84, 86	5.6, 6, 1.6	CCl_2^+
83, 86, 87	100, 71, 19	$CHCl_2^+$
101, 103, 105	7, 4, 1	$CFCl_2^+$
117, 119, 121, 123	1.6, 2, 1, 0.3	CCl_3^+
118, 120, 122, 124	1.6, 2, 1, 0.3	$CHCl_3^+$
145, 147, 149	1, 1, 0.3	$CFBrCl^+$

Peak identified as chloroform ($CHCl_3$) with traces of peak 3 ($CFBrCl_2$). Confirmation was by comparison of retention time with authentic material.

Peak 5

Peak unidentified and was not detected in any of the kinetic experiments.

Peak 6 Multiplier 5.50

m/e	Relative Intensity	Assignment
36, 38	58, 20	HCl^+
47, 49	8, 4	CCl^+
82, 84, 86	25, 20, 8	CCl_2^+
117, 119, 121, 123	100, 83, 29, 4	CCl_3^+
161, 163, 165, 167	20, 38, 25, 4	CCl_2Br^+

Peak identified as bromotrichloromethane (CCl_3Br). Confirmation was by comparison of retention time with authentic material.

Peak 7

Peak was unidentified and was not present in detectable quantities in the kinetic experiments.

Peak 8 Multiplier 6.00

m/e	Relative Intensity	Assignment
36, 38	100, 79	HCl^+
82, 84, 86	30, 21, 15	CCl_2^+
94, 96, 98	55, 32, 21	$C_2Cl_2^+$
117, 119, 121, 123	100, 89, 57, 25	CCl_3^+
129, 131, 133, 135	81, 81, 51, 19	$C_2Cl_3^+$
164, 166, 168, 170, 172	87, 100, 74, 28, 11	$C_2Cl_4^+$
199, 201, 203, 205, 207, 209	47, 87, 75, 36, 26, 9	$C_2Cl_5^+$

Peak identified as hexachloroethane (C_2Cl_6). Confirmation was by comparison of retention time with authentic material.

For the analytical chromatograms, the order of peak elution was:- $CHFCl_2$, $CFCl_2Br$, $CHCl_3$, CCl_3Br and C_2Cl_6. (fig. 14)

RESULTS

THE REACTIONS OF BROMOTRICHLOROMETHANE WITH DICHLOROFLUOROMETHANE

In all the kinetic experiments performed, five peaks only were found by analytical gas chromatography. In elution order, these peaks were found to correspond to dichlorofluoromethane, bromodichlorofluoromethane, chloroform, bromotrichloromethane and hexachloroethane. The bromine formed was undetected by gas chromatography but was assumed to equal the amount of hexachloroethane formed in each experiment.

As in section I, a series of experiments was carried out in which one variable at a time was varied while all the others were held constant. In all cases the lamp to reaction cell distance was 6 in.. The experiments were carried out in order to further develop the possible reaction mechanism operative with these halomethanes.

1) Variation of Reaction Time

A series of experiments was carried out in which the reaction time was varied while the temperature, reactant pressures and light intensity were held constant. The results are shown in the following table.

TABLE I.4, 1.

$[CHCl_2F]_i = 3.73 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l;

Reaction temperature = 162 ± 2°C

Reaction Time Secs.	$[CHCl_3]_f / [C_2Cl_6]_f$	$[CCl_2FBr]_f / [C_2Cl_6]_f$	$[C_2Cl_6]_f / [CCl_3Br]_f$
1800	0.93	0.83	1.13×10^{-2}
3600	1.34	1.45	2.24×10^{-2}
5400	1.97	2.10	3.12×10^{-2}
7200	2.79	2.96	3.99×10^{-2}
9000	2.95	3.30	5.50×10^{-2}

The ratio $[C_2Cl_6]_f/[CCl_3Br]_f$ was plotted against time and gave a straight line passing close to the origin. A least squares calculation on the data gave for the time intercept - 49 sec. and slope $\emptyset I_a/2[CCl_3Br]_i = 0.59 \times 10^{-5} sec.^{-1}$ (fig. 2)

2) Variation of Reaction Temperature

A series was carried out in which the reaction temperature was the only variable.

TABLE I.4, 2

$[CHCl_2F]_i = 3.73 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l;

Reaction time = 7200 secs.

Temp. °C	$[CHCl_3]_f / [C_2Cl_6]_f$	$[CCl_2FBr]_f / [C_2Cl_6]_f$	$[C_2Cl_6]_f / [CCl_3Br]_f$
176	2.71	3.00	6.14×10^{-2}
160	2.11	2.41	4.32×10^{-2}
150	1.88	2.30	3.65×10^{-2}
138	1.44	1.62	2.72×10^{-2}
125	1.19	1.32	2.05×10^{-2}
113	1.02	0.96	1.56×10^{-2}

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs $10^3/T$ gave a straight line with a 'least squares' slope $(E_2-\frac{1}{2}E_6)/2.303R = 1.19 \pm 0.19$ and intercept $\log \sqrt{2}A_2[CHCl_2F]_i/(A_6\phi I_a)^{\frac{1}{2}} = 3.06 \pm 0.08$. (fig. 4)

A plot of log $[CCl_2FBr]_f/[C_2Cl_6]_f$ vs $10^3/T$ gave a straight line with a 'least squares' slope $(E_2-\frac{1}{2}E_6)/2.303R = 1.35 \pm 0.22$ and intercept $\log \sqrt{2}A_2[CHCl_2F]_i/(A_6\phi I_a)^{\frac{1}{2}} = 3.51 \pm 0.09$.

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs $10^3/T$ was a straight line with a slope $= -1.62 \pm 0.10$ and intercept $= 2.38 \pm 0.04$. (fig. 3)

3) Variation of Incident Light Intensity

A series of light variation experiments was carried out by placing calibrated wire gauzes between the light source and the reaction vessel.

TABLE I.4, 3

$[CHCl_2F]_i = 3.73 \times 10^{-3}$ moles/l; $[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l;

Reaction time = 7200 secs.; Reaction temperature = $161 \pm 2^\circ C$

Relative Intensity %	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CCl_2FBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
100	2.11	2.41	4.32×10^{-2}
66	1.78	1.87	3.01×10^{-2}
59	1.93	2.00	2.78×10^{-2}
46	1.64	1.60	2.13×10^{-2}
33	1.50	1.39	1.62×10^{-2}

The above data was combined in a least squares calculation which gave slope and intercept values for the following straight line plots.

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log (R.I.) had slope $= 0.31 \pm 0.11$ and intercept $= -0.29 \pm 0.06$. (fig. 5)

A log $[CCl_2FBr]_f/[C_2Cl_6]_f$ vs log (R.I.) had slope $= 0.49 \pm 0.12$ and intercept $= -0.61 \pm 0.07$.

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log (R.I.) had slope = 0.89 ± 0.05 and intercept = -3.15 ± 0.03. (fig. 6)

4) Variation of Concentration of Bromotrichloromethane

The experimental results for the variation of bromotrichloromethane concentration are tabulated below.

TABLE I.4, 4

$[CHCl_2F]_i = 3.73 \times 10^{-3}$ moles/l; Reaction time = 7200 secs.
Reaction temperature = 163 ± 1°C

$[CCl_3Br]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CCl_2FBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
1.24×10^{-3}	2.48	2.79	4.35×10^{-2}
1.02×10^{-3}	2.63	2.95	4.46×10^{-2}
0.79×10^{-3}	2.91	3:27	4.41×10^{-2}
0.57×10^{-3}	3.27	3.81	3.98×10^{-2}
0.34×10^{-3}	3.63	4.12	4.15×10^{-2}

The least squares method applied to the above data gave slope and intercept values for the following plots.

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CCl_3Br]_i$ had slope = -0.30 ± 0.13 and intercept = -0.48 ± 0.04.

A plot of log $[CCl_2FBr]_f/[C_2Cl_6]_f$ vs log $[CCl_3Br]_i$ had slope = -0.32 ± 0.13 and intercept = -0.48 ± 0.04.

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CCl_3Br]_i$ had slope = 0.07 ± 0.08 and intercept = -1.16 ± 0.02.

FIG 10'

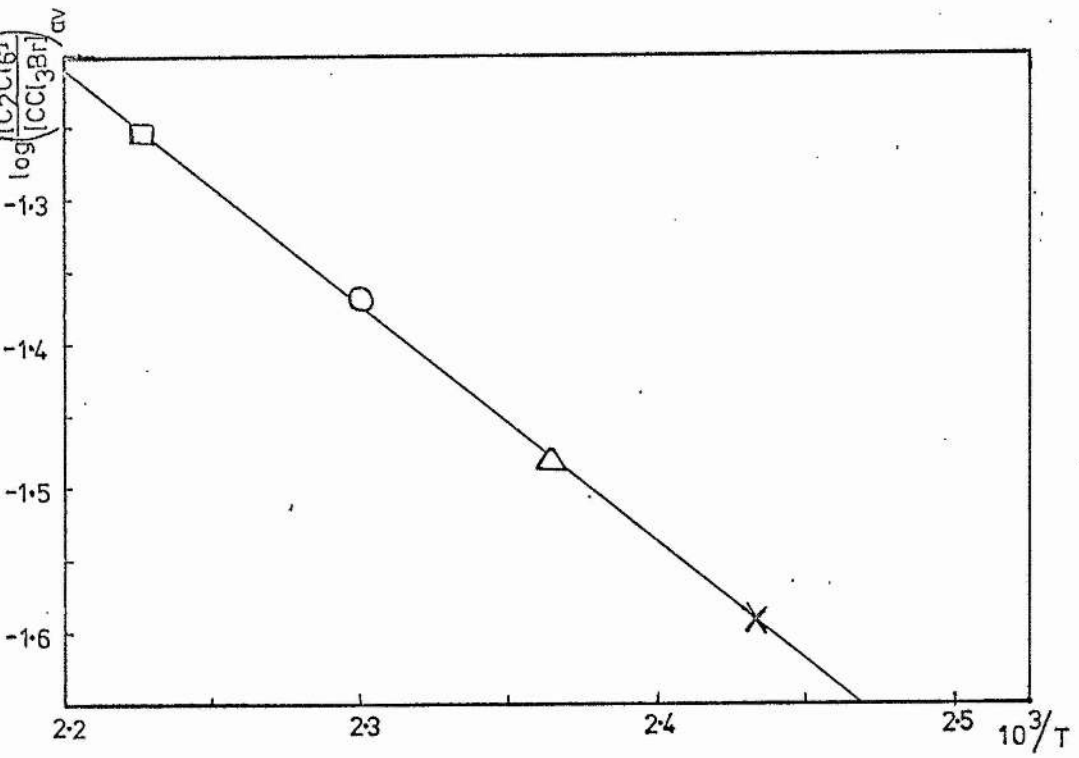
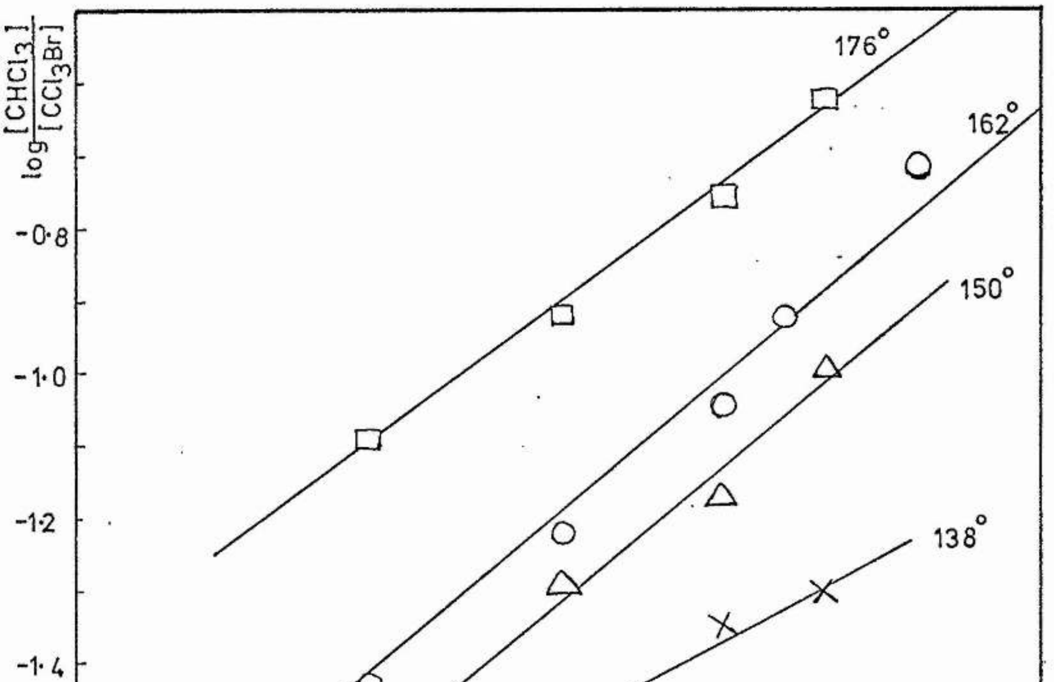

log$\left(\frac{[C_2Cl_6]}{[CCl_3Br]}\right)_{av}$
-1·3
-1·4
-1·5
-1·6
2·2
2·3
2·4
2·5
$10^3/T$

FIG 10


log$\frac{[CHCl_3]}{[CCl_3Br]}$
176°
162°
150°
138°
-0·8
-1·0
-1·2
-1·4
-1·6
-1·8
-3·3
-3·1
-2·9
-2·7
-2·5
-2·3
-2·1
log[$CHCl_2F$]

5) Variation of Concentration of Dichlorofluoromethane at T = 176°C

These experiments formed part of a set in which the concentration of dichlorofluoromethane was varied at several set temperatures.

TABLE I.4, 5

$[CCl_3Br]_i$ = 1.24 x 10^{-3} moles/l; Reaction time = 7200 secs.
Reaction temperature = 176 ± 2°C

$[CHCl_2F]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CCl_2FBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
5.09 x 10^{-3}	4.19	4.59	5.66 x 10^{-2}
3.73 x 10^{-3}	3.48	3.73	4.99 x 10^{-2}
2.26 x 10^{-3}	2.16	2.26	5.55 x 10^{-2}
1.24 x 10^{-3}	1.33	1.42	6.11 x 10^{-2}

Application of the least squares method to the above data gave the slope and intercept values for the following plots.
A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CHCl_2F]_i$ had slope = 0.83 ± 0.08 and intercept = 2.54 ± 0.03. (fig. 10)
A plot of log $[CCl_2FBr]_f/[C_2Cl_6]_f$ vs log $[CHCl_2F]_i$ had slope = 0.85 ± 0.07 and intercept = 2.61 ± 0.03.
A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CHCl_2F]_i$ had slope = -0.07 ± 0.09 and intercept = -1.44 ± 0.03.

6) Variation of Concentration of Dichlorofluoromethane at T = 162°C

The results of this set of experiments are tabulated below.

$[CCl_3Br]_i$ = 1.24 x 10^{-3} moles/l; Reaction time = 7200 secs.;
Reaction temperature = 162 ± 1°C

$[CHCl_2F]_i$ moles/l	$[CHCl_3]_f/[C_2Cl_6]_f$	$[CCl_2FBr]_f/[C_2Cl_6]_f$	$[C_2Cl_6]_f/[CCl_3Br]_f$
0.57×10^{-3}	0.52	0.53	4.28×10^{-2}
1.24×10^{-3}	0.87	0.91	4.24×10^{-2}
2.26×10^{-3}	1.37	1.58	4.34×10^{-2}
3.73×10^{-3}	2.42	2.81	3.82×10^{-2}
4.52×10^{-3}	2.92	3.24	4.09×10^{-2}
6.78×10^{-3}	3.92	4.39	4.92×10^{-2}

The least squares method applied to the above data gave slope and intercept values for the following plots.

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CHCl_2F]_i$ had slope = 0.84 ± 0.07 and intercept = 2.40 ± 0.02. (fig. 10)

A plot of log $[CCl_2FBr]_f/[C_2Cl_6]_f$ vs log $[CHCl_2F]_i$ had slope = 0.88 ± 0.07 and intercept = 2.55 ± 0.03.

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CHCl_2F]_i$ had slope = 0.02 ± 0.06 and intercept = -1.32 ± 0.02.

7) Variation of Concentration of Dichlorofluoromethane at T = 150°C

The experimental results are tabulated below.

TABLE I.4, 7

$[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction time = 7200 secs.;
Reaction temperature = 150 ± 2°C

$[CHCl_2F]_i$ moles/l	$[CHCl_3]_f/[C_2Cl_6]_f$	$[CCl_2FBr]_f/[C_2Cl_6]_f$	$[C_2Cl_6]_f/[CCl_3Br]_f$
5.09×10^{-3}	3.12	3.28	3.20×10^{-2}
3.73×10^{-3}	2.33	2.58	2.91×10^{-2}
2.26×10^{-3}	1.52	1.62	3.35×10^{-2}
1.24×10^{-3}	0.77	0.79	3.69×10^{-2}

The least squares method applied to the above data gave slope and intercept values for the following plots.

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CHCl_2F]_i$ had slope = 0.97 ± 0.10 and intercept = 2.73 ± 0.04. (fig. 10)

A plot of log $[CCl_2FBr]_f/[C_2Cl_6]_f$ vs log $[CHCl_2F]_i$ had slope = 1.01 ± 0.10 and intercept = 2.85 ± 0.04.

A plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CHCl_2F]_i$ had slope = -0.13 ± 0.08 and intercept = -1.81 ± 0.03.

8) Variation of Concentration of Dichlorofluoromethane at T = 138°C

The results of these concentration variation experiments are listed below.

TABLE I.4, 8

$[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; Reaction time = 7200 secs.;

Reaction temperature = 138 ± 2°C

$[CHCl_2F]_i$ moles/l	$\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$	$\frac{[CCl_2FBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$
5.09×10^{-3}	2.29	2.43	2.15×10^{-2}
3.73×10^{-3}	1.82	1.90	2.45×10^{-2}
2.26×10^{-3}	1.14	1.08	2.77×10^{-2}
1.24×10^{-3}	0.82	0.71	2.80×10^{-2}

The above data was combined in least squares calculations which gave the slope and intercept values for the following straight line plots.

A plot of log $[CHCl_3]_f/[C_2Cl_6]_f$ vs log $[CHCl_2F]_i$ had its slope = 0.74 ± 0.11 and intercept = 2.05 ± 0.04. (fig. 10)

A plot of log $[CCl_2FBr]_f/[C_2Cl_6]_f$ vs log $[CHCl_2F]_i$ had its slopo = 0.89 ± 0.12 and intercept = 2.43 ± 0.05.

Finally, a plot of log $[C_2Cl_6]_f/[CCl_3Br]_f$ vs log $[CHCl_2F]_i$ had its slope = -0.18 ± 0.09 and intercept = -2.07 ± 0.04.

9) Variation of Concentration of Chloroform

A series of experiments was performed in which the concentration of chloroform was varied. The results are listed below.

TABLE I.4, 9

$[CCl_3Br]_i = 1.24 \times 10^{-3}$ moles/l; $[CHCl_2F]_i = 3.73 \times 10^{-3}$ moles/l;

Reaction time = 7200 secs.; Reaction temperature = 163 ± 2°C

$[CHCl_3]_i$ moles/l	$\frac{[CCl_2FBr]_f}{[C_2Cl_6]_f}$	$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$	$\frac{[CHCl_3]_f}{[CCl_3Br]_f}$
0.00	3.01	4.41×10^{-2}	0.11
0.34×10^{-3}	2.11	4.30×10^{-2}	0.47
0.57×10^{-3}	1.86	4.58×10^{-2}	0.67
0.79×10^{-3}	1.49	4.25×10^{-2}	0.80
1.02×10^{-3}	1.26	4.62×10^{-2}	0.96
1.24×10^{-3}	1.07	4.77×10^{-2}	1.11
1.47×10^{-3}	1.04	4.45×10^{-2}	1.30
1.70×10^{-3}	1.02	4.75×10^{-2}	1.55
2.25×10^{-3}	0.84	4.61×10^{-2}	1.88
2.83×10^{-3}	0.66	4.73×10^{-2}	2.28

A least squares plot of log $[CCl_2FBr]_f/[C_2Cl_6]_f$ vs log $[CHCl_3]_i$ gave a straight line of slope = -0.54 ± 0.06 and intercept = -1.53 ± 0.02.

DISCUSSION

It will be more convenient to consider, in one discussion section rather than four, the results of the reactions of bromotrichloromethane with each of the four halomethanes studied. Generally it has been shown[73] that only the weakest bond of a polyhalogenated methane is ruptured on photolysis. Thus the observed initiation when bromotrichloromethane is photolysed under the influence of the light from a medium pressure mercury arc filtered through 'Pyrex' (i.e. wavelengths 3130 Å and 3660 Å) is

$$CCl_3Br + h\nu \longrightarrow CCl_3\cdot + Br\cdot \quad (1) \quad D(CCl_3-Br) \sim 49 \text{ Kcal/mole}$$

and not

$$CCl_3Br + h\nu \longrightarrow CCl_2Br\cdot + Cl\cdot \quad D(CCl_2Br-Cl) \sim 68 \text{ Kcal/mole}$$

Any thermal contribution to the initiation is insignificant as a dark experiment in which bromotrichloromethane and dichloromethane were heated at 200°C overnight gave insignificant amounts of products on analysis. All analytical experiments were performed below 190°C and generally within the temperature range 100°C to 180°C. Each of the four hydrogen containing halomethanes reacted with bromotrichloromethane gave in general three products which were quantitatively analysed. These were chloroform, monobromohalomethane and hexachloroethane. In addition molecular bromine was present at the end of each experiment and in one experiment only the amount of bromine present was analysed spectrophotometrically and was found to be equal, within experimental error, to the amount of hexachloroethane formed in the reaction. Furthermore, the most reactive halomethane studied, dichloromethane, was photolysed on its own for three hours at 170°C. Analysis showed no detectable products under these reaction conditions and hence any photolytic decomposition of the reactant halomethanes can be discounted.

For all halomethanes studied trace amounts of dibromodichloromethane were found at high reaction temperature. Dichloromethane was the exception in that quite large amounts of dibromodichloromethane were found at quite low temperatures. These differences can be accounted for by changes in the mechanism of formation of dibromodichloromethane. At high temperatures the formation of dibromodichloromethane can be explained by the reaction sequence

$$CCl_3\cdot + CCl_3Br \longrightarrow CCl_4 + CCl_2Br\cdot \qquad a)$$

$$CCl_2Br\cdot + CCl_3Br \longrightarrow CCl_2Br_2 + CCl_3\cdot \qquad b)$$

Reaction a) has a high activation energy[74,75]

$$k_a = 1.4 \times 10^8 \exp -(13,600)/RT \text{ l. mole}^{-1}\text{sec}^{-1},$$

and will only occur to any extent at high temperature. The bromodichloromethyl radical formed in a) will rapidly abstract a bromine atom from bromotrichloromethane to form the observed dibromodichloromethane. This mechanism implies that the amount of carbon tetrachloride formed should equal the amount of dibromodichloromethane. Careful analysis of a few reaction mixtures at low column temperatures, which enabled the trace amount of carbon tetrachloride to be distinguished from the tail of the chloroform peak, indicated that this was so. The above reaction sequence is an attack by a trichloromethyl radical on a reactant, but it appears that to rationalize the larger amounts of dibromodichloromethane formed when dichloromethane is reacted with bromotrichloromethane, that the reaction of trichloromethyl radicals with a product must be proposed. With dichloromethane the product ratio $[CHCl_3]_f/[CHCl_2Br]_f$ is always greater than unity. It appears that the amount of dibromodichloromethane formed is somehow related to the concentration of bromodichloromethane. The reaction of trichloromethyl radicals with bromodichloromethane appears to be very facile.

$$CCl_3\cdot \ + \ CHCl_2Br \longrightarrow CHCl_3 \ + \ CCl_2Br\cdot \qquad c)$$

$$CCl_2Br\cdot \ + \ CCl_3Br \longrightarrow CCl_2Br_2 \ + \ CCl_3\cdot \qquad d)$$

This reaction scheme would explain the increasing formation of dibromodichloromethane with temperature and also explain why the ratio $[CHCl_3]_f/[CHCl_2Br]_f$ is significantly different from unity. Dichloromethane also produced another small trace product in the large percentage conversion experiments which can be accounted for by considering the possibility of the cross termination reaction,

$$CCl_3\cdot \ + \ CHCl_2\cdot \longrightarrow CCl_3\text{-}CHCl_2 \qquad e)$$

The small trace peak can be assigned to pentachloroethane by comparison of retention times with authentic material but at the most the amount of pentachloroethane formed was approximately 5% of the hexachloroethane formed. The overall effect of this cross termination reaction is probably negligible. No cross termination products were detected with the other halomethanes which were reacted with bromotrichloromethane.

The formation of the major products in all these reactions should be explicable with the following simple mechanism in which the trichloromethyl radical acts as the main chain carrier.

$$CCl_3Br + h\nu \longrightarrow CCl_3\cdot + Br\cdot \tag{1}$$

$$CCl_3\cdot + RH \longrightarrow CCl_3H + R\cdot \tag{2}$$

$$R\cdot + CCl_3Br \longrightarrow RBr + CCl_3\cdot \tag{3}$$

$$2CCl_3\cdot \longrightarrow C_2Cl_6 \tag{6}$$

Application of the steady-state approximation to this mechanism gives the conditions

$$\frac{d[CCl_3\cdot]}{dt} = 0; \qquad \frac{d[R\cdot]}{dt} = 0.$$

The rate of initiation can be expressed by Rate (1) = $\emptyset I_a$ where $\emptyset$ is the quantum yield of the bromotrichlormethane photolysis and I_a is the absorbed light intensity.

Therefore

$$\frac{d[CCl_3\cdot]}{dt} = 0 = \emptyset I_a - k_2[CCl_3\cdot][RH] + k_3[R\cdot][CCl_3Br] - 2k_6[CCl_3\cdot]^2 \tag{1}$$

$$\frac{d[R\cdot]}{dt} = 0 = k_2[CCl_3\cdot][RH] - k_3[R\cdot][CCl_3Br] \tag{2}$$

Addition of (1) and (2) yields

$$\phi I_a = 2k_6[CCl_3\cdot]^2$$

$$\therefore \quad [CCl_3\cdot] = \left(\frac{\phi I_a}{2k_6}\right)^{\frac{1}{2}} \tag{3}$$

Substituting (3) in (2) leads to

$$[R\cdot] = \frac{k_2[RH]}{k_3[CCl_3Br]} \cdot \left(\frac{\phi I_a}{2k_6}\right)^{\frac{1}{2}} \tag{4}$$

When the values for (3) and (4) are substituted in the rate equations, the rates of formation of the products are given by:

$$\frac{d[CHCl_3]}{dt} = k_2[RH]\left(\frac{\phi I_a}{2k_6}\right)^{\frac{1}{2}} \tag{5}$$

$$\frac{d[RBr]}{dt} = k_2[RH]\left(\frac{\phi I_a}{2k_6}\right)^{\frac{1}{2}} \tag{6}$$

$$\frac{d[C_2Cl_6]}{dt} = \frac{\phi I_a}{2} \tag{7}$$

From the above, division of (5) or (6) by (7) leads to

$$\frac{d[CHCl_3]}{d[C_2Cl_6]} = \frac{\sqrt{2}\ k_2[RH]}{(\phi I_a\ k_6)^{\frac{1}{2}}} = \frac{d[RBr]}{d[C_2Cl_6]} \tag{8}$$

Generally, if the extent of reaction is small, the above expression can be used in its integrated form

$$\frac{[CHCl_3]_f}{[C_2Cl_6]_f} = \frac{[RBr]_f}{[C_2Cl_6]_f} \doteq \frac{\sqrt{2}\,k_2[RH]_i}{(\phi I_a\ k_6)^{\frac{1}{2}}} \tag{9}$$

By using the Arrhenius equation in the form $k = A\ e^{-E/RT}$ and taking logarithms of (9) we have,

$$\log_{10}\frac{[CHCl_3]_f}{[C_2Cl_6]_f} = \log_{10}\frac{[RBr]_f}{[C_2Cl_6]_f} = \log_{10}\frac{\sqrt{2}\,A_2[RH]_i}{(\phi I_a\,A_6)^{\frac{1}{2}}} - \frac{(E_2-\frac{1}{2}E_6)}{2.303\ RT} \qquad (10)$$

Furthermore integration of (7) leads to

$$[C_2Cl_6]_f = \frac{\phi I_a}{2}\,.\,t \qquad (11)$$

and hence

$$\frac{[C_2Cl_6]_f}{[CCl_3Br]_f} = \frac{\phi I_a}{2[CCl_3Br]_f}\,.\,t \qquad (12)$$

A straight forward relationship between the incident light intensity I_o, and the absorbed light intensity I_a can be derived by assuming that the Lambert-Beer law is obeyed

$$\text{i.e.}\quad \log_{10}\frac{I_o}{I_o-I_a} = \varepsilon\ l\ [CCl_3Br]$$

where ε = the molar extinction coefficient of bromotrichloromethane ($\sim 5\times10^{-3}$ at 3660 Å)[60] and l = the reaction cell path length in cm. Hence

$$\ln\frac{I_o}{I_o-I_a} = \beta\ l\ [CCl_3Br] \qquad \text{where } \beta = 2.303\,\varepsilon\ (\text{cm}^{-1}\ \text{litre mole}^{-1})$$

$$\therefore\ \frac{I_o}{I_o-I_a} = \exp\,(\beta l[CCl_3Br])$$

$$\therefore\ 1-\frac{I_a}{I_o} = \exp\,(-\beta l[CCl_3Br])$$

$$\therefore\ 1-\frac{I_a}{I_o} = 1-\beta l[CCl_3Br] + \frac{(\beta l[CCl_3Br])^2}{2!} - \cdots$$

As β and $[CCl_3Br]$ are both small, the third and subsequent terms of the expansion are negligible.

$$\text{Hence} \qquad 1 - \frac{I_a}{I_o} = 1 - \beta l[CCl_3Br]$$

$$\therefore \quad I_a = I_o \, \beta l[CCl_3Br] \tag{13}$$

Therefore I_a is directly proportional to I_o.

In the main, all quantitative experiments were carried out with the initial halomethane concentration equal to or greater than the initial bromotrichloromethane concentration, for only under these initial conditions was the product ratio $\frac{[CHCl_3]_f}{[RBr]_f}$ close to unity as is required by the simple mechanism.

When the bromotrichloromethane was in excess the ratio $\frac{[CHCl_3]_f}{[RBr]_f}$ was substantially greater than unity. With this restriction on the initial experimental conditions, the experimental results can be compared and contrasted to the predicted results of the 'simple' mechanism.

From the results of tables I (1,1); (2,1); (3,1); (4,1) plots of $\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ vs. t were made and as shown in fig. 2 they were all straight lines passing close to the origin in agreement with the predictions of equation (12). From the slopes and intercepts obtained by the least squares method the time axis intercepts and rates of initiation ϕI_a were calculated and are shown in the following table.

TABLE A

RH	ϕI_a moles $l^{-1}s^{-1}$	Time intercept secs	Reaction temperature
CH_2F_2	1.64×10^{-8}	- 1060	163°C
CH_2FCl	1.81×10^{-8}	15	163°C
CH_2Cl_2	0.50×10^{-8}	- 1500	108°C
$CHCl_2F$	1.46×10^{-8}	- 49	162°C

As can be seen from this table the values of ϕI_a are temperature dependent. The temperature dependence of ϕI_a is further confirmed by the results shown in table I (1,2); (2,2); (3,2); (4,2). In all cases the ratio $\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ increases with increasing temperature

Plots of log $\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ vs. $10^3/T$ are shown in fig. 3.

For all RH except dichloromethane the slopes and intercepts obtained by the least squares method are identical within experimental error. The results are tabulated below.

TABLE B

RH	Slope	Intercept
CH_2F_2	-1.57 ± 0.12	2.32 ± 0.05
CH_2FCl	-1.54 ± 0.12	2.10 ± 0.05
CH_2Cl_2	-1.16 ± 0.11	1.31 ± 0.04
$CHCl_2F$	-1.62 ± 0.10	2.38 ± 0.04

It would be possible from these results to obtain a pseudo Arrhenius equation for the temperature dependence of ϕI_a. This will be dealt with later when further experimental results can be drawn upon to give a more accurate temperature dependence equation for ϕI_a. Why the rate of initiation should be temperature dependent is not quite clear but it appears[74] that the initial process must involve electronically excited bromotrichloromethane molecules, where only a few vibrational levels of the excited state are involved in collisional deactivation.

Beside the temperature dependence of the ratio $\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$, the tables also give the temperature dependence of the ratios $\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ and $\frac{[RBr]_f}{[C_2Cl_6]_f}$ in all cases except for RH = difluoromethane where the bromide peak was so volatile as to invalidate its quantitative analysis. In general the results of least squares treatments for plots of $\log \frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ vs. $10^3/T$ and $\log \frac{[RBr]_f}{[C_2Cl_6]_f}$ vs $10^3/T$ for each halomethane gave virtually identical slopes and intercepts. The results are tabulated below and the plots of $\log \frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ vs $10^3/T$ are shown in fig. 4

TABLE C

RH	$(E_2-\frac{1}{2}E_6)$ kcal/mole	$\log_{10}\frac{\sqrt{2}\,A_2[RH]_i}{(\phi I_a A_6)^{\frac{1}{2}}}$	A_2 l m^{-1}s^{-1}
CH_2F_2	9.2 ± 0.9	4.18 ± 0.09	1.03×10^8
CH_2FCl	8.1 ± 1.2	4.40 ± 0.11	1.85×10^8
CH_2Cl_2	4.7 ± 0.7	3.53 ± 0.06	1.27×10^7
$CHCl_2F$	5.5 ± 0.8	3.06 ± 0.08	0.72×10^7

By utilizing the value of $\emptyset I_a$ obtained from the time variation series and the value of Tedder and Walton[70] for $A_6 = 10^{10.9} l\ m^{-1} s^{-1}$, and $E_6 = 0$ Kcal/mole a value of A_2 can be determined for each RH.

Discussion of these results will be dealt with more fully later on. At present it suffices to point out that the activation energies, while paralleling the expected activation energy order, are all too low. Similarly the pre-exponential terms are low in value. The neglect of the temperature dependence of $\emptyset I_a$ partially contributes to these low values.

The results in Tables I (1,3) (2,3) (3,3) (4,3) were obtained by varying incident light intensity I_o which has been shown to be directly proportional to the absorbed light intensity I_a. From (9) plots of $\log \frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ vs log (Relative light intensity) should be straight lines of slope = -0.50. It is apparent from the tables and fig. 5 that in no case is the slope equal to -0.50, even within experimental error. Plots of $\log \frac{[RBr]_f}{[C_2Cl_6]_f}$ vs. log (R.I.) should also have slopes equal to -0.50, but they are again identical to the results obtained for the corresponding chloroform plots.

However, from (12), plots of $\log \frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ vs log (R.I.) should be straight lines with unit slopes. Table D and fig. 6 show that this was generally true within experimental error.

TABLE D

	$\log \frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ vs log RI Slope	$\log \frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ vs log RI Slope
CH_2F_2	-0.006 ± 0.05	0.99 ± 0.04
CH_2FCl	0.36 ± 0.12	0.94 ± 0.06
CH_2Cl_2	0.13 ± 0.09	0.90 ± 0.10
$CHCl_2F$	0.31 ± 0.11	0.89 ± 0.05

Similar results were obtained with the photolysis of bromotrichloromethane with propene and 2-fluoropropene[91]. Besides hydrogen abstraction from the methyl group CCl_3Br added to the double bond. For the light intensity variation experiments plots of log $[CHCl_3]/[CCl_3Br]$ and log $[CH_3CXBrCH_2CCl_3]/[C_2Cl_6]$ vs log (Relative Intensity) were made and gave 0.84 and -0.63 respectively for X = H and 1.5 and -0.71 respectively for X = F. The latter plots in each case should have had slopes equal to -0.50. The discrepancy was taken to imply the existence of another termination step, namely dimerisation of the allyl radicals of which small quantities were observed.

In the present work plots of log $[CHCl_3]/[CCl_3Br]$ vs log (Relative Intensity) gave straight lines with slopes equal to 0.99; 1.28; 1.03; 1.20 for RH = CH_2F_2; CH_2FCl; CH_2Cl_2; $CHCl_2F$ respectively. These results represent a major discrepancy between the mechanism predictions and the experimentally observed values. It appears that the termination step is adequately dealt with by the present mechanism, but that too little chloroform is produced at the lower light intensities over the amount demanded by the 'simple' mechanism. It is conceivable that step (2) of the mechanism is reversible, as this reaction would presumably have similar Arrhenius parameters to the reaction of the trifluoromethyl radical with chloroform[40] ($k = 10^{8.0} \exp(-6{,}600/RT)\ \mathrm{l.m^{-1}s^{-1}}$). On the other hand the reactions of the trichloromethyl radical with the halomethanes will generally have similar pre-exponential terms but they will probably have greater activation energies.

Inclusion of the reverse of step (2)

$$R\cdot \ + \ CHCl_3 \longrightarrow RH \ + \ CCl_3^{\cdot} \tag{8}$$

and the application of the steady state approximations to the new mechanism leads to the result

$$\frac{[CHCl_3]_f}{[C_2Cl_6]_f} = \frac{[RBr]_f}{[C_2Cl_6]_f} = \frac{\sqrt{2}\ k_2[RH]_i}{(k_6\ \phi I_a)^{\frac{1}{2}}} \left(\frac{k_3[CCl_3Br]}{k_8[CHCl_3] + k_3[CCl_3Br]} \right) \tag{14}$$

It is probable that $k_8 \sim k_3 \sim 10^5$ at 164°C. On this assumption, the predominant term in the denominator will be $k_3[CCl_3Br]$ as the concentration of bromotrichloromethane will be greater than for chloroform. Therefore equation (14) reduces to equation (9) obtained for the 'simple' mechanism. In full form, equation (14) similarly predicts that the ratio $\frac{[CHCl_3]_f}{[C_2Cl_6]_f} = \frac{[RBr]_f}{[C_2Cl_6]_f}$ and both should be dependent on $I_o^{-0.50}$

Step (8) is feasible as is shown by the results in Table I (4,9) which were obtained by adding variable amounts of chloroform to a reaction mixture of bromotrichloromethane with dichlorofluoromethane.

The table shows that increasing the initial chloroform concentration has the effect of decreasing the ratio $\frac{[RBr]_f}{[C_2Cl_6]_f}$

A plot of log $\frac{[RBr]_f}{[C_2Cl_6]_f}$ vs log $[CHCl_3]_i$ has its slope = -0.54 ± 0.06.

Assuming that (14) is true and by taking any pair of values for $\frac{[RBr]_f}{[C_2Cl_6]_f}$ and the corresponding values for the concentrations of bromotrichloromethane and dichlorofluoromethane it follows that $k_3 \sim 0.5\ k_8$. It appears that the inclusion of step (8) will be an improvement in the overall mechanism for the reaction, but in itself it does not explain the positive dependence of the ratio $\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ on the incident light intensity.

The results for the concentration variation of bromotrichloromethane are given in Table I (1,4); (2,4); (3,4); (4,4). Plots of log $\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ vs log $[CCl_3Br]_i$ and log $\frac{[RBr]_f}{[C_2Cl_6]_f}$ vs log $[CCl_3Br]_i$ are equal within experimental error for each halomethane studied, but the results are not the same for all four halomethanes. From (9) a plot of log $\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ vs log $[CCl_3Br]_i$ should be a straight line of slope -0.50, assuming that the quantum yield $\emptyset$, is independent of the concentration of bromotrichloromethane. The slope and intercept values for plots of log $\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ vs log $[CCl_3Br]_i$ are shown in the following table.

TABLE E

RH :	Slope	Intercept
CH_2F_2	-0.32 ± 0.09	-1.16 ± 0.03
CH_2FCl	0.03 ± 0.22	0.45 ± 0.07
CH_2Cl_2	0.19 ± 0.09	1.54 ± 0.03
$CHCl_2F$	-0.30 ± 0.13	-0.48 ± 0.04

Previous workers[74] have shown, that when bromotrichloromethane is photolysed on its own, that the quantum yield Ø increases by roughly 20% for a three fold decrease in the initial bromotrichloromethane concentration. Little evidence of this effect is observed with the present results where the ratio $\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ is virtually constant as the concentration of bromotrichloromethane is reduced. Only with dichloromethane is there a general upward trend in the ratio $\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ with decreasing $[CCl_3Br]_i$. Even with this case, for a four fold decrease in bromotrichloromethane concentration there is only a 12% difference between the maximum and minimum values of $\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$. In all cases, the percentage difference between the maximum and minimum values of $\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ is less than 10%. The previous workers[74] have further shown that increasing the concentration of an inert gas in the photolysis of bromotrichloromethane decreases the quantum yield Ø. It is conceivable that, within the present system, there is a virtual balancing of the effects of an increase in Ø with decreasing bromotrichloromethane concentration and a decrease in Ø with an effective increase in the quenching power of the halomethane reactant. The slope and intercept values for plots of log $\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ vs log $[CCl_3Br]_i$ are tabulated below.

TABLE F

RH	Slope	Intercept
CH_2F_2	0.03 ± 0.08	-1.26 ± 0.03
CH_2FCl	0.01 ± 0.11	-1.40 ± 0.03
CH_2Cl_2	-0.08 ± 0.08	-2.01 ± 0.03
$CHCl_2F$	0.07 ± 0.08	-1.16 ± 0.02

In all cases, the results for the slopes are zero within experimental error, which would be expected from (11) if Ø was independent of the concentrations of bromotrichloromethane or halomethane which could act as a quencher for any electronically excited bromotrichloromethane molecule.

A further test of (9) is afforded by the concentration variation of the halomethane reactant. Plots of $\log \frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ or $\log \frac{[RBr]_f}{[C_2Cl_6]_f}$ versus $\log [RH]_i$ should be straight lines with slopes equal to unity and intercepts equal to $\log \frac{\sqrt{2}.k_2}{(\emptyset I_a k_6)^{\frac{1}{2}}}$. Generally, the slope and intercept values for the plots relating to the two products, chloroform and bromohalomethane are identical within experimental error. The results, shown in Tables I (1,5), (1,6), (1,7), (1,8); (2,5), (2,6), (2,7), (2,8); (3,5), (3,6), (3,7), (3,8); (4,5), (4,6), (4,7), (4,8), are tabularly summarised in the form of the slope and intercept values of plots of $\log \frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ vs $\log [RH]_i$. These plots are shown in figs. 7,8,9,10.

TABLE F'

RH	Reaction Temperature °C	Slope	Intercept
CH_2F_2	188	0.74 ± 0.09	+1.46 ± 0.03
	176	0.70 ± 0.08	+1.27 ± 0.03
	162	0.63 ± 0.10	0.90 ± 0.02
	150	0.57 ± 0.06	0.60 ± 0.02
CH_2FCl	177	0.83 ± 0.08	2.47 ± 0.03
	163	0.70 ± 0.06	2.08 ± 0.02
	151	0.69 ± 0.08	1.93 ± 0.03
	140	0.78 ± 0.10	1.98 ± 0.05
CH_2Cl_2	123	0.62 ± 0.06	2.50 ± 0.02
	112	0.60 ± 0.03	2.38 ± 0.01
	100	0.77 ± 0.07	2.76 ± 0.03
	87	0.60 ± 0.07	2.28 ± 0.03
$CHCl_2F$	176	0.83 ± 0.08	2.54 ± 0.03
	162	0.84 ± 0.07	2.40 ± 0.02
	150	0.97 ± 0.10	2.73 ± 0.04
	138	0.74 ± 0.11	2.05 ± 0.04

From these results there are few obvious trends with increasing temperature. The slope values are all substantially less than unity and in general the maximum slope values are also less than unity. It is difficult to reconcile this less than unity dependence on halomethane concentration with any postulated simple mechanism. Partial order within these series is observed with the general increase in the value of the intercept with increasing temperature. Indeed, assuming that (9) is valid and using the calculated values of ϕI_a listed in Table A, along with $\log_{10} k_6 = 10.9$[70], reasonably accurate rate constants k_2 can be calculated from the relation $\log \frac{\sqrt{2}.k_2}{(\phi I_a\ k_6)^{\frac{1}{2}}}$ = Intercept. The results are compared with the same rate constants obtained from table C

TABLE G

RH	Temp °C	k_2 l $m^{-1}s^{-1}$	k_2 (temp series)
CH_2F_2	162	$\sim$ 20	$\sim 2.5 \times 10^3$
CH_2FCl	163	$\sim 3 \times 10^3$	$\sim 1.6 \times 10^4$
CH_2Cl_2	112	$\sim 5 \times 10^3$	$\sim 2.8 \times 10^4$
$CHCl_2F$	162	$\sim 6 \times 10^3$	$\sim 1.3 \times 10^4$

The results by the intercept method are approximately a fifth of the results obtained from the temperature series, and are probably the least accurate. Both sets of figures parallel the observed reactivity of the four halomethanes.

Finally the results of plots of $\log \frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ versus $\log\,[RH]_i$ should be straight lines of zero slope if the quantum yield ϕ is independent of the concentration of RH.

The slope and intercept values obtained from plots of $\log \frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ vs $\log\,[RH]_i$ are shown in Table H.

TABLE H

RH	Reaction Temperature	Slope	Intercept
CH_2F_2	188	-0.009 ± 0.05	-1.05 ± 0.02
	176	-0.06 ± 0.04	-1.30 ± 0.02
	162	-0.03 ± 0.05	-1.31 ± 0.02
	150	-0.07 ± 0.04	-1.14 ± 0.01
CH_2FCl	177	-0.04 ± 0.03	-1.42 ± 0.01
	163	-0.002 ± 0.05	-1.43 ± 0.02
	151	-0.03 ± 0.06	-1.64 ± 0.02
	140	-0.05 ± 0.05	-1.76 ± 0.02
CH_2Cl_2	123	-0.06 ± 0.06	-1.79 ± 0.02
	112	+0.02 ± 0.02	-1.67 ± 0.01
	100	-0.09 ± 0.06	-2.05 ± 0.02
	87	-0.003 ± 0.05	-1.95 ± 0.02
$CHCl_2F$	176	-0.07 ± 0.09	-1.44 ± 0.03
	162	+0.02 ± 0.06	-1.32 ± 0.02
	150	-0.13 ± 0.08	-1.81 ± 0.03
	138	-0.18 ± 0.09	-2.07 ± 0.04

The table shows that the slope values are all equal to zero within experimental error, but that the general negative slope values could be further indication of a decrease in Ø with increasing halomethane concentration. There is an approximate 10% decrease in the ratio $\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ with a 10 fold increase in the halomethane reactant. This change is probably not significant in relation to the experimental scatter on the measurements of $[C_2Cl_6]_f/[CCl_3Br]_f$.

The results for the concentration variation of each halomethane at the set temperatures can be used to confirm the experimental reproducibility for these reaction systems. As indicated previously, there is little change for the ratio $[C_2Cl_6]_f/[CCl_3Br]_f$ at any one temperature while the halomethane concentration is varied. Thus, each halomethane studied can yield a plot of $\log \frac{[C_2Cl_6]_f}{[CCl_3Br]_f}$ versus $10^3/T$. The slope and intercept values for these plots (figs 7', 8', 9', 10') should be identical to those obtained from the straightforward temperature variation experiments with each halomethane. The values are shown in the following table.

TABLE I

RH	Slope	Intercept
CH_2F_2	-1.55 ± 0.12	2.33 ± 0.05
CH_2FCl	-1.73 ± 0.12	2.54 ± 0.05
CH_2Cl_2	-1.21 ± 0.12	1.40 ± 0.05
$CHCl_2F$	-1.67 ± 0.12	2.46 ± 0.05

The good correspondence to the values obtained from the temperature variation experiments (TABLE B) confirms the experimental reproducibility in these systems.

All the basic results have now been dealt with, and it is now possible to derive the pseudo Arrhenius equation for the temperature dependence of the rate of initiation, $\emptyset I_a$. As has been shown equation (12) is generally true. By considering only those experiments where the physical constraints are identical (i.e. lamp to reaction cell distance = 6 inches), values of $\emptyset I_a$ can be calculated from the ratio $[C_2Cl_6]_f/[CCl_3Br]_f$ obtained from the experimental series for all halomethanes in which the following parameters were allowed to vary:- Reaction temperature, reaction time, and halomethane concentration at all temperatures. A plot of (10 + log $\emptyset I_a$) vs $10^3/T$ gave a good straight line of slope -1.383 ± 0.073 and intercept = 5.4086 ± 0.0304. Therefore $\emptyset I_a(T) = (2.56 \pm 0.17) \times 10^{-5} \exp(-6{,}330 \pm 330)/RT$ quanta $l.^{-1}s^{-1}$.

This activation energy, obtained for the rate of initiation, is virtually identical to the corresponding value obtained from the addition reactions of bromotrichloromethane with halogenated ethylenes[75] where a value of E = (6260 ± 900) cals/mole was obtained. It appears that the activation energy is solely dependent on the bromotrichloromethane and is constant regardless of the other reactant, be it saturated or unsaturated.

The effect of the temperature dependence of $\emptyset I_a$ on the Arrhenius factors shown in table C can be eliminated by considering expressions for the rates of formation of chloroform and hexachloroethane, derived from the simple mechanism. The rate of formation of chloroform is given by:-

$$R_{CHCl_3} = \frac{d[CHCl_3]}{dt} = k_2[CCl_3\cdot][RH]$$

Assuming that there is no significant change in the concentration of bromotrichloromethane during the course of the reaction, it is permissible to equate $[CCl_3Br]_f$ to $[CCl_3Br]_i$

$$\text{Hence} \quad R_{CHCl_3} = \frac{[CHCl_3]_f}{[CCl_3Br]_f} \cdot \frac{[CCl_3Br]_i}{t} = k_2[CCl_3\cdot][RH]_i \quad (a)$$

where t = Reaction time in seconds.

$[RH]_i$ = initial halomethane concentration

Similarly the rate of formation of hexachloroethane is given by

$$R_{C_2Cl_6} = \frac{[C_2Cl_6]_f}{[CCl_3Br]_f} \cdot \frac{[CCl_3Br]_i}{t} = k_6[CCl_3\cdot]^2 \qquad (b)$$

By dividing (a) by the square root of (b), the following expression, which does not contain any radical species is obtained,

$$\frac{R_{CHCl_3}}{(R_{C_2Cl_6})^{\frac{1}{2}}} = \frac{[CHCl_3]_f/[CCl_3Br]_f}{([C_2Cl_6]_f/[CCl_3Br]_f)^{\frac{1}{2}}} \left(\frac{[CCl_3Br]_f}{t}\right)^{\frac{1}{2}} = \frac{k_2[RH]}{k_6^{\frac{1}{2}}} \qquad (c)$$

Taking logarithms of (c) leads to

$$\log_{10} \frac{R_{CHCl_3}}{(R_{C_2Cl_6})^{\frac{1}{2}}} = \log_{10} \frac{A_2[RH]}{A_6^{\frac{1}{2}}} - \frac{(E_2 - \frac{1}{2}E6)}{2.303\ RT} \qquad (d)$$

Plots of $\log_{10} \frac{R_{CHCl_3}}{(R_{C_2Cl_6})^{\frac{1}{2}}}$ vs. $10^3/T$ should be straight lines of slopes = $(E_2 - \frac{1}{2}E_6)/2.303\ R$ and intercepts = $\log_{10}(A_2[RH]_i/A_6^{\frac{1}{2}})$. Re-estimates of the A factor and activation energy for the hydrogen abstraction step from the halomethanes by trichloromethyl radicals can be made by using Tedder and Walton's[70] value for $A_6 = 10^{10.9}\ l\ m^{-1}s^{-1}$ and $E_6 = 0$ in conjunction with the above approach. In addition to the normal temperature variation experiments, the results for the variation of halomethane concentration at several temperatures, can be used to yield several temperature variation 'experiments' at various initial concentrations of halomethanes. The A factors and activation energies derived from least squares plots of log $(R_{CHCl_3}/R^{\frac{1}{2}}_{C_2Cl_6})$ vs $10^3/T$ are tabulated below for each halomethane.

All temperature variation series were carried out with $[RH]_i$ = 3.73×10^{-3} moles litre^{-1}. Results for temperature variation series are listed in Tables 1 (1,2); (2,2); (3,2); (4,2).

TABLE J

$[CH_2F_2]$ m.l.$^{-1}$	A_2 l.m.$^{-1}$s.$^{-1}$	E_2 Kcal/mol
Temp. variation series	$(4.92 \pm 0.95) \times 10^{9}$	12.80 ± 0.82
5.09×10^{-3}	$(31.57 \pm 5.98) \times 10^{9}$	14.48 ± 0.78
3.73×10^{-3}	$(12.21 \pm 2.82) \times 10^{9}$	13.59 ± 0.94
2.26×10^{-3}	$(5.36 \pm 1.76) \times 10^{9}$	12.69 ± 1.28
1.24×10^{-3}	$(1.96 \pm 0.89) \times 10^{9}$	11.71 ± 1.69
0.57×10^{-3}	$(1.67 \pm 0.77) \times 10^{9}$	11.21 ± 1.70
Average	$(9.62 \pm 8.0) \times 10^{9}$	12.75 ± 1.8

$[CH_2FCl]_i$ m.l.$^{-1}$	A_2 l.m.$^{-1}$s.$^{-1}$	E_2 Kcal/mol
Temp. variation series	$(1.02 \pm 0.23) \times 10^{10}$	11.61 ± 0.96
6.78×10^{-3}	$(0.73 \pm 0.24) \times 10^{10}$	11.46 ± 1.33
5.09×10^{-3}	$(11.74 \pm 5.43) \times 10^{10}$	13.76 ± 1.76
3.73×10^{-3}	$(3.55 \pm 1.73) \times 10^{10}$	12.69 ± 1.84
2.26×10^{-3}	$(1.46 \pm 0.70) \times 10^{10}$	11.80 ± 1.80
1.24×10^{-3}	$(1.42 \pm 1.06) \times 10^{10}$	11.65 ± 2.57
0.57×10^{-3}	$(1.98 \pm 1.57) \times 10^{10}$	11.75 ± 2.71
Average	$(3.13 \pm 3.00) \times 10^{10}$	12.10 ± 1.8

$[CH_2Cl_2]_i$ m.l.$^{-1}$	A_2 l.m.$^{-1}$s.$^{-1}$	E_2 Kcal/mole
Temp. Variation series	$(4.79 \pm 0.65) \times 10^8$	7.29 ± 0.69
5.09×10^{-3}	$(0.83 \pm 0.18) \times 10^8$	5.98 ± 1.06
3.73×10^{-3}	$(0.27 \pm 0.04) \times 10^8$	5.05 ± 0.68
2.26×10^{-3}	$(0.80 \pm 0.11) \times 10^8$	5.73 ± 0.68
1.24×10^{-3}	$(0.12 \pm 0.02) \times 10^8$	5.90 ± 0.83
Average	$(1.36 \pm 1.00) \times 10^8$	6.00 ± 1.00

$[CHCl_2F]_i$ m.l.$^{-1}$	A_2 l.m.$^{-1}$s^{-1}	E_2 Kcal/mole
Temp. Variation series	$(5.48 \pm 0.85) \times 10^8$	9.11 ± 0.71
5.09×10^{-3}	$(20.41 \pm 7.44) \times 10^8$	10.15 ± 1.45
3.73×10^{-3}	$(6.57 \pm 2.86) \times 10^8$	9.17 ± 1.68
2.26×10^{-3}	$(4.34 \pm 1.87) \times 10^8$	8.74 ± 1.66
1.24×10^{-3}	$(2.67 \pm 1.63) \times 10^8$	8.22 ± 2.21
Average	$(7.89 \pm 5.0) \times 10^8$	9.08 ± 1.54

The average values obtained by this treatment appear to be a substantial improvement over those shown in table C. For all halomethanes except dichloromethane there is an increase of roughly 3.5 Kcal/mole in the activation energy. For dichloromethane the increase is more modest, 1.3 Kcal/mole. There is also an increase of approximately 10^2 in the pre-exponential term for all the halomethanes except dichloromethane where the increase is only a factor of ten.

The results are compared in table K with the values obtained for abstraction by bromine atoms, trifluoromethyl and methyl radicals.

TABLE K

log A in litre mole^{-1} sec^{-1}: E in Kcal/mole.

RH	$Br\cdot$[27]		$CF_3\cdot$[39,40]		$CCl_3\cdot$		CH_3[39,91]	
	log A	E	log A	E	log A	E	log A	E
CH_4	10.9	18.3	9.1	11.2	(9.6)	(17.0)	8.8	14.8
CH_3F	10.7	16.1	9.1	11.2			8.2	11.4
CH_2F_2	10.4	16.6	8.9	11.2	10.0	12.8*	8.0	10.2
CHF_3	10.1	22.3					7.4	13.6 (38) 11.4 (39)
CH_3Cl	10.9	14.7	9.1	10.6			8.9	9.4^x
CH_2Cl_2	9.9	10.9*	8.2	7.6	8.1	6.0*	8.5	7.2^x
$CHCl_3$	9.3	9.3	8.1	6.6			7.8	5.8^x
CH_2FCl	10.9	14.8*			10.5	12.1*		
$CHCl_2F$	10.0	13.3*			8.9	9.1*		
$CHClF_2$			8.1	10.8^a				
HCl			8.2	5.1				4.4
HBr			8.8	2.9			8.8	1.4

* This work X Uncertain values

a) Abstraction from CHF_3 by $CF_2Cl\cdot$ log A = 8.9 E = 13.7
Ref. 77

Abstraction from $CHCl_3$ by $CHCl_2\cdot$ E = 6.4 Ref. 55

These results for hydrogen abstraction by trichloromethyl radicals, while an improvement over the estimates obtained by assuming a temperature independent ϕI_a term, are not directly comparable to the results obtained for hydrogen abstraction by trifluoromethyl or methyl radicals.

The A factors for difluoromethane and fluorochloromethane are at least a factor of ten too large while the activation energy for dichloromethane is probably 2 Kcals/mole too small in relation to the values obtained for the hydrogen abstraction by trifluoromethyl radicals from dichloromethane and chloroform. Furthermore, it is conceivable that all the activation energies are low by about 4 Kcals/mole if direct comparisons, between the results for the hydrogen abstraction from alkanes by bromine atoms, methyl, trifluoromethyl and trichloromethyl radicals and the results of hydrogen abstraction by these radicals from halomethanes, are valid.

TABLE L

Hydrogen abstraction from alkanes			(E Kcal/mole)	log A(av) l $m^{-1}s^{-1}$	
R	Prim(CH_3-)	Sec(CH_2<)	Tert(CH<)		
Br.	13.4	10.2	7.5	10.5	Ref 7
$CH_3\cdot$	11.7	10.1	8.0	8.5	Ref 91
$CF_3\cdot$	7.5	5.3	3.0	9.2	Ref 91
$CCl_3\cdot$	14.3	10.7		9.6	Ref 75

From table L the trichloromethyl radical is less reactive than the trifluoromethyl radical but is similar in reactivity to the methyl radical. Attack by each of these radicals on a particular substrate (RH) would lead one to expect the activation energies to be related to the bond strength of the formed methane. Thus, as $D(CCl_3-H) \sim 93$ Kcal/mole; $D(CH_3-H) \sim 104$ Kcal/mole and $D(CF_3-H) \sim 106$ Kcal/mole, the activation energies for hydrogen abstraction from a particular halomethane ought to vary as follows $E_{CCl_3\cdot} > E_{CH_3\cdot} > E_{CF_3\cdot}$. On top of this decrease, polar effects are important, in deciding the overall activation energy for a particular reaction. Hydrogen abstraction by CF_3 radicals from the fluoromethane series shows no decrease (CH_4= 11.2; CH_3F = 11.2; CH_2F_2 = 11.2)[39,40] in the activation energies in comparison with the results for hydrogen abstraction by methyl radicals from the same fluoromethanes. (CH_4 = 14.8; CH_3F = 11.8; CH_2F_2 = 10.4; CHF_3 = 11.4)[39]. These results indicate that there is a strong polar effect with trifluoromethyl radicals as the bond strength probably decreases in going from CH_4 to CH_3F to CH_2F_2. The repulsion between the CF_3 radical and a fluoromethane is probably sufficient to give the observed invariance of the activation energies. This can be represented as follows

$$\overset{\delta-}{FH_2C}-\overset{\delta+}{H} \qquad \overset{\delta+\delta-}{\cdot CF_3}$$

This polar repulsion effect is probably less important for the trichloromethyl radical and least important for the methyl radical. Thus, for the fluoromethanes, the activation energies for hydrogen abstraction by methyl radicals decreases down the series in line with the drop in the bond strengths. Although the activation energy for hydrogen abstraction from an alkane is generally much higher ($\sim$4 kcal) for methyl radicals than for trifluoromethyl radicals, the polar effects for halomethanes alter the reactivities of the CF_3 and CH_3 radicals so much so that the activation energies can be lower for hydrogen abstraction by CH_3 radicals than for CF_3 radicals. Again, hydrogen abstraction from the chloromethane series by CF_3 and CH_3 radicals show similar trends (table K). The results for methyl radicals are uncertain, but within bounds, in going from methane to chloroform there is a greater decrease in the activation energies for methyl radicals than for trifluoromethyl radicals. These trends can be explained by assuming that the bond energy decrease in going from methane to chloroform is predominant for both CH_3 and CF_3 radicals. The smaller decrease observed for the hydrogen abstraction by trifluoromethyl radicals is probably due to a polar effect still exerting some influence though insufficient to overcome the general decrease.

Thus the magnitude of the polar effect for trichloromethyl radicals should be less than for trifluoromethyl radicals but greater than for methyl radicals. Confirmation of these trends comes from the activation energy for hydrogen abstraction from chloroform by a dichloromethyl radical[55]. The value of 6.4 Kcal/mole is intermediate between those for abstraction by $CF_3\cdot$ (6.6) and $CH_3\cdot$ (5.8) from chloroform. By applying these arguments to the results for hydrogen abstraction by trichloromethyl radicals from halomethanes it appears that the low activation energy for dichloromethane is too low by at least 1 Kcal/mole, and possibly is low by as much as 2 Kcal/mole. Given that the trichloromethyl radical is least reactive and more likely to be subject to a polar effect in the transition state than a methyl radical, it is difficult to see how the activation energy for hydrogen abstraction from dichloromethane can be less than that for a methyl radical unless this value is greatly in error. It would be reasonable to assume that for the reaction $CCl_3\cdot + CH_4 \longrightarrow CHCl_3 + CH_3\cdot$ the activation energy should be about 17 Kcal/mole. This places an upper limit on the activation energies for hydrogen abstraction by trichloromethyl radicals from the halomethanes under discussion, for only with fluoroform does the activation energy for hydrogen abstraction by a chlorodifluoromethyl radical[77] become greater than the activation energy for abstraction from methane. Fluoroform has a higher bond dissociation energy ($D(CF_3-H) = 106$ Kcal/mole)[27] than methane or any of the other halomethanes under discussion, thus a high activation energy for abstraction by $CF_2Cl\cdot$ radicals is not surprising. The activation energies for difluoromethane, chlorofluoromethane and dichlorofluoromethane are probably reasonably accurate. At the most they are probably one 1 Kcal/mole too low. This assertion can be justified by assuming that the activation energy for the abstraction by $CCl_3\cdot$ radicals from methane is 17 Kcals with a pre-exponential term of $10^{9.6}$ $l\ m^{-1}s^{-1}$. It would be reasonable to assume that the decrease in the activation energy for the abstraction from methane and difluoromethane by methyl radicals should be greater than the difference encountered with $CCl_3\cdot$ radicals. The difference occurs but it is only about 0.5 Kcal/mole in magnitude, which does not seem sufficient as there should be an appreciable polar effect with trichloromethyl radicals. Again it appears that the reported activation energies are consistently underestimated by about 1-2 Kcal/mole. The results closely follow the trends observed for the bromination of these compounds. The underestimation of the activation energies is accompanied by an overestimation of the pre-exponential term. This term generally appears to be about a power of ten too large in relation to the values obtained for abstraction by either trifluoromethyl or methyl radicals.

Within the constraints caused by the non-conformity of these reaction systems to the simple mechanism the 'best' estimates for the hydrogen abstraction step are as follows:-

TABLE M

[RH]	log A l $m^{-1}s^{-1}$	E Kcal/mole	$k_2(T)$ l $m^{-1}s^{-1}$	
CH_2F_2	10.00 ± 1.00	12.8 ± 2.0	4×10^3	(164)
CH_2FCl	10.5 ± 1.00	12.1 ± 2.0	3×10^4	(164)
CH_2Cl_2	8.1 ± 1.00	6.0 ± 2.0	5×10^4	(112)
$CHCl_2F$	8.9 ± 1.00	9.1 ± 2.0	2.5×10^4	(164)

The rate constants given in Table M can be compared with those obtained in table G. There is good correspondence between the results obtained by the present treatment and by the 'simple' mechanism treatment of the temperature variation series.

Previous workers[66,67] who studied the reaction of bromotrichloromethane with substituted butanes considered the following mechanism

$$CCl_3Br + h\nu \longrightarrow CCl_3\cdot + Br\cdot \quad (1)$$

$$CCl_3\cdot + RH \longrightarrow CHCl_3 + R\cdot \quad (2)$$

$$R\cdot + CCl_3Br \longrightarrow RBr + CCl_3\cdot \quad (3)$$

$$Br\cdot + RH \longrightarrow HBr + R\cdot \quad (4)$$

$$CCl_3\cdot + HBr \longrightarrow CHCl_3 + Br\cdot \quad (5)$$

$$2\,CCl_3\cdot \longrightarrow C_2Cl_6 \quad (6)$$

Applying the steady state approximations to this sequence leads to the following conditions

$$\frac{d[CCl_3\cdot]}{dt} = \phi I_a - k_2[CCl_3\cdot][RH] + k_3[R\cdot][CCl_3Br] - k_5[CCl_3\cdot][HBr] - 2\,k_6[CCl_3\cdot] = 0 \qquad (15)$$

$$\frac{d[Br\cdot]}{dt} = -k_4[Br\cdot][RH] + k_5[CCl_3\cdot][HBr] + \phi I_a = 0 \qquad (16)$$

$$\frac{d[R\cdot]}{dt} = k_2[CCl_3\cdot][RH] + k_4[Br\cdot][RH] - k_3[R\cdot][CCl_3Br] = 0 \qquad (17)$$

Adding (15), (16) (17) leads to

$$2\,\phi I_a - 2\,k_6[CCl_3\cdot]^2 = 0$$

$$\therefore \quad [CCl_3\cdot] = \left(\frac{\phi I_a}{k_6}\right)^{\frac{1}{2}}$$

Substitution in (16) gives

$$[Br\cdot] = \frac{1}{k_4[RH]}\left(\phi I_a + k_5[HBr]\left(\frac{\phi I_a}{k_6}\right)^{\frac{1}{2}}\right)$$

Addition of (16) and (17) and substituting for $[CCl_3\cdot]$ yields

$$[R\cdot] = \frac{\phi I_a}{k_3[CCl_3Br]} + \frac{k_2[RH] + k_5[HBr]}{k_3[CCl_3Br]}\left(\frac{\phi I_a}{k_6}\right)^{\frac{1}{2}}$$

The rates of formation of products are given by

$$\frac{d[CHCl_3]}{dt} = k_2[CCl_3\cdot][RH] + k_5[CCl_3\cdot][HBr]$$

$$d[RBr] = k_3[R\cdot][CCl_3Br]$$

$$d[C_2Cl_6] = k_6[CCl_3\cdot]^2 = \phi I_a$$

Substitution for the radical concentrations yields

$$\frac{d[CHCl_3]}{d[C_2Cl_6]} = \frac{k_2[RH]}{(\phi I_a\ k_6)^{\frac{1}{2}}} + \frac{k_5[HBr]}{(\phi I_a\ k_6)^{\frac{1}{2}}} \qquad (18)$$

$$\frac{d[RBr]}{d[C_2Cl_6]} = 1 + \frac{k_2[RH]}{(\emptyset I_a\ k_6)^{\frac{1}{2}}} + \frac{k_5[HBr]}{(\emptyset I_a\ k_6)^{\frac{1}{2}}} \qquad (19)$$

For a small extent of reaction the above equations (18) and (19) can be used in their integrated forms

$$\frac{[CHCl_3]_f}{[C_2Cl_6]_f} = \frac{[RBr]_f}{[C_2Cl_6]_f} - 1 = \frac{k_2[RH]_i}{(\emptyset I_a\ k_6)^{\frac{1}{2}}} + \frac{k_5[HBr]_i}{(\emptyset I_a\ k_6)^{\frac{1}{2}}} \qquad (20)$$

By using the following argument, these workers showed that bromine atoms could not be the principal chain carriers. Initially there is no hydrogen bromide present and hence reaction (5) cannot occur. In general reaction (4) is faster than reaction (2) but the concentration of hydrogen bromide will only increase if k_5 is small which again implies that bromine atoms cannot be the principal chain carriers. In contrast, if k_5 is very large, the hydrogen bromide will never accumulate and reaction (5) will remain unimportant as long as the chain length is greater than unity. It appears that k_5 is indeed large[67]. These workers give $k_5^{463} = 10^{8.5 \pm 0.6}\ l\ m^{-1} s^{-1}$ in comparison with $k_2^{463} = 10^{3.2 \pm 0.25}\ l\ m^{-1} s^{-1}$ for RH = Butane. These workers further showed that the addition of hydrogen bromide to an experiment had a profound effect on the relative proportions of the bromo butanes formed. In fact, with added hydrogen bromide the Relative Selectivity was almost identical to the selectivity of bromine atoms. This fact implies that the main chain propagator is the trichloromethyl radical, for addition of hydrogen bromide would have no effect on the relative proportions of bromobutanes formed if the main chain carriers were bromine atoms[23]. This test is not applicable to the present system.

For all halomethanes studied here, the chain length must be shorter than for the reaction of bromotrichloromethane with substituted butanes. Only for dichloromethane is the ratio $\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ significantly greater than unity (between 5 and 15.) For dichlorofluoromethane and chlorofluoromethane this ratio varies from about 0.2 to about 5 whereas for difluoromethane the ratio is always less than unity and within the range 0.01 to 0.6. In the study with substituted butanes, this ratio was between 5 and 30, with the bulk of the results between 10 and 20. Thus it appears that the reaction of bromotrichloromethane with halomethanes occurs near or in the non-chain region. As this would invalidate the above argument, reaction due to bromine atoms must make a considerable contribution to any proposed mechanism for the reaction of bromotrichloromethane with these halomethanes. The following reaction mechanism

$CCl_3Br + h\nu \rightarrow CCl_3\cdot + Br\cdot$ (1)
$CCl_3\cdot + RH \rightleftharpoons CHCl_3 + R\cdot$ (2)(8)
$R\cdot + CCl_3Br \rightarrow RBr + CCl_3\cdot$ (3)
$Br\cdot + RH \rightarrow HBr + R\cdot$ (4)
$CCl_3\cdot + HBr \rightleftharpoons CHCl_3 + Br\cdot$ (5)(9)
$CCl_3\cdot + CCl_3\cdot \rightarrow C_2Cl_6$ (6)
$Br\cdot + Br\cdot + M \rightarrow Br_2 + M$ (7)
$CCl_3\cdot + Br\cdot \rightarrow CCl_3Br$ (10)

probably represents the nearest to the truth obtainable with this approach. Reaction (10), which is a chain termination reaction, probably occurs but it is kinetically indistinguishable as the product, bromotrichloromethane, is an initial reactant. Other possible reactions are

$$CCl_3\cdot + CCl_3Br \longrightarrow CCl_3Br + CCl_3\cdot \qquad (11)$$

$$Br. + CCl_3Br \longrightarrow Br_2 + CCl_3^{\cdot} \qquad (12)$$

Reaction (11), although it undoubtably occurs, is kinetically indistinguishable as the products are identical to the reactants. Reaction (12) has been shown[74] not to occur below 200°C, and furthermore bromotrichloromethane is the minor constituent of an initial reaction mixture and hence (12) would be less favourable than reaction (4). Chloroform, a product, is a very reactive molecule towards attack by a bromine atom and presumably to attack by a trichloromethyl radical. It is about 100 times more reactive towards bromine atoms than any of the reactant halomethanes under consideration. Therefore both step (2) and (5) are likely to be reversible. Step (4) is likely to be reversible as well.

Although termination in bromine is unfavourable because of third body restrictions, this must be the mode of production of the observed bromine in a reaction mixture as previous work has shown that reaction (12)

$$Br\cdot + CCl_3Br \rightarrow Br_2 + CCl_3\cdot \qquad (12)$$

does not occur to any significant extent below 200°C.

Consideration of the rates of product formation from the reaction steps (1) to (7) and (9) yields the following

$$R_{CHCl_3} = k_2[CCl_3\cdot][RH] + k_5[CCl_3\cdot][HBr] - k_9[Br\cdot][CHCl_3].$$

$$R_{RBr} = k_3[R\cdot][CCl_3Br]$$

$$R_{C_2Cl_6} = k_6[CCl_3\cdot]^2$$

$$R_{Br_2} = k_7[Br\cdot]^2[M]$$

$$R_{HBr} = k_4[Br\cdot][RH] - k_5[CCl_3\cdot][HBr] + k_9[Br\cdot][CHCl_3].$$

$$\text{Now } [CCl_3\cdot] = \left(\frac{R_{C_2Cl_6}}{k_6}\right)^{\frac{1}{2}}$$

$$\therefore R_{CHCl_3} = k_2[RH]\left(\frac{R_{C_2Cl_6}}{k_6}\right)^{\frac{1}{2}} + k_5[HBr]\left(\frac{R_{C_2Cl_6}}{k_6}\right)^{\frac{1}{2}} - k_9\left(\frac{R_{Br_2}}{k_7[M]}\right)^{\frac{1}{2}}[CHCl_3]$$

As one experiment indicated that the amount of bromine formed in a reaction equalled the amount of hexachloroethane the rates of formation of these two products were equated and to an approximation we have:-

$$R_{CHCl_3} = k_2[RH]\left(\frac{R_{C_2Cl_6}}{k_6}\right)^{\frac{1}{2}} + k_5[HBr]\left(\frac{R_{C_2Cl_6}}{k_6}\right)^{\frac{1}{2}} - k_9\left(\frac{R_{C_2Cl_6}}{k_6}\right)^{\frac{1}{2}}[CHCl_3]$$

$$\text{i.e. } \frac{R_{CHCl_3}}{(R_{C_2Cl_6})^{\frac{1}{2}}}\cdot k_6^{\frac{1}{2}} + k_9\left(\frac{[CHCl_3]_f}{[CCl_3Br]_f}\right)[CCl_3Br]_i = k_2[RH]_i + k_5[HBr]$$

For small extents of reaction, this equation gives

$$\frac{\left(\frac{[CHCl_3]_f}{[CCl_3Br]_f}\right)}{\left(\frac{[C_2Cl_6]_f}{[CCl_3Br]_f}\right)^{\frac{1}{2}}};\left(\frac{[CCl_3Br]_i}{t}\right)^{\frac{1}{2}}\cdot k_6^{\frac{1}{2}} + k_9\left(\frac{[CHCl_3]_f}{[CCl_3Br]_f}\right)\cdot[CCl_3Br]_{\frac{i}{t}}$$

$$= k_2[RH] + k_5[HBr]$$

By plotting the left hand side of this equation against the concentration of halomethane, straight line plots with slope equal to k_2 and intercept equal to $k_5[HBr]$ should be obtained. This treatment further assumes that the concentration of hydrogen bromide is independent of the halomethane concentration. By performing series of experiments where the concentration of halomethane was varied at several temperatures the values of k_2 obtained can be used to give a plot of log k_2 vs $10^3/T$, the slope being equal to the activation energy E_2 and the intercept equal to A_2. The results obtained by this method are given in the following table

TABLE N

RH	log A_2 l $m^{-1}s^{-1}$	E_2 Kcal/mole	k
CH_2F_2	12.2	18.3	1.2×10^3 (163)
CH_2FCl	10.86	13.8	1.0×10^4 (163)
CH_2Cl_2	7.13	5.2	3.39×10^4(112)
$CHFCl_2$	10.69	12.2	3.9×10^4 (163)

The most noticeable results are for dichloromethane in that the values for log A and E have decreased slightly whereas for the other halomethanes there have been increases, some considerable. It appears that this treatment gives an indication of the effect that neglect of the bromine atom chains has on the determined activation energies. The virtual constancy of the results for dichloromethane appear to confirm that bromine atoms do not play a large part in the overall kinetics of this reaction. For dichlorofluoromethane and chlorofluoromethane there is an increase in both log A and E which is of greater magnitude for dichlorofluoromethane. This again is in line with the idea of increasing participation by bromine atoms the nearer a reaction is to the non-chain region. The ratio $\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ is smaller for dichlorofluoromethane than for chlorofluoromethane under identical experimental conditions.

For difluoromethane, where the ratio $\frac{[CHCl_3]_f}{[C_2Cl_6]_f}$ is very much less than unity, there is a large increase in both the A factor and the activation energy over those shown in table M.

But it is also apparent that the A factors for all halomethanes, except dichloromethane, are all at least a factor of 10 to 10^2 too large in comparison with the pre-exponential factors obtained for similar hydrogen abstraction reactions by either trifluoromethyl or methyl radicals. The activation energy for difluoromethane is probably also too large by about 2 to 3 Kcal/mole when compared with the activation energies for abstraction by bromine atoms, methyl and trifluoromethyl radicals.

In deriving these rate constants a value for the rate constant for the recombination of trichloromethyl radicals of $k_6 = 10^{10.5}$ $l\ m^{-1}s^{-1}$ was used. This value is less than that of Tedder and Walton[70] ($k_6 = 10^{10.9}\ l\ m^{-1}s^{-1}$) but greater than that obtained by De Mare and Huybrechts[45] ($k_6 = 10^{9.7}\ l\ m^{-1}s^{-1}$). The value used is more in line with that obtained for similar halomethyl radical combinations[43] (CF_3 10.4; CF_2Cl 10.2; CH_3 10.3). The rate equation obtained by Sullivan and Davidson[76] for step 9 was also used.

$$\log k_9 = 9.36 - 9300/4.575\ T \quad l\ m^{-1}s^{-1}.$$

It is possible that even this value of $k_6 = 10^{10.5}\ l\ m^{-1}s^{-1}$ is too large, as this would result in too large a value for the intercept .... but it would have little effect on the calculated activation energy. The maximum effect that using the lower value for k_6 would have on the intercept would be a lowering of A_2 by about a factor of ten. Neglect of the change in concentration of hydrogen bromide with halomethane concentration should only have a minor effect on these determined A factors and activation energies.

In conclusion the results most likely to be close to the true values are those given in table M, with the activation energy more likely to lie between the stated value and the upper limit.

The trends in the results can be explained by considering the opposed effects of decreasing bond strength in the halomethane reactant and increased polar repulsion between the trichloromethyl radical and the halomethane.

Details of Reaction

Chromatographic Analysis:-

Column 20% Silicone Oil on 60-100 mesh Embacel

Temperature 65° until elution of CCl_3Br then raised to 110°C for elution of C_2Cl_6

Nitrogen flow rate 120 ml./min.

Chart speed 48 in./hr.

1) Variation of Reaction Time

Temp. 162°C; Reactant pressures $CHCl_2F$ 66 mm., CCl_3Br 22 mm.

Relative final concentrations of products:-

a) Time 1800 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	0.88	0.75	1.10×10^{-2}	
1.0	0.87	0.90	1.14×10^{-2}	
1.0	0.97	0.84	1.20×10^{-2}	
1.0	1.08	0.88	1.01×10^{-2}	
1.0	0.85	0.78	1.19×10^{-2}	
1.0	0.93	0.83	1.13×10^{-2}	Mean

b) Time 3600 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.43	1.59	2.25×10^{-2}	
1.0	1.37	1.44	2.31×10^{-2}	
1.0	1.49	1.53	2.20×10^{-2}	
1.0	1.26	1.45	2.21×10^{-2}	
1.0	1.15	1.22	2.23×10^{-2}	
1.0	1.34	1.45	2.24×10^{-2}	Mean

c) Time 5400 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.67	1.75	3.49×10^{-2}	
1.0	1.92	2.06	3.10×10^{-2}	
1.0	2.11	2.15	3.05×10^{-2}	
1.0	2.11	2.39	2.94×10^{-2}	
1.0	2.04	2.15	3.02×10^{-2}	
1.0	1.97	2.10	3.12×10^{-2}	Mean

d) Time 7200 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.05	3.35	3.59×10^{-2}	
1.0	2.58	2.82	4.21×10^{-2}	
1.0	2.79	2.69	4.14×10^{-2}	
1.0	2.75	2.96	4.00×10^{-2}	
1.0	2.79	2.96	3.99×10^{-2}	Mean

e) Time 9000 secs.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.28	3.73	5.36×10^{-2}	
1.0	3.03	3.45	5.42×10^{-2}	
1.0	2.64	2.75	5.52×10^{-2}	
1.0	2.89	3.26	5.65×10^{-2}	
1.0	2.93	3.28	5.57×10^{-2}	
1.0	2.95	3.30	5.50×10^{-2}	Mean

2) Variation of Reaction Temperature

Time 7200 secs; Reactant pressures $CHCl_2F$ 66 mm., CCl_3Br 22 mm.
Relative final concentration of products:-

a) Temp. 176°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.23	3.89	5.72×10^{-2}	
1.0	2.40	2.56	6.26×10^{-2}	
1.0	2.32	2.49	6.80×10^{-2}	
1.0	3.04	3.40	5.75×10^{-2}	
1.0	2.56	2.94	6.20×10^{-2}	
1.0	2.71	3.00	6.14×10^{-2}	Mean

b) Temp. 160°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.98	2.20	4.40×10^{-2}	
1.0	2.04	2.28	4.39×10^{-2}	
1.0	2.64	3.01	3.82×10^{-2}	
1.0	1.96	2.35	4.69×10^{-2}	
1.0	1.91	2.20	4.31×10^{-2}	
1.0	2.11	2.41	4.32×10^{-2}	Mean

c) Temp. 150°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.09	2.30	3.48×10^{-2}	
1.0	1.90	2.40	3.50×10^{-2}	
1.0	1.90	2.33	3.43×10^{-2}	
1.0	1.85	2.40	3.89×10^{-2}	
1.0	1.68	2.07	3.93×10^{-2}	
1.0	1.88	2.30	3.65×10^{-2}	Mean

d) Temp. 138°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.31	1.36	2.70×10^{-2}	
1.0	1.75	2.17	2.45×10^{-2}	
1.0	1.38	1.51	2.77×10^{-2}	
1.0	1.34	1.49	2.86×10^{-2}	
1.0	1.39	1.58	2.80×10^{-2}	
1.0	1.43	1.62	2.72×10^{-2}	Mean

e) Temp. 125°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.13	1.37	1.93×10^{-2}	
1.0	1.36	1.46	2.04×10^{-2}	
1.0	1.29	1.32	2.06×10^{-2}	
1.0	1.15	1.33	2.02×10^{-2}	
1.0	1.03	1.13	2.19×10^{-2}	
1.0	1.19	1.32	2.05×10^{-2}	Mean

f) Temp. 113°C

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.25	1.18	1.43×10^{-2}	
1.0	0.89	0.80	1.65×10^{-2}	
1.0	0.94	0.93	1.65×10^{-2}	
1.0	1.03	0.97	1.46×10^{-2}	
1.0	0.99	0.93	1.62×10^{-2}	
1.0	1.02	0.96	1.56×10^{-2}	Mean

3) Variation of Incident Light Intensity

Time 7200 secs., Reactant pressures, $CHCl_2F$ 66 mm., CCl_3Br 22 mm.
Temp. 161°C
Relative final concentrations of products:-

Transmissions

a) 100%

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.98	2.20	4.40×10^{-2}	
1.0	2.04	2.28	4.39×10^{-2}	
1.0	2.64	3.01	3.82×10^{-2}	
1.0	1.96	2.35	4.69×10^{-2}	
1.0	1.91	2.20	4.31×10^{-2}	
1.0	2.11	2.41	4.32×10^{-2}	Mean

b) 66%

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.02	2.10	2.81×10^{-2}	
1.0	1.84	1.95	2.97×10^{-2}	
1.0	1.79	1.86	2.93×10^{-2}	
1.0	1.66	1.75	3.27×10^{-2}	
1.0	1.61	1.68	3.05×10^{-2}	
1.0	1.78	1.87	3.01×10^{-2}	Mean

c) 59%

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.09	2.25	2.76×10^{-2}	
1.0	2.24	2.34	2.56×10^{-2}	
1.0	1.73	1.72	2.69×10^{-2}	
1.0	1.77	1.84	2.93×10^{-2}	
1.0	1.82	1.86	2.97×10^{-2}	
1.0	1.93	2.00	2.78×10^{-2}	Mean

d) 46%

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.91	1.89	2.08×10^{-2}	
1.0	1.61	1.60	2.10×10^{-2}	
1.0	1.74	1.75	2.01×10^{-2}	
1.0	1.44	1.30	2.19×10^{-2}	
1.0	1.50	1.46	2.28×10^{-2}	
1.0	1.64	1.60	2.13×10^{-2}	Mean

e) 33%

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.69	1.57	1.52×10^{-2}	
1.0	1.61	1.47	1.65×10^{-2}	
1.0	1.51	1.44	1.65×10^{-2}	
1.0	1.21	1.15	1.68×10^{-2}	
1.0	1.48	1.35	1.58×10^{-2}	
1.0	1.50	1.39	1.62×10^{-2}	Mean

4) Variation of Concentration of Bromotrichloromethane

Time 7200 secs., Reactant pressure $CHCl_2F$ 66 mm., Temp. 163°C

Relative final concentrations of products:-

CCl_3Br pressures

a) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.70	3.10	4.27×10^{-2}	
1.0	2.61	2.92	4.36×10^{-2}	
1.0	2.50	2.77	4.42×10^{-2}	
1.0	2.37	2.65	4.24×10^{-2}	
1.0	2.24	2.52	4.48×10^{-2}	
1.0	2.48	2.79	4.35×10^{-2}	Mean

b) 18 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.63	2.96	4.64×10^{-2}	
1.0	2.68	3.06	4.41×10^{-2}	
1.0	2.81	3.03	4.37×10^{-2}	
1.0	2.82	3.23	4.06×10^{-2}	
1.0	2.19	2.45	4.83×10^{-2}	
1.0	2.63	2.95	4.46×10^{-2}	Mean

c) 14 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.81	3.18	4.47×10^{-2}	
1.0	3.10	3.45	4.43×10^{-2}	
1.0	3.02	3.40	4.45×10^{-2}	
1.0	2.88	3.29	4.31×10^{-2}	
1.0	2.73	3.03	4.39×10^{-2}	
1.0	2.91	3.27	4.41×10^{-2}	Mean

d) 10 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.66	4.27	3.70×10^{-2}	
1.0	3.25	3.80	4.00×10^{-2}	
1.0	3.12	3.60	3.94×10^{-2}	
1.0	3.55	4.09	4.01×10^{-2}	
1.0	2.79	3.30	4.27×10^{-2}	
1.0	3.27	3.81	3.98×10^{-2}	Mean

e) 6 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	4.24	4.70	3.90×10^{-2}	
1.0	3.58	4.18	4.10×10^{-2}	
1.0	3.35	3.73	4.46×10^{-2}	
1.0	3.33	3.85	4.12×10^{-2}	
1.0	3.63	4.12	4.15×10^{-2}	Mean

5) Variation of Concentration of Dichlorofluoromethane at T = 176°C

Time 7200 secs., Reactant pressure, CCl_3Br 22 mm.,

Relative final concentrations of products:-

$CHCl_2F$ pressures

a) 90 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	4.33	4.69	5.28×10^{-2}	
1.0	4.05	4.39	5.88×10^{-2}	
1.0	3.81	4.17	6.16×10^{-2}	
1.0	4.56	5.10	5.61×10^{-2}	
1.0	4.22	4.60	5.38×10^{-2}	
1.0	4.19	4.59	5.66×10^{-2}	Mean

b) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.25	3.47	5.36×10^{-2}	
1.0	3.98	4.09	5.11×10^{-2}	
1.0	3.26	3.64	4.75×10^{-2}	
1.0	3.43	3.72	4.74×10^{-2}	
1.0	3.48	3.73	4.99×10^{-2}	Mean

c) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.19	2.28	5.26×10^{-2}	
1.0	1.98	2.15	5.52×10^{-2}	
1.0	2.27	2.38	5.58×10^{-2}	
1.0	1.96	2.08	6.18×10^{-2}	
1.0	2.38	2.38	5.23×10^{-2}	
1.0	2.16	2.26	5.55×10^{-2}	Mean

d) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.35	1.44	5.81×10^{-2}	
1.0	1.23	1.33	6.31×10^{-2}	
1.0	1.32	1.39	6.50×10^{-2}	
1.0	1.38	1.49	6.01×10^{-2}	
1.0	1.34	1.44	5.93×10^{-2}	
1.0	1.33	1.42	6.11×10^{-2}	Mean

6) Variation of Concentration of Dichlorofluoromethane at T = 162°C

Time 7200 secs., Reactant pressure, CCl_3Br 22 mm.

Relative final concentrations of products:-

$CHCl_2F$ pressures

a) 120 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	4.11	4.47	4.83×10^{-2}	
1.0	3.75	3.96	5.33×10^{-2}	
1.0	3.96	4.37	5.16×10^{-2}	
1.0	4.07	4.75	4.69×10^{-2}	
1.0	3.71	4.37	4.58×10^{-2}	
1.0	3.92	4.39	4.92×10^{-2}	Mean

b) 80 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.30	3.72	3.55×10^{-2}	
1.0	2.49	2.91	4.34×10^{-2}	
1.0	3.23	3.52	3.69×10^{-2}	
1.0	2.83	3.11	4.50×10^{-2}	
1.0	2.75	2.92	4.36×10^{-2}	
1.0	2.92	3.24	4.09×10^{-2}	Mean

c) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.23	2.55	4.08×10^{-2}	
1.0	2.73	3.27	3.48×10^{-2}	
1.0	2.77	3.24	3.90×10^{-2}	
1.0	2.04	2.43	3.83×10^{-2}	
1.0	2.32	2.58	Analysis failure	
1.0	2.42	2.81	3.82×10^{-2}	Mean

d) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.36	1.55	4.16×10^{-2}	
1.0	1.31	1.47	4.73×10^{-2}	
1.0	1.47	1.76	4.25×10^{-2}	
1.0	1.44	1.70	4.05×10^{-2}	
1.0	1.28	1.42	4.53×10^{-2}	
1.0	1.37	1.58	4.34×10^{-2}	Mean

e) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	0.74	0.71	4.62×10^{-2}	
1.0	0.90	0.96	4.14×10^{-2}	
1.0	1.03	1.12	4.10×10^{-2}	
1.0	0.86	0.91	4.21×10^{-2}	
1.0	0.81	0.87	4.15×10^{-2}	
1.0	0.87	0.91	4.24×10^{-2}	Mean

f) 10 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	0.49	0.51	4.34×10^{-2}	
1.0	0.55	0.57	4.15×10^{-2}	
1.0	0.55	0.55	4.58×10^{-2}	
1.0	0.47	0.46	4.57×10^{-2}	
1.0	0.55	0.56	3.78×10^{-2}	
1.0	0.52	0.53	4.28×10^{-2}	Mean

7) Variation of Concentration of Dichlorofluoromethane at T = 150°C

Time 7200 secs., Reactant pressure CCl_3Br 22 mm.,

Relative final concentrations of products:-

$CHCl_2F$ pressures

a) 90 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	3.04	3.12	3.06×10^{-2}	
1.0	2.82	3.01	3.42×10^{-2}	
1.0	3.59	3.76	3.30×10^{-2}	
1.0	3.08	3.25	3.18×10^{-2}	
1.0	3.05	3.26	3.02×10^{-2}	
1.0	3.12	3.28	3.20×10^{-2}	Mean

b) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.18	2.34	3.15×10^{-2}	
1.0	2.13	2.53	2.86×10^{-2}	
1.0	2.34	2.44	2.95×10^{-2}	
1.0	2.11	2.62	2.96×10^{-2}	
1.0	2.87	2.98	2.63×10^{-2}	
1.0	2.33	2.58	2.91×10^{-2}	Mean

c) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.45	1.51	3.27×10^{-2}	
1.0	1.64	1.85	3.13×10^{-2}	
1.0	1.50	1.57	3.50×10^{-2}	
1.0	1.54	1.54	3.47×10^{-2}	
1.0	1.49	1.60	3.38×10^{-2}	
1.0	1.52	1.62	3.35×10^{-2}	Mean

d) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	0.74	0.80	3.44×10^{-2}	
1.0	0.86	0.86	3.61×10^{-2}	
1.0	0.75	0.76	3.86×10^{-2}	
1.0	0.74	0.75	3.77×10^{-2}	
1.0	0.78	0.80	3.77×10^{-2}	
1.0	0.77	0.79	3.69×10^{-2}	Mean

8) Variation of Concentration of Dichlorofluoromethane at T = 138°C

Time 7200 secs., Reactant pressure, CCl_3Br 22 mm.,

Relative final concentrations of products:-

$CHCl_2F$ pressures

a) 90 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.22	2.34	2.13×10^{-2}	
1.0	2.27	2.47	2.18×10^{-2}	
1.0	2.32	2.38	2.10×10^{-2}	
1.0	2.62	2.86	2.01×10^{-2}	
1.0	2.01	2.12	2.32×10^{-2}	
1.0	2.29	2.43	2.15×10^{-2}	Mean

b) 66 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	2.04	2.21	2.22×10^{-2}	
1.0	1.83	1.85	2.43×10^{-2}	
1.0	1.94	1.99	2.32×10^{-2}	
1.0	1.55	1.59	2.64×10^{-2}	
1.0	1.75	1.87	2.65×10^{-2}	
1.0	1.82	1.90	2.45×10^{-2}	Mean

c) 40 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	1.17	1.19	2.47×10^{-2}	
1.0	1.01	0.96	2.79×10^{-2}	
1.0	1.20	1.08	2.70×10^{-2}	
1.0	1.10	1.03	3.29×10^{-2}	
1.0	1.22	1.13	2.60×10^{-2}	
1.0	1.14	1.08	2.77×10^{-2}	Mean

d) 22 mm.

$[C_2Cl_6]$	$[CHCl_3]$	$[CCl_2FBr]$	$\frac{[C_2Cl_6]}{[CCl_3Br]}$	
1.0	0.67	0.69	2.74×10^{-2}	
1.0	0.82	0.66	2.89×10^{-2}	
1.0	0.90	0.78	2.87×10^{-2}	
1.0	0.84	0.64	2.99×10^{-2}	
1.0	0.87	0.78	2.52×10^{-2}	
1.0	0.82	0.71	2.80×10^{-2}	Mean

9) Variation of Concentration of Chloroform

Time = 7200 secs., Reactant pressures, CCl_3Br 22 mm., $CHCl_2F$ 66 mm., Temperature 163°C

Relative final concentrations of products:-

$CHCl_3$ pressures

a) 0.0 mm.

$[CCl_3Br]$	$[CCl_2FBr] \times 10^2$	$[CHCl_3]_f$	$[C_2Cl_6] \times 10^2$	
1.0	14.76	0.123	4.27	
1.0	12.98	0.110	4.32	
1.0	13.18	0.115	4.47	
1.0	12.70	0.110	4.50	
1.0	12.58	0.110	4.47	
1.0	13.24	0.113	4.41	Mean

b) 6 mm.

$[CCl_3Br]$	$[CCl_2FBr] \times 10^2$	$[CHCl_3]_f$	$[C_2Cl_6] \times 10^2$	
1.0	9.63	0.502	4.06	
1.0	8.94	0.465	4.55	
1.0	8.93	0.464	4.16	
1.0	9.40	0.486	4.70	
1.0	8.42	0.452	4.03	
1.0	9.06	0.474	4.30	Mean

c) 10 mm.

$[CCl_3Br]$	$[CCl_2FBr] \times 10^2$	$[CHCl_3]_f$	$[C_2Cl_6] \times 10^2$	
1.0	8.34	0.620	4.31	
1.0	9.41	0.745	4.55	
1.0	8.24	0.658	4.78	
1.0	8.52	0.664	4.78	
1.0	8.09	0.641	4.49	
1.0	8.52	0.666	4.58	Mean

d) 14 mm.

$[CCl_3Br]$	$[CCl_2FBr] \times 10^2$	$[CHCl_3]_f$	$[C_2Cl_6] \times 10^2$	
1.0	6.99	0.847	4.39	
1.0	6.67	0.818	4.21	
1.0	6.19	0.782	4.19	
1.0	5.61	0.754	4.21	
1.0	6.26	0.779	4.24	
1.0	6.34	0.796	4.25	Mean

e) 18 mm.

$[CCl_3Br]$	$[CCl_2FBr] \times 10^2$	$[CHCl_3]_f$	$[C_2Cl_6] \times 10^2$
1.0	6.41	1.002	4.32
1.0	6.25	1.01	4.49
1.0	5.59	0.93	4.69
1.0	5.29	0.95	4.91
1.0	5.35	0.92	4.72
1.0	5.78	0.96	4.62

f) 22 mm.

$[CCl_3Br]$	$[CCl_2FBr] \times 10^2$	$[CHCl_3]_f$	$[C_2Cl_6] \times 10^2$	
1.0	5.60	1.20	4.61	
1.0	5.35	1.19	4.93	
1.0	4.93	1.04	4.94	
1.0	4.93	1.07	4.44	
1.0	4.66	1.03	4.94	
1.0	5.10	1.11	4.77	Mean

g) 26 mm.

$[CCl_3Br]$	$[CCl_2FBr] \times 10^2$	$[CHCl_3]_f$	$[C_2Cl_6] \times 10^2$	
1.0	4.52	1.26	4.27	
1.0	4.88	1.35	4.41	
1.0	4.17	1.24	4.60	
1.0	4.99	1.33	4.41	
1.0	4.44	1.30	4.57	
1.0	4.60	1.30	4.45	Mean

h) 30 mm.

$[CCl_3Br]$	$[CCl_2FBr] \times 10^2$	$[CHCl_3]_f$	$[C_2Cl_6] \times 10^2$	
1.0	4.40	1.52	4.78	
1.0	4.55	1.48	5.02	
1.0	4.60	1.60	4.27	
1.0	5.28	1.61	4.95	
1.0	5.28	1.55	4.74	
1.0	4.82	1.55	4.75	Mean

i) 40 mm.

$[CCl_3Br]$	$[CCl_2FBr] \times 10^2$	$[CHCl_3]_f$	$[C_2Cl_6] \times 10^2$	
1.0	3.89	1.93	4.68	
1.0	3.77	1.81	4.85	
1.0	4.11	1.93	4.39	
1.0	3.85	1.90	4.41	
1.0	3.66	1.84	4.70	
1.0	3.86	1.88	4.61	Mean

j) 50 mm.

$[CCl_3Br]$	$[CCl_2FBr] \times 10^2$	$[CHCl_3]_f$	$[C_2Cl_6] \times 10^2$	
1.0	3.28	2.40	4.69	
1.0	2.95	2.32	4.91	
1.0	3.06	2.34	4.49	
1.0	3.39	2.26	4.46	
1.0	2.85	2.07	5.07	
1.0	3.11	2.28	4.73	Mean

PART II

THE COMPETITIVE GAS-PHASE PHOTOBROMINATIONS OF HALOMETHANES

PART II

INTRODUCTION

Many competitive brominations of the type

$$Br\cdot + R_1H \longrightarrow HBr + R_1\cdot$$

$$Br\cdot + R_2H \longrightarrow HBr + R_2\cdot$$

have been studied.[7] These experiments have yielded ratios of A factors and activation energy differences: i.e. A_1/A_2 and (E_1-E_2) for many pairs of compounds. Absolute values of A and E can then be assigned to individual reactions if the absolute values can be found for at least one reaction. Kistiakowsky and Van Artsdalen[26] measured rate constants for the reactions $Br\cdot + CH_4 \longrightarrow HBr + CH_3\cdot$ and $Br\cdot + CH_3Br \longrightarrow HBr + CH_2Br\cdot$, and subsequent competitive bromination studies have been dependent on the accuracy of these 'standard' rate constants. They obtained absolute A factors by combining rate constants for the above reaction at one temperature with the activation energies obtained from the corresponding photobromination reactions. Amphlett and Whittle[27] have studied the thermal bromination of fluoroform (CF_3H) and pentafluoroethane (C_2F_5H) by measurement of initial rates of removal of bromine. The absolute rate constants they determined were then combined with the competitive results for $(CH_4 + CHF_3)$ and for $(C_2H_6 + CH_4)$ in conjunction with $(C_2H_6 + CH_3Br)$.

This method leads to a more accurate estimate of the absolute rate constants for the reactions $Br\cdot + CH_4$ and $Br\cdot + CH_3Br$ as it does not involve the combination of thermal and photobromination results which leads to larger errors.

Further to these two standard reactions, Sullivan and Davidson[76] have studied the thermal bromination of chloroform and have obtain values of A and E for $Br\cdot + CHCl_3 \longrightarrow HBr + CCl_3^\cdot$. The competitive results of Fettis, Knox and Trotman-Dickenson[23] gave absolute values for the reaction $Br\cdot + CH_3Cl \longrightarrow HBr + CH_2Cl\cdot$ with $Br\cdot + CH_3Br$ used as the standard reaction.

In the present work the competitive photobrominations were predominantly dependent on the absolute values of A and E obtained by Sullivan and Davidson, with an internal cross-check provided by the estimates of Trotman-Dickenson of the absolute rate constants for the bromination of methyl chloride.

Besides being of interest on their own, the pre-exponential factors and the activation energies, obtained from these photobrominations, were made use of in the computational treatment involved with the results of Part I.

EXPERIMENTAL

Reactants

1) BROMINE:- was 'Fisons' Laboratory reagent and was used without further purification.

2) CHLOROFORM:- was 'Fisons" Analar reagent and was purified using a Pye 105 preparative g.l.c.. 200μl samples were injected onto a 15 ft. glass column packed with 15% Tritolyl phosphate on 40-60 mesh Embacel. The column temperature was 91°C and the nitrogen pressures were: Injector 60 lb/sq.in., Column 48 lb/sq.in. With these conditions, the chloroform collected in the high-efficiency trap cooled in liquid nitrogen, was better than 99.9% pure when analysed on the Griffin and George D6 chromatograph.

3) DICHLOROMETHANE:- was 'British Drug Houses' material and was used without further purification, as analytical gas chromatography showed it to be better than 99.7% pure.

4) CHLOROFLUOROMETHANE:- was 'Du Ponts' Freon 31 and was found to be better than 99.9% pure by analytical gas chromatography and as such was used without further purification.

5) DICHLOROFLUOROMETHANE and METHYL CHLORIDE:- were both products of "Cambrian Chemicals Ltd.' and, as they were both better than 99.5% pure, they were used without further purification.

6) DIFLUOROMETHANE:- was 'Peninsular Chemical Research' material and being better than 99.5% pure it was used without further treatment.

7) HYDROGEN BROMIDE:- was prepared by dropping liquid bromine into tetralin. The hydrogen bromide evolved, was bubbled through a trap containing more tetralin to remove any bromine carried over. The purified hydrogen bromide was then collected in a three way trap; cooled in liquid nitrogen. The resultant hydrogen bromide was then transferred immediately to the vacuum line where it was degassed and trap to bulb distilled to remove any water. The purified hydrogen bromide was then stored in the black bulb on the vacuum line. (Bulb D in fig I).

APPARATUS

The apparatus was essentially that described in Part I. The only major modification was that instead of initiating the reaction with a medium pressure mercury arc lamp, an ordinary 150 watt tungsten lamp, held about 7 in. from the front face of the pyrex reaction vessel, was used.

EXPERIMENTAL PROCEDURE

The compounds to be brominated were individually 'degassed' several times. Each component of the initial reaction mixture was allowed to expand into the main line and bulb B (see fig I) until the required pressure of the component was reached. The bulb tap was then closed and the main line evacuated, by initially distilling the bulk of the component into its storage tube, by cooling with liquid nitrogen. The line was then properly evacuated. The measured amount of reactant was then distilled into the reaction vessel. After sufficient time for complete transfer the procedure was repeated for the other halomethane constituent. Finally bromine was added in a like manner. The pre-heated furnace was then raised round the reaction vessel. The reaction was initiated by switching on the tungsten lamp and at the end of the reaction, the products were transferred by distillation to a small trap, from which samples were taken for injection into the chromatography apparatus.

For the reaction series which involved added hydrogen bromide, a slightly different technique was used, in that the hydrogen bromide was directly measured in the reaction vessel (Volume = 142 ml) and then frozen. In all other respects, the transfer of the halomethane and of the bromine was as described above.

The pressures of bromine and HBr were measured using a mercury manometer and for the pressures of the halomethane a capsule dial gauge was used.

Analysis:

Quantitative analyses were carried out on a Griffin and George D6 gas density balance chromatograph as described in Part I. The chromatogram peak areas were measured using solely a Honeywell precision integrator.

Identification of Products

In all cases the product identification was based predominantly on comparisons of retention times. All the corresponding bromides obtained from the reactant halomethanes had previously been formed in the reactions of the halomethanes with bromotrichloromethane. In these cases the peak corresponding to the bromide had been positively identified from its mass spectrum.

For a few reactants it was possible to compare the retention times with those for authentic materials. The methods used for each pair of halomethanes were as follows:-

A) CHLOROFORM AND DICHLOROMETHANE

The chromatogram of a reaction mixture showed four peaks (Fig 15) with trace amounts of a fifth peak at higher temperatures. For these halomethanes, it was possible to compare the retention times of the four peaks, with those of authentic materials. In order of elution, the peaks were found to be

CH_2Cl_2; $CHCl_3$; $CHCl_2Br$ and CCl_3Br

The fifth peak was probably dibromodichloromethane as its retention time coincided with that of the known CCl_2Br_2 impurity in the authentic sample of bromotrichloromethane.

B) CHLOROFORM AND DICHLOROFLUOROMETHANE

The chromatogram consisted of four peaks only (fig 15). The peaks corresponding to chloroform and bromotrichloromethane were confirmed by comparison of their retention times, with those for authentic material. The peaks corresponding to dichlorofluoromethane and bromodichlorofluoromethane, were confirmed by comparing their retention times with those obtained from the reaction of bromotrichloromethane with dichlorofluoromethane. In order of elution the peaks were

$CHCl_2F$; CCl_2FBr; $CHCl_3$ and CCl_3Br.

C) CHLOROFORM AND CHLOROFLUOROMETHANE

The chromatogram again consisted of four peaks (fig 15) in which the chloroform and bromotrichloromethane peaks were identified as before. For the other halomethane and its bromide derivative, they were identified by comparison of their retention times, with those from the reaction of chlorofluoromethane with bromotrichloromethane. The elution order was

CH_2FCl; $CHFClBr$; $CHCl_3$ and CCl_3Br.

D) CHLOROFORM AND DICHLOROFLUOROMETHANE

The four peaks of the chromatogram (fig15) were identified by comparison of their retention times, with those obtained from the previous two sections. The elution order was

CH_2FCl; $CHCl_2F$; $CHClFBr$ and CCl_2FBr.

E) METHYL CHLORIDE AND DICHLOROMETHANE

The chromatogram consisted of four major peaks and two minor ones (fig 16). By comparison of the retention times of authentic dichloromethane and bromodichloromethane with the retention times of the reaction products, the peaks corresponding to these compounds were identified. Mass spectra of the reaction mixture were complimentary to the above retention time comparisons. The resolution obtained on the MS12 was extremely poor and spectra were scanned at points of inflection, in the monitor readings. The spectra obtained were sufficient to give the order of elution as

CH_3Cl; CH_2Cl_2; CH_2ClBr and $CHCl_2Br$

for the four major peaks. The fifth and sixth peaks were probably $CHClBr_2$ and CCl_2Br_2 respectively.

Mass spectral analysis:-

Perkin Elmer F11, Helium pressure 1 lb/sq.in., Temperature 40°C 50 metre Silicon Oil capillary column.

A.E.I. MS12 Ionization current 20 e.v., accelerating potential 8 k.v., decrease 6; band width 500 C. sec^{-1}, chart speed 1.5 in sec^{-1}; magnet range 5.

Peak 1

Multiplier 2.50 Monitor reading 0.7 ascending

m/e	Relative Intensity	Assignment
35, 37	0.7, 0.2	Cl^+
36, 38	5, 2	HCl^+
49, 51	10, 5	CH_2Cl^+
50, 52	100, 30	CH_3Cl^+

Peak identified as methyl chloride (CH_3Cl)

Peak 2

Multiplier 2.5 Monitor reading 2.8 maximum

m/e	Relative Intensity	Assignment
35, 37	0.7, 0.2	Cl^+
36, 38	1.4, 0.4	HCl^+
47, 49	10, 100	CCl^+
48, 50	9, 17	$CHCl^+$
49, 51	100, 30	CH_2Cl^+
50, 52	17, 5	CH_3Cl^+
84, 86, 88	13, 9, 1.4	$CH_2Cl_2^+$

Peak identified as dichloromethane (CH_2Cl_2)

Confirmed by comparison of retention time with an authentic sample.

Peak 3

Multiplier 2.0 Monitor reading 2.0 descending

m/e	Relative Intensity	Assignment
35, 37	Weak	Cl^+
36, 38	Weak	HCl^+
47, 49	14, 100	CCl^+
48, 50	12, 16	$CHCl^+$
49, 51	100, 42	CH_2Cl^+
50, 52	16, 4	CH_3Cl^+
79, 81	2, 2	Br^+
83, 85, 87	Weak	$CHCl_2^+$
84, 86, 87	12, 8, 1	$CH_2Cl_2^+$
93, 95	4, 4	CH_2Br^+
Pattern for	Weak	CH_xClBr^+

Peak identified as bromochloromethane (CH_2ClBr) with traces of dichloromethane (CH_2Cl_2)

Peak 4

Multiplier 2.5 Monitor reading 1.2 descending

m/e	Relative Intensity	Assignment
35, 37	Weak	Cl^+
36, 38	Weak	HCl^+
47, 49	24, 96	CCl^+
48, 50	29, 16	$CHCl^+$
49, 51	96, 29	CH_2Cl^+
79, 81	2, 2	Br^+
83, 85, 87	100, 59, 8	$CHCl_2^+$
84, 86, 88	8, 4, 1	$CH_2Cl_2^+$
92, 94	Weak	$CHBr^+$
93, 95	4, 4	CH_2Br^+
Pattern for ClBr 1 mass unit below that for peak 3	4, 6, 1	$CH_{(x-1)}ClBr$

Peak identified as bromodichloromethane ($CHCl_2Br$) with traces of dichloromethane and bromochloromethane. Confirmed by comparison of retention time with an authentic sample.

F) CONCENTRATION VARIATION OF DICHLOROMETHANE IN THE BROMINATION OF CHLOROFORM AND DICHLOROMETHANE

Reaction products were identified as in section A.

G) BROMINATION OF CHLOROFORM WITH ADDED HYDROGEN BROMIDE

Reaction products were identified by comparison of their retention times, with those of authentic chloroform and bromotrichloromethane.

RESULTS

COMPETITIVE BROMINATION OF PAIRS OF HALOMETHANES

A series of experiments were carried out in which the initial concentrations of the halomethanes and of the bromine were fixed. The reaction time and incident light intensity, were also held constant for each experiment, while the temperature was varied. A thermal reaction, carried out for 1800 secs at 175°C with chloroform and dichloromethane as the halomethane, gave trace amounts of the corresponding bromides. This was taken as a fair indication that, under the experimental conditions used in the photolytic experiments, the thermal contribution could be neglected.

The results of the temperature variation experiments are shown in the following tables along with the results for the dichloromethane concentration variation and the effect of added hydrogen bromide experiments.

A) CHLOROFORM AND DICHLOROMETHANE

TABLE II.1

$[CHCl_3]_i = 2.26 \times 10^{-3}$ moles/l.; $[CH_2Cl_2]_i = 2.26 \times 10^{-3}$ moles/l.;
$[Br_2]_i = 1.13 \times 10^{-3}$ moles/l.; Reaction time = 900 secs.

Temp°C	$[CHCl_2Br]_f/[CCl_3Br]_f$
121	0.582
109	0.557
94	0.496
82	0.469
74	0.442
66	0.423
59	0.406

FIG 17 The Competitive Brominations of A($CHCl_3 + CH_2Cl_2$) ; B($CHCl_3 + CHCl_2F$) ; C($CHCl_3 + CH_2FCl$) ; D($CH_2FCl + CHCl_2F$) ; and E($CH_3Cl + CH_2Cl_2$)

The plots are as follows:

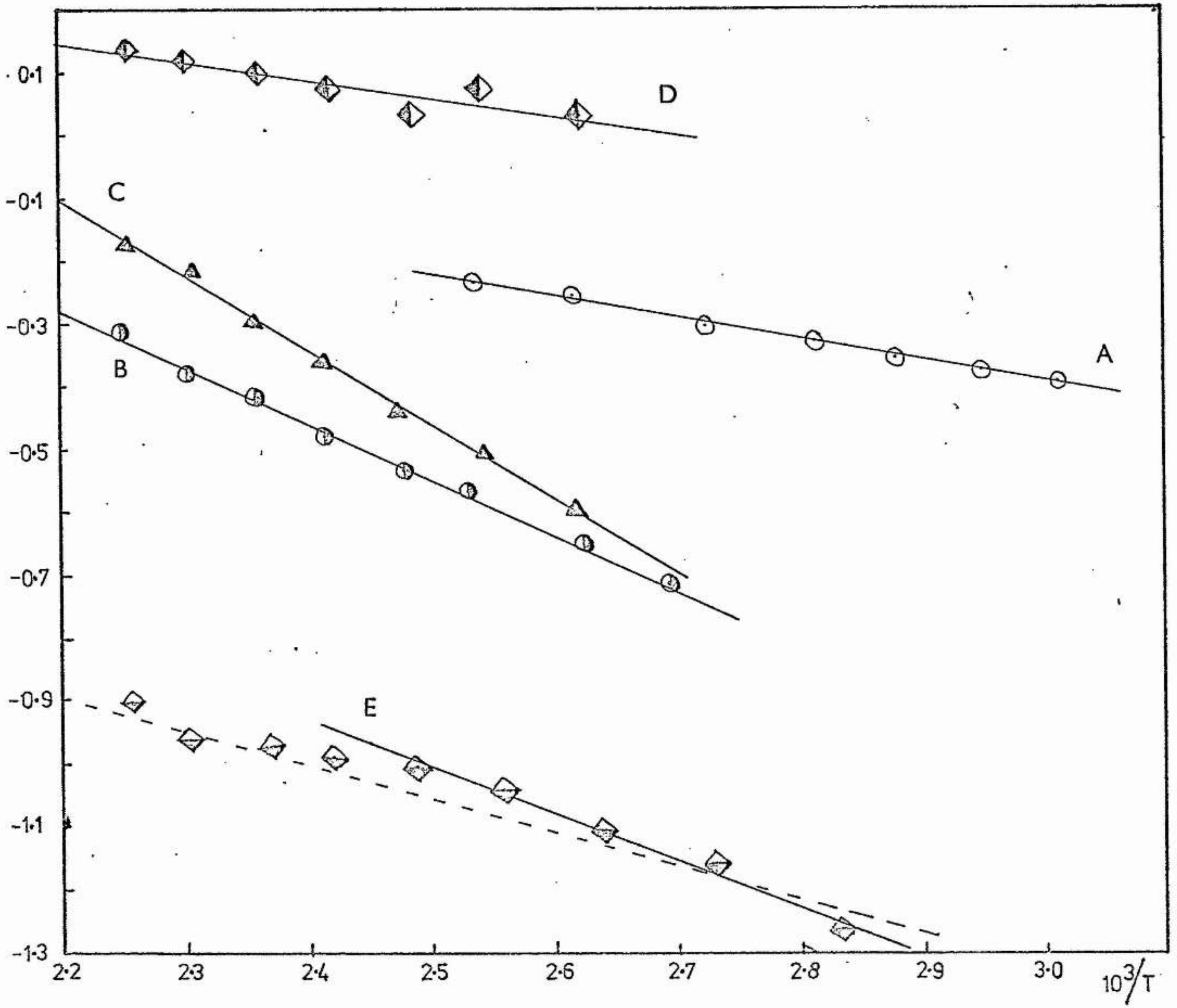
A $\log\frac{[CHCl_2Br]_f[CHCl_3]_i}{[CCl_3Br]_f[CH_2Cl_2]_i}$ vs $\frac{10^3}{T}$

B $1 + \log\frac{[CCl_2FBr]_f[CHCl_3]_i}{[CCl_3Br]_f[CHCl_2F]_i}$ vs $\frac{10^3}{T}$

C $1 + \log\frac{[CHClFBr]_f[CHCl_3]_i}{[CCl_3Br]_f[CH_2FCl]_i}$ vs $\frac{10^3}{T}$

D $\log\frac{[CHClFBr]_f[CHCl_2F]_i}{[CCl_2FBr]_f[CH_2FCl]_i}$ vs $\frac{10^3}{T}$

E $\log\frac{[CH_2ClBr]_f[CH_2Cl_2]_i}{[CHCl_2Br]_f[CH_3Cl]_i}$ vs $\frac{10^3}{T}$



The subscripts i and f refer to initial and final concentrations respectively.

A least squares plot of $\log_{10} [CHCl_2Br]_f[CHCl_3]_i/[CCl_3Br]_f[CH_2Cl_2]_i$ Vs $10^3/T$ gave a good straight line (Fig 17) of gradient $(E_{CH_2Cl_2} - E_{CHCl_3})/2.303R = 0.34 \pm 0.04$. The extrapolated intercept was $\log A_{CH_2Cl_2} - \log A_{CHCl_3} = 0.63 \pm 0.01$

B) CHLOROFORM AND DICHLOROFLUOROMETHANE

TABLE II.2

$[CHCl_3]_i = 1.13 \times 10^{-3}$ moles/l; $[CHCl_2F]_i = 4.52 \times 10^{-3}$ moles/l;

$[Br_2]_i = 0.57 \times 10^{-3}$ moles/l; Reaction time = 900 secs.

Temp °C	$\frac{[CCl_2FBr]_f[CHCl_3]_i}{[CCl_3Br]_f[CHCl_2F]_i}$
171	4.870×10^{-2}
161	4.16×10^{-2}
151	3.86×10^{-2}
141	3.33×10^{-2}
130	2.93×10^{-2}
122	2.72×10^{-2}
108	2.24×10^{-2}
98	1.93×10^{-2}

A least squares plot of $\log_{10} [CCl_2FBr]_f[CHCl_3]_i/[CCl_3Br]_f[CHCl_2F]_i$ vs $10^3/T$ gave a good straight line of gradient $(E_{CHCl_2F} - E_{CHCl_3})/2.303R = 0.88 \pm 0.06$. The intercept was $(\log A_{CHCl_2F} - \log A_{CHCl_3}) = 0.66 \pm 0.02$ (fig 17).

C) CHLOROFORM AND CHLOROFLUOROMETHANE

TABLE II.3

$[CHCl_3]_i = 1.13 \times 10^{-3}$ moles/l; $[CH_2FCl]_i = 4.52 \times 10^{-3}$ moles/l;

$[Br_2]_i = 0.57 \times 10^{-3}$ moles/l; Reaction time = 900 secs.

Temp °C	$\dfrac{[CHFClBr]_f[CHCl_3]_i}{[CCl_3Br]_f[CH_2FCl]_i}$
170	6.70×10^{-2}
160	6.10×10^{-2}
151	5.06×10^{-2}
141	4.37×10^{-2}
131	3.62×10^{-2}
120	3.13×10^{-2}
109	2.56×10^{-2}

A plot of $\log_{10}$ $[CHFClBr]_f[CHCl_3]_i/[CCl_3Br]_f[CH_2FCl]_i$ vs $10^3/T$ gave a good straight line. The least squares method gave for the gradient $(E_{CH_2FCl} - E_{CHCl_3})/2.303R = 1.20 \pm 0.11$ and for the intercept $(\log_{10} A_{CH_2FCl} - \log_{10} A_{CHCl_3}) = 1.53 \pm 0.05$ (Fig 17).

D) CHLOROFLUOROMETHANE AND DICHLOROFLUOROMETHANE

TABLE II.4

$[CH_2FCl]_i = 2.26 \times 10^{-3}$ moles/l; $[CHCl_2F]_i = 2.26 \times 10^{-3}$ moles/l;

$[Br_2]_i = 0.57 \times 10^{-3}$ moles/l; Reaction time = 900 secs.

Temp °C	$\dfrac{[CHClFBr]_f[CHCl_2F]_i}{[CCl_2FBr]_f[CH_2FCl]_i}$
170	1.37
161	1.32
150	1.27
140	1.18
129	1.08
120	1.19
108	1.07

From a plot of $\log_{10}$ $[CHClFBr]_f[CHCl_2F]_i/[CCl_2FBr]_f[CH_2FCl]_i$ vs $10^3/T$ a [illegible] straight line was obtained (Fig 17). The least squares method gave for the gradient $(E_{CH_2FCl} - E_{CHCl_2F})/2.303R$ = 0.28 ± 0.09 and for the extrapolated intercept $(\log_{10} A_{CH_2FCl} - \log A_{CHCl_2F}) = 0.76 \pm 0.04$.

E) METHYL CHLORIDE AND DICHLOROMETHANE

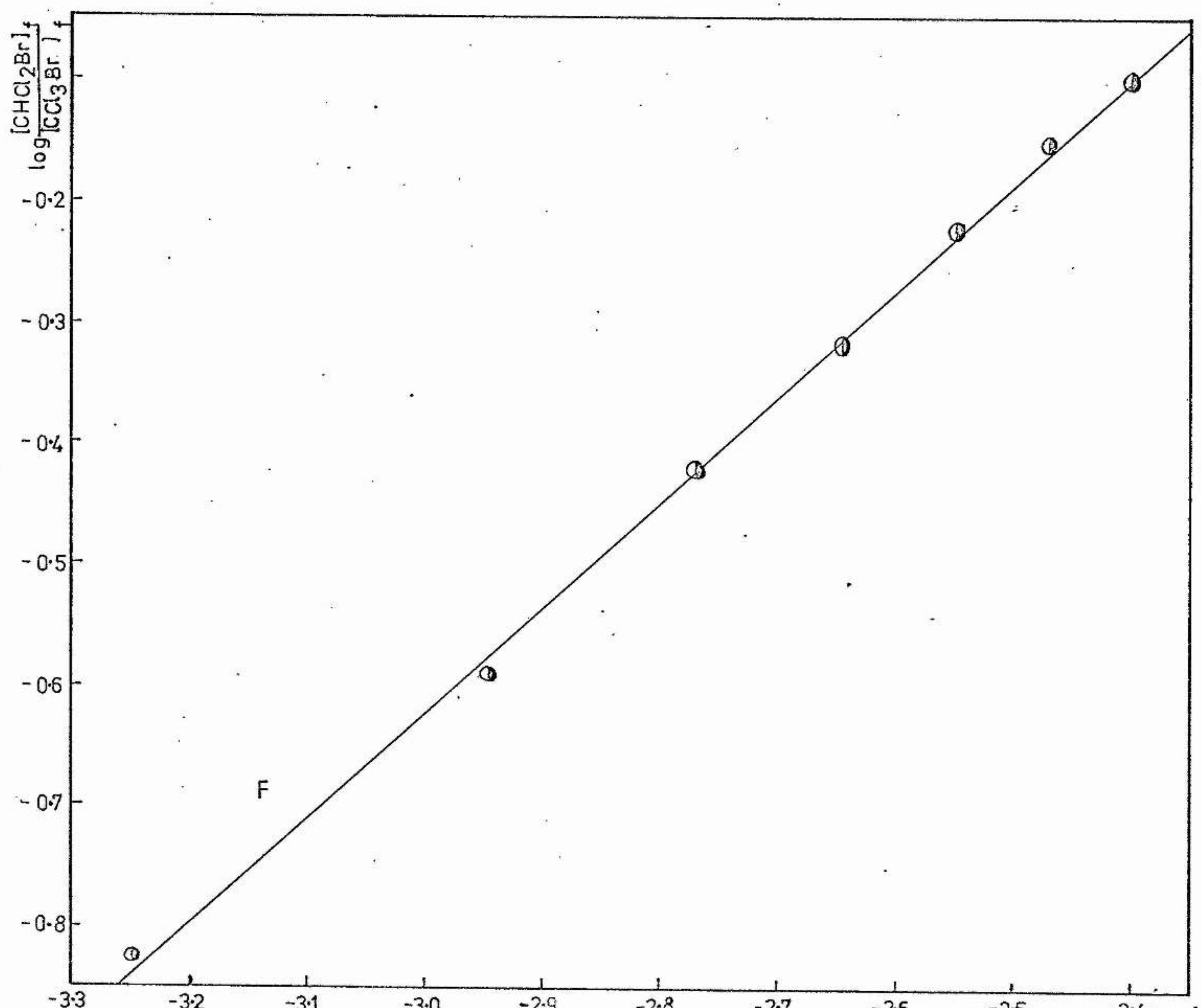
TABLE II.5

$[CH_3Cl]_i = 4.52 \times 10^{-3}$ moles/l; $[CH_2Cl_2]_i = 1.13 \times 10^{-3}$ moles/l;
$[Br_2]_i = 0.57 \times 10^{-3}$ moles/l; Reaction time = 900 secs.

Temp °C	$\dfrac{[CH_2ClBr]_f[CH_2Cl_2]_i}{[CHCl_2Br]_f\,[CH_3Cl]_i}$
170	0.126
161	0.109
149	0.107
140	0.103
129	9.83×10^{-2}
118	9.11×10^{-2}
106	7.86×10^{-2}
93	6.90×10^{-2}
80	5.45×10^{-2}

A least squares plot of $\log_{10}$ $[CH_2ClBr]_f[CH_2Cl_2]_i/[CHCl_2Br]_f[CH_3Cl]_i$ vs $10^3/T$ gave a straight line (fig 17) of gradient $(E_{CH_3Cl} - E_{CH_2Cl_2})/2.303R = 0.57 \pm 0.07$ and extrapolated intercept $(\log A_{CH_3Cl} - \log A_{CH_2Cl_2}) = 0.39 \pm 0.03$

FIG 18


log $\frac{[CHCl_2Br]_f}{[CCl_3Br]_f}$
-0·2
-0·3
-0·4
-0·5
-0·6
-0·7
-0·8
F
-3·3
-3·2
-3·1
-3·0
-2·9
-2·8
-2·7
-2·6
-2·5
-2·4

F) CONCENTRATION VARIATION OF DICHLOROMETHANE IN THE BROMINATION OF CHLOROFORM AND DICHLOROMETHANE

TABLE II.6

$[CHCl_3]_i = 2.26 \times 10^{-3}$ moles/l; $[Br_2]_i = 0.57 \times 10^{-3}$ moles/l;

Reaction time = 900 secs.; Reaction temperature 82 ± 2°C

$[CH_2Cl_2]_i$ moles/l x 10^3	$\frac{[CHCl_2Br]_f}{[CCl_3Br]_f}$	$\frac{[CHCl_3Br]_f[CHCl_3]_i}{[CCl_3Br]_f[CH_2Cl_2]_i}$
0.57	0.150	0.598
1.13	0.257	0.513
1.70	0.380	0.506
2.26	0.479	0.479
2.83	0.596	0.476
3.39	0.704	0.470
3.96	0.794	0.454

A least square plot of log $[CHCl_2Br]_f/[CCl_3Br]_f$ vs log $[CH_2Cl_2]_i$ gave a straight line of gradient = 0.87 ± 0.02 and intercept = 1.99 ± 0.01 (fig 18)

G) BROMINATION OF CHLOROFORM WITH ADDED HYDROGEN BROMIDE

TABLE II.7

$[CHCl_3]_i = 2.26 \times 10^{-3}$ moles/l; $[Br_2]_i = 0.57 \times 10^{-3}$ moles/l;

Reaction time = 900 secs; Reaction temperature = 76 ± 2°C

Pressure HBr in mm	$\frac{[CCl_3Br]_f}{[CHCl_3]_f} \times 10^2$
0.0	9.73
6.0	9.60 Time corrected
12.0	8.75
20.0	8.39
30.0	8.41
46.0	7.89
60.0	7.34
82.0	6.24

DISCUSSION

The first accurate rate constant determination for a bromination reaction, was carried out by Bodenstein and Lind[78] who evaluated the rate constants involved in the thermal bromination of hydrogen. Succeeding workers[23,26] have amply confirmed, that the free radical mechanism proposed for the bromination of hydrogen, is almost always obeyed no matter what is the reactant to be brominated. The exceptions tend to be very reactive molecules, for example, toluene and 2-methylpropane. The mechanism generally applicable is as follows:-

Thermal initiation $Br_2 + M \rightleftharpoons 2Br\cdot + M \quad k_1 k_{-1}$

Photolytic initiation $Br_2 \xrightarrow{hv} 2Br^\cdot$

$$Br\cdot + RH \rightleftharpoons R^\cdot + HBr \qquad k_2 k_{-2}$$

$$R\cdot + Br_2 \longrightarrow RBr + Br \qquad k_4$$

$$2Br\cdot + M \longrightarrow Br_2 + M \qquad k_6$$

For the more reactive molecules, where the steady state concentrations of $R^\cdot$ and $Br\cdot$ are comparable, ($R\cdot/Br\cdot \gg 1$) there are additional termination steps over the previous situation where, at steady state concentrations[79], $R^\cdot/Br^\cdot \ll 1$. The additional terminations are

$$R\cdot + Br. \longrightarrow RBr \qquad k_7$$

$$2R\cdot \longrightarrow RR \qquad k_8$$

By adopting a competitive method to study brominations, no assumptions have to be made about the rate of attainment of steady state concentrations of radical species.

The reactions occurring competitively are as follows

$$Br_2 \xrightarrow{h\nu} 2Br\cdot$$

$$Br\cdot + R_1H \rightleftharpoons R_1^{\cdot} + HBr \qquad k_2, k_{-2}$$

$$Br^{\cdot} + R_2H \rightleftharpoons R_2^{\cdot} + HBr \quad k_3, k_{-3}$$

$$\begin{array}{l} R_1^{\cdot} \\ R_2^{\cdot} \end{array} + Br_2 \begin{array}{l} \nearrow R_1Br + Br\cdot k_4 \\ \searrow R_2Br + Br\cdot k_5 \end{array}$$

$$2Br\cdot + M \longrightarrow Br_2 + M \quad k_6$$

By carrying the reaction out under conditions where reactions -2 and -3 are not significant, R_1 and R_2 are only removed by further reaction with bromine to give the corresponding bromides. The rates of bromination of the substrates are given by

$$-\,d[R_1H]/dt \;=\; d[R_1Br]/dt \;=\; k_2[R_1H][Br\cdot]$$

$$\text{and } -\,d[R_2H]/dt \;=\; d[R_2Br]/dt \;=\; k_3[R_2H][Br\cdot]$$

As each reactant experiences the same concentration of bromine atoms, regardless of the manner of initiation, the above equations can be rearranged to give

$$\frac{d[R_1H]}{k_2[R_1H]} = \frac{d[R_2H]}{k_3[R_2H]}$$

Integrating the above, and using $[RH]_{final} = [RH]_{orig} - [RBr]$ which assumes that the reaction of each reactant gives solely monobrominated product, gives:-

$$\frac{k_2}{k_3} = \frac{\ln([R_1H]_o - [R_1Br])/[R_1H]_o}{\ln([R_2H]_o - [R_2Br])/[R_2H]_o}$$

For low conversions (say 10%) a valid approximation is to equate $\ln([RH]_o - [RBr])/[RH]_o = \ln(1 - [RBr]/[RH]_o)$ to $-[RBr]/[RH\cdot]_o$

$$\therefore \quad \underline{\frac{k_2}{k_3} = \frac{R_1Br}{R_2Br}\,\left(\frac{[R_2H]}{[R_1H]}\right)_{orig}} \qquad (A)$$

This relation has been used and validated by many workers[23,80], who have studied competitive brominations. The rate constant ratio should be independent of the initial concentration of bromine, the ratio $[R_1H]/[R_2H]$ and the percentage of bromine reacted. The latter stipulation would be untrue if secondary bromination of either R_1Br or R_2Br occurred. Under the experimental conditions used in the present work, analytical gas chromatography indicated that very little secondary bromination occurred with the halomethanes where this was possible.

Comparison of the rate constant ratio for the bromination of dichloromethane and chloroform at 82°C, with 40 mm. of each halomethane but 20 mm. of bromine in one case and 10 mm. of bromine in the other, gave $k_2/k_3 = 0.47$ (20 mm.) and $k_2/k_3 = 0.48$ (10 mm.).

This indicates that for this system also, the rate constant ratio was indeed independent of the initial bromine concentration.

A final check on the validity of the above relation was obtained from series F, in which the ratio of chloroform to dichloromethane was varied.

The results, shown in Table II.6, for the rate constant ratio, show very little change with a seven fold increase in the dichloromethane concentration. The high rate constant ratio obtained for the lowest dichloromethane concentration, is anomalous within the remainder of the series.

These checks seem to indicate, that for the competitive reactions now studied, the mechanism applicable is indeed that given by steps 1-6. Further, similar checks, on the applicability of (A) to the other less reactive halomethanes studied, were not performed as reactions by (7) or (8), would be even less likely than for dichloromethane.

The bromination of chloroform with various added amounts of hydrogen bromide, showed that the rate of formation of bromotrichloromethane, was indeed inhibited by the addition. The ratio of $[CCl_3Br]/[CHCl_3]$ was about 70% of the uninhibited ratio even when 80 mm.of hydrogen bromide had been added. In a competitive system, reactions (2) and (3) would both be inhibited by the presence of hydrogen bromide, and as such very little change would be expected in the rate constant ratio, as the effects would tend to cancel out. Fettis, Knox and Trotman-Dickenson[23], have shown that the ratio k_2/k_3 was only slightly altered by the addition of quantities of hydrogen bromide, that were in vast excess of the amount formed in a normal competitive reaction.

Sullivan and Davidson[76] have obtained absolute rate parameters for the thermal brominations of chloroform. For $Br\cdot + CHCl_3 \longrightarrow CCl_3\cdot + HBr$ they obtain

$$\log k_2(\mathrm{l.m.^{-1}s.^{-1}}) = 9.36 \pm 0.15 - (9{,}300 \pm 300)/2.303RT$$

(N.B. all rate constants are in units litre $\mathrm{mole^{-1}sec^{-1}}$)

Using these absolute values, and the results from the competitive reactions of the following pairs of halomethanes $(CHCl_3, CH_2Cl_2)$; $(CHCl_3, CHCl_2F)$ and $(CHCl_3, CH_2ClF)$, it was possible to obtain absolute rate parameters for $Br\cdot + RH \longrightarrow R\cdot + HBr$ (where RH = CH_2Cl_2; $CHCl_2F$ and CH_2ClF).

The values obtained were cross-checked by brominating a mixture of $CHCl_2F$ and CH_2ClF. A further cross-check was obtained by the bromination of CH_3Cl and CH_2Cl_2. In this case, absolute values have been assigned to the bromination of methyl chloride, by Fettis, Knox and Trotman-Dickenson[23] who used the results for methyl bromide[82] as their 'standard' for their competitive reactions. They obtain for $Br\cdot + CH_3Cl \longrightarrow CH_3\cdot + HBr$

$$\log k_{CH_3Cl} = (10.62 \pm 0.06) - (14,451 \pm 156)/2.303RT$$

Amphlett and Whittle[27] using the competitive results of Fettis, Knox and Trotman-Dickenson re-estimate for

$$\log k_{CH_3Cl} = (10.86 \pm 0.06) - (14,720 \pm 160)/2.303RT)$$

The results obtained from the competitive brominations of chloroform with 1) dichloromethane 2) dichlorofluoromethane and 3) chlorofluoromethane were as follows.

<u>1) For CH_2Cl_2</u> A plot of $\log k_{CH_2Cl_2}/k_{CHCl_3}$ vs $10^3/T$ gave

$$(E_{CH_2Cl_2} - E_{CHCl_3})/2.303R = 0.34 \pm 0.04$$

and $\log A_{CH_2Cl_2} - \log A_{CHCl_3} = 0.63 \pm 0.01$

By substituting,

$$E_{CHCl_3} = (9.30 \pm 0.30) \text{ Kcal/mole}$$

and $\log A_{CHCl_3} = (9.36 \pm 0.15)\ 1\ m^{-1}s^{-1}$

in the above equations, the rate constant for $Br\cdot + CH_2Cl_2 \longrightarrow CHCl_2\cdot + HBr$ was found to be

$$\log k_{CH_2Cl_2} = (9.99 \pm 0.16) - (10860 \pm 480)/2.303\ RT$$

with $\log A^1_{CH_2Cl_2}$ per hydrogen $= 9.69 \pm 0.16$

2) For $CHCl_2F$ A plot of log k_{CHCl_2F}/k_{CHCl_3} vs $10^3/T$ gave

$(E_{CHCl_2F} - E_{CHCl_3})/2.303R = 0.88 \pm 0.06$

and $\log A_{CHCl_2F} - \log A_{CHCl_3} = 0.66 \pm 0.02$

As previously, substitution of E_{CHCl_3} and $\log A_{CHCl_3}$, gave for the reaction $Br^{\cdot} + CHCl_2F \longrightarrow CCl_2F\cdot + HBr$

$$\log k_{CHCl_2F} = (10.02 \pm 0.17) - (13,300 \pm 570)/2.303RT$$

3) For CH_2ClF A plot of log k_{CH_2ClF}/k_{CHCl_3} vs $10^3/T$ gave

$(E_{CH_2ClF} - E_{CHCl_3})/2.303R = 1.20 \pm 0.11$

and $\log A_{CH_2ClF} - \log A_{CHCl_3} = 1.53 \pm 0.05$

As previously, substitution of E_{CHCl_3} and $\log A_{CHCl_3}$ gave for the reaction $Br\cdot + CH_2ClF \longrightarrow CHClF. + HBr$

$$\log k_{CH_2FCl} = (10.89 \pm 0.20) - (14,800 \pm 800)/2.303RT$$

with A^1 per hydrogen $= 3.89 \times 10^{10}$ $l\ m^{-1}s^{-1}$

4) The competitive bromination of CH_2FCl and $CHCl_2F$ gave from a plot of log k_{CH_2FCl}/k_{CHCl_2F} vs $10^3/T$

$(E_{CH_2ClF} - E_{CHCl_2F})/2.303R = 0.28 \pm 0.09$

and $\log A_{CH_2ClF} - \log A_{CHCl_2F} = 0.76 \pm 0.04$

i.e. $$\log \frac{k_{CH_2ClF}}{k_{CHCl_2F}} = (0.76 \pm 0.04) - (1,280 \pm 400)/2.303RT$$

5) The competitive bromination of CH_3Cl and CH_2Cl_2 gave from a plot of log $k_{CH_3Cl}/k_{CH_2Cl_2}$ vs $10^3/T$

$$\log \frac{k_{CH_3Cl}}{k_{CH_2Cl_2}} = (0.39 \pm 0.03) - (2,610 \pm 410)/2.303RT$$

For this series, there was a noticeable curve to the plot at higher temperatures, which could be due to secondary bromination, or to the large percentage conversion. By using the results between 80 and 130°C

$$\log \frac{k_{CH_3Cl}}{k_{CH_2Cl_2}} = (0.84 \pm 0.04) - (3400 \pm 300)/2.303RT$$

6) The competitive bromination of $CHCl_3$ with various concentrations of CH_2Cl_2, gave from a plot of log $CHCl_2Br/CCl_3Br$ vs $\log[CH_2Cl_2]_i$ a straight line of slope 0.87 ± 0.02 and intercept = 1.99 ± 0.01

From $$\frac{[CHCl_2Br]}{[CCl_3Br]} = \frac{k_{CH_2Cl_2}}{k_{CHCl_3}} \frac{[CH_2Cl_2]_i}{[CHCl_3]_i}$$

a plot of log $CHCl_2Br/CCl_3Br$ v $\log[CH_2Cl_2]_i$ should be a straight line of slope unity and intercept equal to $\log(k_{CH_2Cl_2}/k_{CHCl_3}[CHCl_3])$.

Also $$\frac{[CHCl_2Br]}{[CCl_3Br]} \times \frac{[CHCl_3]_i}{[CH_2Cl_2]_i}$$ should be a constant (B)

equal to $k_{CH_2Cl_2}/k_{CHCl_3}$

By using Sullivan and Davidson's[76] results for $CHCl_3$ and the derived rate parameters for CH_2Cl_2, the rate constant ratio $k_{CH_2Cl_2}/k_{CHCl_3}$ at 82°C, was 0.48. This value is, within experimental error, equal to the experimentally observed values of (B). Using the calculated value of $k_{CH_2Cl_2}/k_{CH\ Cl_3}$ in conjunction with the initial concentration of chloroform, the value for $\log(k_{CH_2Cl_2}/k_{CHCl_3} \times [CHCl_3]_i)$ at 82°C, was 2.33.

This compares well with the intercept value from the initial plot of 1.99 ± 0.01.

In summary the competitive reactions with chloroform as standard, indicate that the rate constants for dichloromethane, chlorofluoromethane and dichlorofluoromethane are:-

1) $\log k_{CH_2Cl_2} = (9.99 \pm 0.16) - (10860 \pm 480)/2.303RT$

2) $\log k_{CHCl_2F} = (10.02 \pm 0.17) - (13,300 \pm 570)/2.303RT$

3) $\log k_{CH_2FCl} = (10.89 \pm 0.20) - (14800 \pm 800)/2.303RT$

Combination of the competitive experiments 2 and 3 gave

$$\log \frac{k_{CH_2FCl}}{k_{CHCl_2F}} = (0.87 \pm 0.07) - (1500 \pm 800)/2.303RT$$

This value compares well with the result from the fourth competitive reaction (CH_2ClF + $CHCl_2F$) which gave

4) $\log \frac{k_{CH_2FCl}}{k_{CHCl_2F}} = (0.76 \pm 0.04) - (1280 \pm 400)/2.303RT$

5) The competitive results for 5 ($CH_3Cl + CH_2Cl_2$) in the range 80 - 130°C gave

$$\log \frac{k_{CH_3Cl}}{k_{CH_2Cl_2}} = (0.84 \pm 0.04) - (3400 \pm 300)/2.303RT$$

In combination with the absolute rate parameters listed by Amphlett and Whittle[27] for methyl chloride

i.e. $\log k_{CH_3Cl} = (10.86 \pm 0.06) - (14720 \pm 160)/2.303RT$

a new estimate for dichloromethane was obtained.

$$\log k_{CH_2Cl_2} = (10.02 \pm 0.10) - (11320 \pm 600)/2.303RT$$

This compares well with the value from 1)

i.e. $\log k_{CH_2Cl_2} = (9.99 \pm 0.16) - (10860 \pm 480)/2.303RT$

6) The power dependence on the concentration of dichloromethane, appears to be 0.87. It appears that this is a real effect and not just experimental error. Previous workers[83] using a similar system have found an order in fluoroform = 0.78. Later work by Amphlett and Whittle[27] indicated that for halomethanes there was a critical pressure above which the order became unity. This pressure effect on reactant order was not observed for pentafluoroethane, which was also studied by Amphlett and Whittle.

The rate constants, determined where the order was 0.78 and where it was unity, are comparable.

$$\log k_{CHF_3} = (10.11 \pm 0.04) - (22320 \pm 110)/2.303RT \quad \text{Order} = 1.0$$

$$\log k_{CHF_3} = (10.46 \pm 0.23) - (23000 \pm 700)/2.303RT \quad \text{Order} = 0.78$$

These results are sufficiently similar to be justified in assuming the order in halomethane to be unity, and to obtain good estimates of the rate parameters using the aforementioned method.

The rate constants obtained are compared with those of other workers who have used similar systems.

From Table II.8 it can be seen that progressive substitution of fluorine for hydrogen leads to a steady decrease in the pre-exponential factor but there is a distinct minimum in the values of the activation energies. After the initial drop in E in going from methane to fluoromethane, there is a small rise in going to difluoromethane, and a large increase in going to fluoroform. It therefore appears, that the introduction of one or two fluorines into methane, activate the remaining hydrogens. The phenomena is also observed with the fluorinated ethanes. For these compounds,

TABLE II.8

Rate parameters for Br· + RH $\longrightarrow$ HBr + R·

RH	log A ($l\ m^{-1} s^{-1}$)	E (Kcal $mole^{-1}$)	Ref
CH_4	10.99 ± 0.05	18.58 ± 0.14	80
CH_3F	10.74 ± 0.05	16.10 ± 0.14	80
CH_2F_2	10.37 ± 0.05	16.59 ± 0.14	80
CHF_3	10.11 ± 0.04	22.32 ± 0.11	82
CH_3Cl	10.86 ± 0.06	14.72 ± 0.16	23
CH_2Cl_2	9.99 ± 0.16	10.86 ± 0.48	This Work
$CHCl_3$	9.36 ± 0.15	9.30 ± 0.30	76
CH_2FCl	10.89 ± 0.20	14.80 ± 0.80	This Work
$CHCl_2F$	10.02 ± 0.17	13.30 ± 0.57	This Work
CH_3CH_3	11.14 ± 0.06	13.66 ± 0.14	23,24,80
$CH_3\overset{*}{C}H_2F$	10.12 ± 0.08	11.59 ± 0.17	80
$CH_3\overset{*}{C}HF_2$	10.36 ± 0.05	14.55 ± 0.14	80
CH_3CF_3	11.01 ± 0.04	23.46 ± 0.13	80
CH_2FCF_3	10.59 ± 0.06	19.50 ± 0.16	80
CHF_2CF_3	10.03 ± 0.02	19.31 ± 0.06	27

besides the activation of the hydrogens on the fluorinated carbon atom, strong deactivation of the hydrogens on the β carbon atom, is observed.

For the fluorinated methanes, there is a minima in the bond dissociation energy, in going from CH_4 to CHF_3. This, combined with an increased polar effect in the transition state for fluoroform, leads to the observed increase in activation energy.

The activation of α hydrogens and the deactivation of β hydrogens, is also shown in the bromination of 1-fluorobutane relative to butane.[84]

Relative Selectivities ($R.S^{x}_{4}$) at 150°C

	X	CH_2	CH_2	CH_2	CH_3
X≡H		1	80	80	1
X≡F		9	7	90	1

The bromination of methane and the chloromethanes, shows a steady decrease in the pre-exponential factor. This is identical to the results for the fluoromethanes, but in contrast there is no minimum in the activation energies, instead, a steady decrease in going from methane to chloroform, is observed. This is reasonable, as it is almost certain that there is no minima in the bond dissociation energy in going from CH_4 to $CHCl_3$, only a steady decrease.

With these ideas, it was possible to rationalise the results obtained from the bromination of chlorofluoromethane (CH_2FCl) and dichlorofluoromethane ($CHCl_2F$). The changes observed in going from CH_2Cl_2 to $CHCl_3$, were a decrease in the A factor and a decrease in E of about 1.5 kcal/mole. This decrease was probably the result of a decrease in D(C-H) which still offsets the increase in repulsive polar forces in the transition state. The magnitude of the decrease in log A and E was similar to those observed in going from CH_2FCl

to $CHFCl_2$, where presumably the same effects were operative.

The change in E in going from CH_3F to CH_2F_2 can be attributed to a balancing of the effects of a decrease in D(C-H) and an increase in the transition state polar effects. For the change in E in going from CH_3Cl to CH_2ClF, the decrease in D(C-H) can probably be compensated for by an increase in polar effect. It therefore appears reasonable, that the introduction of a fluorine atom into methyl chloride, would not decrease the activation energy from that observed for methyl chloride, as the decrease in D(C-H) would be compensated for by an increase in repulsive polar forces in the transition state.

From these naive arguments it appears that the Arrhenius parameters obtained here, beside being internally consistent, are consistent with the results of other workers using similar systems.

A final comparison of the activation energies obtained from the halogenation of halomethanes by fluorine, chlorine and bromine is made in Table II.9. From the table, it is apparent that there is a minimum in the activation energies, for the halogenation of the chloromethanes with both fluorine and chlorine, but no minimum is observed for the bromination. This fact could be explained, by the decreasing dipole moments of the hydrogen halides. The dipoles are HF 1.91; HCl 1.05; HBr 0.80. It has been proposed[29,86,30] that the obtained activation energies, can be explained by a balancing of the bond strengths of the haloalkane and the repulsion of the incipient products in the transition state.[89,90] Allowing for the changes in the activation energy magnitudes because of the varying bond strengths of the hydrogen halides formed, the minimum observed for both fluorine and chlorine attack can be explained by proposing that in these cases, the polar effect is sufficiently large to overcome the decrease in bond strengths in going from methane to chloroform. For the brominations of these chloromethanes, the polar effect is not sufficient to overcome the effect of decreasing bond strength, within the series. The polar effect can be represented as follows:-

$$\overset{\delta-}{\mathrm{Br}}\text{--------}\overset{\delta+}{\mathrm{H}}\text{-------}\overset{\delta\mp\,\delta\pm}{\mathrm{CCl_3}}$$

and experimental evidence for this effect, is that the hydrogen abstraction from hydrogen bromide by CF_3 radicals, has a higher activation energy than that for the reaction of CH_3 radicals with hydrogen bromide.[87]

Further evidence that the activation energy obtained for the bromination of dichloromethane, is substantially correct, comes from the use of the Polanyi relationship, used in conjunction with the known activation energies and bond dissociation energies for other halomethanes. By using the Polanyi relationship in the form $E = 0.86\ (D(R\text{-}H) - 82.5)$[85], and the known values of the activation energies for the bromination of the chloromethanes, an estimate of the bond dissociation energy D(R-H) can be obtained. The comparison between these calculated and the observed values of D(R-H) from other methods, is extremely good and implies that the activation energy for the bromination of dichloromethane is reasonably accurate.

This also implies that the results for chlorofluoromethane and dichlorofluoromethane, are accurate. These rate parameters were of considerable use in the computation involved with the results of Part I.

TABLE II.9

	19 Fluorine	29,80 Chlorine	B,27 Bromine	27,A D(C-H)	85 $D(C-H)_i$	88 Dipole
CH_4	1.21	3.85	18.58	104	104	0
CH_3Cl	1.07	3.30	14.72	98	99	1.87
CH_2Cl_2	0.16	3.00	10.86	95	95	1.55
$CHCl_3$	0.66	3.34	9.30	92	93	1.02
CH_2ClF			14.80		100	
$CHCl_2F$	1.34		13.30		98	1.35
$CHClF_2$	1.32					1.44
CH_3F	1.07		16.10			1.82
CH_2F_2	2.4		16.59			1.93
CHF_3		8.4	22.32	106		1.62

Ref

19 Foon and McAskill, Trans Farad. Soc. 1969, 65, 3005

29 For chloromethanes, Knox, Trans. Farad. Soc. 1962, 53, 275

80 For fluoroform, Coomber and Whittle, ibid., 1968, 64, 2130

B This work for CH_2Cl_2, CH_2ClF, $CHCl_2F$

27 Amphlett and Whittle, Trans. Farad. Soc., 1968, 64, 2130

85 Calculated D(C-H) for bromination of RH using Polanyi expression of Thaler, Methods in free radical chemistry, vol. 2, Dekker, 1969, page 151. $E = \alpha[D(R-H)-C_i]$ where $\alpha = 0.86$ and C_i = 82.5 Kcal/mole

(A) Bond dissociation energies as follows

CH_4, CHF_3 ref 27

CH_3Cl, CH_2Cl_2, $CHCl_3$ Goldfinger and Martens 1961 Trans. Farad. Soc., 57, 2220

The bond dissociation energies for the chloromethanes obtained, by the electron impact method, by Martin, Lampe and Taft, J. Amer. Chem. Soc. 1966, 88, 1353 and Farmer, Henderson, Lassing and Marsden, J. Chem. Phys. (1956) 24, 348 although in broad agreement with one another are about 10 Kcal less than the bond dissociation energies obtained by other methods. The values of Benson, J. Amer. Chem. Soc. 91, 7564 (1969) are in broad agreement with those listed.

DETAILS OF REACTIONS

A) COMPETITIVE BROMINATION OF DICHLOROMETHANE AND CHLOROFORM

Chromatographic Analysis:-

Column 20% Silicone Oil on 60-100 mesh Embacel
Temperature 90°C
Nitrogen flow rate 120 ml. min.^{-1}
Chart speed 48 in./hr.

Variation of Reaction Temperature

Time 900 secs., Reactant pressures, CH_2Cl_2 40 mm., $CHCl_3$ 40 mm., Br_2 20 mm. Maximum % decomposition of CH_2Cl_2 = 10% and of $CHCl_3$ = 20%

a) Temp. 121± 1°C $\frac{[CHCl_2Br]}{[CCl_3Br]}$	b) Temp. 109 ± 1°C $\frac{[CHCl_2Br]}{[CCl_3Br]}$
0.577	0.559
0.584	0.544
0.581	0.573
0.586	0.574
0.580	0.535
0.582 Mean	0.557 Mean

c) Temp. 94 ± 1°C $\frac{[CHCl_2Br]}{[CCl_3Br]}$	d) Temp. 82 ± 1°C $\frac{[CHCl_2Br]}{[CCl_3Br]}$
0.501	0.474
0.510	0.474
0.472	0.477
0.499	0.458
0.500	0.461
0.496 Mean	0.469 Mean

e) Temp. 74 ± 1°C	f) Temp. 66 ± 1°C	g) Temp. 59 ± 1°C
$\frac{[CHCl_2Br]}{[CCl_3Br]}$	$\frac{[CHCl_2Br]}{[CCl_3Br]}$	$\frac{[CHCl_2Br]}{[CCl_3Br]}$
0.436	0.425	0.420
0.446	0.436	0.425
0.439	0.410	0.399
0.453	0.447	0.395
0.433	0.398	0.390
0.442 Mean	0.423 Mean	0.406 Mean

B) COMPETITIVE BROMINATION OF CHLOROFORM AND DICHLOROFLUOROMETHANE

Chromatographic Analysis:-

Column 20% Silicone Oil on 60-100 mesh Embacel
Temperature 65°C
Nitrogen flow rate 120 ml.min.$^{-1}$
Chart speed 48 in./hr.

Variation of Reaction Temperature

Time 900 secs., Reactant pressures, $CHCl_2F$ 80 mm., $CHCl_3$ 20 mm., Br_2 10 mm. Maximum % decomposition of $CHCl_2F$ = 4% and of $CHCl_3$ = 50%

a) Temp. 171 ± 1°C	b) Temp. 161 ± 1°C
$\frac{[CCl_2FBr]\ [CHCl_3]_i}{[CCl_3Br]\ [CHCl_2F]_i}$	$\frac{[CCl_2FBr]\ [CHCl_3]_i}{[CCl_3Br]\ [CHCl_2F]_i}$
4.90×10^{-2}	4.43×10^{-2}
4.44×10^{-2}	4.29×10^{-2}
5.07×10^{-2}	4.12×10^{-2}
4.91×10^{-2}	3.80×10^{-2}
5.04×10^{-2}	4.15×10^{-2}
4.87×10^{-2} Mean	4.16×10^{-2} Mean

c) Temp. 151 ± 2°C

$$\frac{[CCl_2FBr]\,[CHCl_3]_i}{[CCl_3Br]\,[CHCl_2F]_i}$$

3.65×10^{-2}
3.89×10^{-2}
3.90×10^{-2}
3.76×10^{-2}
4.09×10^{-2}

3.86×10^{-2} Mean

d) Temp. 141 ± 1°C

$$\frac{[CCl_2FBr]\,[CHCl_3]_i}{[CCl_3Br]\,[CHCl_2F]_i}$$

3.54×10^{-2}
3.35×10^{-2}
3.17×10^{-2}
3.19×10^{-2}
3.37×10^{-2}

3.33×10^{-2} Mean

e) Temp. 130 ± 1°C

$$\frac{[CCl_2FBr]\,[CHCl_3]_i}{[CCl_3Br]\,[CHCl_2F]_i}$$

2.99×10^{-2}
3.01×10^{-2}
3.13×10^{-2}
2.75×10^{-2}
2.77×10^{-2}

2.93×10^{-2} Mean

f) Temp. 122 ± 2°C

$$\frac{[CCl_2FBr]\,[CHCl_3]_i}{[CCl_3Br]\,[CHCl_2F]_i}$$

2.75×10^{-2}
2.64×10^{-2}
2.73×10^{-2}
2.82×10^{-2}
2.64×10^{-2}

2.72×10^{-2} Mean

g) Temp. 108 ± 1°C

$$\frac{[CCl_2FBr]\,[CHCl_3]_i}{[CCl_3Br]\,[CHCl_2F]_i}$$

2.02×10^{-2}
2.31×10^{-2}
2.32×10^{-2}
2.36×10^{-2}
2.19×10^{-2}

2.24×10^{-2} Mean

h) Temp. 98 ± 1°C

$$\frac{[CCl_2FBr]\,[CHCl_3]_i}{[CCl_3Br]\,[CHCl_2F]_i}$$

1.97×10^{-2}
1.93×10^{-2}
1.83×10^{-2}
1.96×10^{-2}
1.96×10^{-2}

1.93×10^{-2} Mean

C) COMPETITIVE BROMINATION OF CHLOROFORM AND CHLOROFLUOROMETHANE

Chromatographic Analysis:-

Column 20% Silicone Oil on 60-100 mesh Embacel
Temperature 90°C
Nitrogen flow rate 120 ml.min.^{-1}
Chart speed 48 in./hr.

Variation of Reaction Temperature

Time 900 secs., Reactant pressures, CH_2FCl 80 mm., $CHCl_3$ 20 mm., Br_2 10 mm. Maximum % decomposition of CH_2FCl = 5% and of $CHCl_3$ = 30%

a) Temp. 170 ± 1°C

$$\frac{[CHClFBr]}{[CCl_3Br]}\ \frac{[CHCl_3]_i}{[CH_2ClF]_i}$$

6.80×10^{-2}
6.62×10^{-2}
6.53×10^{-2}
6.26×10^{-2}
7.28×10^{-2}

6.70×10^{-2} Mean

b) Temp. 160 ± 1°C

$$\frac{[CHClFBr]}{[CCl_3Br]}\ \frac{[CHCl_3]_i}{[CH_2ClF]_i}$$

5.65×10^{-2}
6.60×10^{-2}
6.11×10^{-2}
6.16×10^{-2}
5.96×10^{-2}

6.10×10^{-2} Mean

c) Temp. 151 ± 1°C

$$\frac{[CHClFBr]}{[CCl_3Br]}\ \frac{[CHCl_3]_i}{[CH_2ClF]_i}$$

5.38×10^{-2}
4.87×10^{-2}
5.32×10^{-2}
4.63×10^{-2}
5.11×10^{-2}

5.06×10^{-2} Mean

d) Temp. 141 ± 2°C

$$\frac{[CHClFBr]}{[CCl_3Br]}\ \frac{[CHCl_3]_i}{[CH_2ClF]_i}$$

4.68×10^{-2}
4.37×10^{-2}
3.98×10^{-2}
4.70×10^{-2}
4.13×10^{-2}

4.37×10^{-2} Mean

e) Temp. 131 ± 1°C	f) Temp. 120 ± 1°C	g) Temp. 109 ± 1°C
$\frac{[CHClFBr]}{[CCl_3Br]} \frac{[CHCl_3]_i}{[CH_2FCl]_i}$	$\frac{[CHClFBr]}{[CCl_3Br]} \frac{[CHCl_3]_i}{[CH_2FCl]_i}$	$\frac{[CHClFBr]}{[CCl_3Br]} \frac{[CHCl_3]_i}{[CH_2FCl]_i}$
3.74×10^{-2}	3.10×10^{-2}	2.46×10^{-2}
3.45×10^{-2}	3.15×10^{-2}	2.68×10^{-2}
3.85×10^{-2}	3.05×10^{-2}	2.56×10^{-2}
3.71×10^{-2}	3.15×10^{-2}	2.53×10^{-2}
3.34×10^{-2}	3.18×10^{-2}	2.57×10^{-2}
3.62×10^{-2} Mean	3.13×10^{-2} Mean	2.56×10^{-2} Mean

D) COMPETITIVE BROMINATION OF DICHLOROFLUOROMETHANE AND CHLOROFLUOROMETHANE

Chromatographic Analysis:-

Column 20% Silicone Oil on 60-100 mesh Embacel
Temperature 65°C
Nitrogen flow rate 120 ml.min.$^{-1}$
Chart speed 48 in./hr.

Variation of Reaction Temperature

Time 900 secs., Reactant pressures, $CHCl_2F$ 40 mm., CH_2FCl 40 mm., Br_2 10 mm. Maximum % decomposition of CH_2FCl = 4% and of $CHCl_2F$ = 3%

a) Temp. 170 ± 1°C	b) Temp. 161 ± 1°C
$\frac{[CHClFBr]}{[CCl_2FBr]}$	$\frac{[CHClFBr]}{[CCl_2FBr]}$
1.37	1.31
1.45	1.42
1.35	1.30
1.28	1.26
1.40	1.29
1.37 Mean	1.32 Mean

c) Temp. 150 ± 1°C	d) Temp. 140 ± 1°C
$\frac{[CHClFBr]}{[CCl_2FBr]}$	$\frac{[CHClFBr]}{[CCl_2FBr]}$
1.26	1.21
1.34	1.19
1.20	1.13
1.27	1.12
1.26	1.27
1.27 Mean	1.18 Mean

e) Temp. 129 ± 1°C	f) Temp. 120 ± 1°C	g) Temp. 108 ± 1°C
$\frac{[CHClFBr]}{[CCl_2FBr]}$	$\frac{[CHClFBr]}{[CCl_2FBr]}$	$\frac{[CHClFBr]}{[CCl_2FBr]}$
1.14	1.27	0.98
1.07	1.18	1.24
1.08	1.10	1.02
1.05	1.24	1.03
1.05	1.14	1.09
1.08 Mean	1.19 Mean	1.07 Mean

E) COMPETITIVE BROMINATIONS OF METHYL CHLORIDE AND DICHLOROMETHANE

Chromatographic Analysis:

Column 20% Silicone Oil on 60-100 mesh Embacel
Temperature 65°C
Nitrogen flow rate 120 ml.min.$^{-1}$
Chart speed 48 in./hr.

Variation of Reaction Temperature

Time 900 secs., Reactant pressures, CH_3Cl 80 mm., CH_2Cl_2 20 mm., Br_2 10 mm. Maximum % decomposition of CH_3Cl = 2% and of CH_2Cl_2 = 20%

a) Temp. 170 ± 1°C

$\frac{[CH_2ClBr]}{[CHCl_2Br]}\frac{[CH_2Cl_2]_i}{[CH_3Cl]_i}$
0.125
0.124
0.130
0.128
0.122
0.126 Mean

b) Temp. 161 ± 1°C

$\frac{[CH_2ClBr]}{[CHCl_2Br]}\frac{[CH_2Cl_2]_i}{[CH_3Cl]_i}$
0.112
0.114
0.109
0.109
0.103
0.109 Mean

c) Temp. 149 ± 1°C

$\frac{[CH_2ClBr]}{[CHCl_2Br]}\frac{[CH_2Cl_2]_i}{[CH_3Cl]_i}$
0.108
0.104
0.119
0.097
0.106
0.107 Mean

d) Temp. 140 ± 1°C

$\frac{[CH_2ClBr]}{[CHCl_2Br]}\frac{[CH_2Cl_2]_i}{[CH_3Cl]_i}$
0.110
0.101
0.103
0.100
0.101
0.103 Mean

e) Temp. 129 ± 1°C

$\frac{[CH_2ClBr]}{[CHCl_2Br]}\frac{[CH_2Cl_2]_i}{[CH_3Cl]_i}$
9.79×10^{-2}
9.85×10^{-2}
10.16×10^{-2}
9.58×10^{-2}
9.78×10^{-2}
9.83×10^{-2} Mean

f) Temp. 118 ± 1°C

$\frac{[CH_2ClBr]}{[CHCl_2Br]}\frac{[CH_2Cl_2]_i}{[CH_3Cl]_i}$
8.81×10^{-2}
9.27×10^{-2}
9.13×10^{-2}
9.16×10^{-2}
9.20×10^{-2}
9.11×10^{-2} Mean

g) Temp. 106 ± 1°C	h) Temp. 93 ± 1°C	i) Temp. 80 ± 1°C
$\frac{[CH_2ClBr]}{[CHCl_2Br]}\frac{[CH_2Cl_2]_i}{[CH_3Cl]_i}$	$\frac{[CH_2ClBr]}{[CHCl_2Br]}\frac{[CH_2Cl_2]_i}{[CH_3Cl]_i}$	$\frac{[CH_2ClBr]}{[CHCl_2Br]}\frac{[CH_2Cl_2]_i}{[CH_3Cl]_i}$
8.42×10^{-2}	6.60×10^{-2}	5.12×10^{-2}
7.29×10^{-2}	6.84×10^{-2}	4.96×10^{-2}
8.37×10^{-2}	6.72×10^{-2}	6.43×10^{-2}
7.26×10^{-2}	7.29×10^{-2}	6.28×10^{-2}
7.96×10^{-2}	7.08×10^{-2}	4.45×10^{-2}
7.86×10^{-2} Mean	6.90×10^{-2} Mean	5.45×10^{-2} Mean

F) BROMINATION OF CHLOROFORM WITH VARIOUS CONCENTRATIONS OF DICHLOROMETHANE

Chromatographic Analysis:-

Column 20% Silicone Oil on 60-100 mesh Embacel
Temperature 90°C
Nitrogen flow rate 120 ml.min.$^{-1}$
Chart speed 48 in./hr.

Variation of Concentration of Dichloromethane

Time 900 secs., Reactant pressures, $CHCl_3$ 40 mm., Br_2 10 mm., Temperature 82 ± 2°C. Maximum % decomposition of CH_2Cl_2 = 4% and of $CHCl_3$ = 7%

CH_2Cl_2 pressures

a) 10 mm.	b) 20 mm.
$\frac{[CHCl_2Br]}{[CCl_3Br]}$	$\frac{[CHCl_2Br]}{[CCl_3Br]}$
0.160	0.241
0.145	0.256
0.149	0.264
0.148	0.265
0.145	0.257
0.150 Mean	0.257 Mean

c) 30 mm.	d) 40 mm.
$\frac{[CHCl_2Br]}{[CCl_3Br]}$	$\frac{[CHCl_2Br]}{[CCl_3Br]}$
0.370	0.490
0.380	0.465
0.376	0.488
0.401	0.475
0.372	0.477
0.380 Mean	0.479 Mean

d) 50 mm.	e) 60 mm.	g) 70 mm.
$\frac{[CHCl_2Br]}{[CCl_3Br]}$	$\frac{[CHCl_2Br]}{[CCl_3Br]}$	$\frac{[CHCl_2Br]}{[CCl_3Br]}$
0.581	0.696	0.801
0.610	0.684	0.778
0.583	0.701	0.770
0.607	0.732	0.800
0.598	0.710	0.823
0.596 Mean	0.704 Mean	0.794 Mean

G) BROMINATION OF CHLOROFORM WITH ADDED HYDROGEN BROMIDE

Chromatographic Analysis:-

Column 20% SiliconeOil on 60-100 mesh Embacel
Temperature 90°C
Nitrogen flow rate 120 ml.min.$^{-1}$
Chart speed 48 in./hr.

Variation of Concentration of HBr

Time 900 secs., Reactant pressures, $CHCl_3$ 40 mm., Br_2 10 mm., Temperature 76 ± 2°C

HBr pressures

a) 0 mm.

$\frac{[CCl_3Br]}{[CHCl_3]_f}$

9.59×10^{-2}
10.05×10^{-2}
9.65×10^{-2}
10.13×10^{-2}
9.24×10^{-2}

9.73×10^{-2} Mean

b) 6 mm. Time = 960 secs

$\frac{[CCl_3Br]}{[CHCl_3]_f}$

10.14×10^{-2}
9.66×10^{-2}
10.03×10^{-2}
9.97×10^{-2}
9.79×10^{-2}

9.92×10^{-2} Mean

Corrected mean for Time = 900 secs
9.30×10^{-2}

c) 12 mm.

$\frac{[CCl_3Br]}{[CHCl_3]_f}$

9.02×10^{-2}
8.75×10^{-2}
8.69×10^{-2}
8.41×10^{-2}
8.88×10^{-2}

8.75×10^{-2} Mean

d) 20 mm.

$\frac{[CCl_3Br]}{[CHCl_3]_f}$

8.56×10^{-2}
7.97×10^{-2}
8.95×10^{-2}
7.91×10^{-2}
8.59×10^{-2}

8.39×10^{-2} Mean

e) 30 mm.

$\frac{[CCl_3Br]}{[CHCl_3]_f}$

8.51×10^{-2}
8.14×10^{-2}
8.36×10^{-2}
8.39×10^{-2}
8.63×10^{-2}

8.41×10^{-2} Mean

f) 46 mm.

$\frac{[CCl_3Br]}{[CHCl_3]_f}$

8.48×10^{-2}
7.66×10^{-2}
7.44×10^{-2}
7.63×10^{-2}
8.23×10^{-2}

7.89×10^{-2} Mean

g) 60 mm.

$\frac{[CCl_3Br]}{[CHCl_3]_f}$

7.86×10^{-2}
7.17×10^{-2}
6.94×10^{-2}
7.27×10^{-2}
7.43×10^{-2}

7.34×10^{-2} Mean

h) 82 mm.

$\frac{[CCl_3Br]}{[CHCl_3]_f}$

6.00×10^{-2}
6.16×10^{-2}
6.02×10^{-2}
6.26×10^{-2}
6.75×10^{-2}

6.24×10^{-2} Mean

APPENDIX

A Brief Description of the Computer program and of the correspondence obtained with the results of Part 1.

The program was written and developed by Mr.A.D. Booth and Mr. M.A. Rothwell of B.P. Chemicals International Ltd., Epsom Division, and consists basically of two parts:-

1) Numerical integration for stiff systems of ordinary differential equations.
2) An optimization package for the fitting of rate parameters to the equations describing the reaction of bromotrichloromethane with halomethanes.

The program was written in ASA Fortran IV except in those instances where computer practice was peculiar to ICL 1900 machines. Because of the minor differences between an ICL 1900 and an IBM 360/44 considerable time was lost in transferring the program from the Epsom ICL machine to the St. Andrews IBM 360 machine. Furthermore, the differences in word lengths (i.e. machine accuracy) between these machines caused further problems, which were cured by time consuming trial and error.

$CCl_3Br \longrightarrow CCl_3\cdot + Br\cdot$	Rate = ϕI_a
$CCl_3 + RH \rightleftharpoons CHCl_3 + R\cdot$	k_2, k_8
$R\cdot + CCl_3Br \longrightarrow RBr + CCl_3\cdot$	k_3
$Br\cdot + RH \longrightarrow HBr + R\cdot$	k_4
$CCl_3\cdot + HBr \rightleftharpoons CHCl_3 + Br\cdot$	k_5, k_9
$CCl_3\cdot + CCl_3\cdot \longrightarrow C_2Cl_6$	k_6
$Br\cdot + Br\cdot \longrightarrow Br_2$	k_7
$CCl_3\cdot + Br\cdot \longrightarrow CCl_3Br$	k_{10}
$R\cdot + Br\cdot \longrightarrow RBr$	k_{11}

Simplifying the notation as follows

$x_1 = [CCl_3Br]$

$x_2 = [RH]$

$x_3 = [CHCl_3]$

$x_4 = [RBr]$

$x_5 = [HBr]$

$x_6 = [C_2Cl_6]$

$x_7 = [Br_2]$

$x_8 = [CCl_3\cdot]$

$x_9 = [Br\cdot]$

$x_{10} = [R\cdot]$

leads to the following differential equations for the concentrations of molecular and radical species in a reaction .

$$
\begin{aligned}
\dot{x}_1 &= -\emptyset I_a - k_3x_1x_{10} + k_{10}x_8x_9 \\
\dot{x}_2 &= -k_2x_2x_8 + k_8x_3x_{10} - k_4x_2x_9 \\
\dot{x}_3 &= k_2x_2x_8 + k_5x_5x_8 - k_8x_3x_{10} - k_9x_3x_9 \\
\dot{x}_4 &= k_3x_1x_{10} + k_{11}x_{10}x_9 \\
\dot{x}_5 &= k_4x_2x_9 - k_5x_5x_8 + k_9x_3x_9 \\
\dot{x}_6 &= k_6{x_8}^2 \\
\dot{x}_7 &= k_7{x_9}^2 \\
\dot{x}_8 &= \emptyset I_a - k_2x_2x_8 + k_8x_3x_{10} + k_3x_1x_{10} - k_5x_5x_8 \\
&\qquad + k_9x_3x_9 - 2\,k_6{x_8}^2 - k_{10}x_8x_9 = 0 \\
\dot{x}_9 &= \emptyset I_a - k_4x_2x_9 + k_5x_5x_8 - k_9x_3x_9 - 2\,k_7{x_9}^2 \\
&\qquad - k_{11}x_9x_{10} - k_{10}x_8x_9 = 0 \\
\dot{x}_{10} &= k_2x_2x_8 - k_8x_3x_{10} - k_3x_1x_{10} + k_4x_2x_9 - k_{11}x_9x_{10}
\end{aligned}
$$

This set of differential equations cannot be solved analytically so a numerical integration method must be used. The three radical species cause some severe numerical problems as the solutions for x_8, x_9 and x_{10} contain terms which cause their value to rapidly change over a brief initial period of time. Their negligible value after this period of time still cause numerical stability problems and differential equations of this type are generally referred to as 'stiff'.[92] By applying the steady-state approximation, where the differential equations for the radical concentrations are set equal to zero, the equations can be solved for the radical concentrations in terms of the molecular species. These values can then be used to solve the differential equations for the molecular species. In this case x_8, x_9, x_{10} can be solved in terms of x_1,------,x_7 then the first seven equations can be numerically integrated. The method of integration used here is that of Gear[93,94] which is specifically designed for stiff systems.

For this reaction mechanism, only a few of the steps have well defined activation energies and Arrhenius parameters. The second part of the program was used to obtain better estimates for the remaining unknown values. This part of the program consisted of an optimization package, 'MINEX', written at Epsom which uses a method based on the Gauss-Newton algorithm with a Marquardt-type improvement, combined with a Fibonacci line search[95]. The program was user provided with initial guesses for all the unknown rate parameters for which simple upper and lower limits were set so that the changes brought about, on optimization, remained within the bounds of chemical feasibility. The objective function was taken as

$$S = \sum_{i=1}^{m} [u_i^2(f_i - \hat{f}_i)^2 + v_i^2(g_i - \hat{g}_i)^2 + w_i^2(h_i - \hat{h}_i)^2]$$

where f_i, g_i and h_i are the calculated values of $[CHCl_3]_f/[CCl_3Br]_f$; $[RBr]_f/[CCl_3Br]_f$ and $[C_2Cl_6]_f/[CCl_3Br]_f$. The corresponding observed values are $\hat{f}_i$, $\hat{g}_i$, $\hat{h}_i$ and u_i, v_i and w_i are weighting factors. The function S was minimized with respect to the unknown activation energies and Arrhenius factors.

The initial choice of weighting factors was

$$u_i = 1/\hat{f}_i ; \quad v_i = 1/\hat{g}_i ; \quad w_i = 1/\hat{h}_i$$

Thus each term in the objective function was treated with equal emphasis. A better fit was observed with the following weighting factors.

$$u_i = v_i = 1 \qquad w_i = 2$$

At this stage the program was transferred to the St. Andrews IBM 360/44.

The rate equation $k = A \exp(-E/RT)$ was used in the form $k_j = A_j \exp[-\frac{E_j}{R}(\frac{1}{T} - \frac{1}{T_o})]$ where $T_o = 436°K = 163°C$; $A_j \exp(E/RT_o) = A$.

Initial values of all the parameters for steps 1-11 of the mechanism were used with appropriate upper and lower bounds to the values of A_j and E_j. The rate parameters, which are known to a reasonable degree of confidence, were frozen at the literature values. In general, the initial values for steps 1, 4, 9, 10 and 11 were user frozen at their initial values. For the other parameters, the estimates which were used, were based upon similar reactions for which literature values of the rate constants were known. Generally, the activation energies (E_j) were allowed to vary by $\pm$ 2 Kcal/mole over the original values and the Arrhenius parameters (A_j) were allowed to vary by $\pm 10^2\ l\ m^{-1} s^{-1}$.

The initial values used for optimization were

$$ØI_a(T) = 2.56 \times 10^{-5} \exp(-6330/RT)$$

Step 2

$k_{CH_2ClF} \sim 10^{10} \exp(-12000/RT)$

$k_{CH_2Cl_2} \sim 3 \times 10^{7} \exp(-7000/RT)$

$k_{CHCl_2F} \sim 5 \times 10^{8} \exp(-10000/RT)$

Step 3

$k_{RH} \sim 10^{8} \exp(-4000/RT)$

Step 4

$k_{CH_2ClF} = 7.76 \times 10^{10} \exp(-14800/RT)$ This work

$k_{CH_2Cl_2} = 0.98 \times 10^{10} \exp(-10860/RT)$ This work

$k_{CHCl_2F} = 1.05 \times 10^{10} \exp(-13300/RT)$ This work

Step 5

$k_{RH} \sim 10^{8} \exp(-3000/RT)$

Step 6

$k_{RH} \sim 3 \times 10^{10} \exp/-0/RT)$

Step 7

$k_{RH} \sim 4 \times 10^{10} \exp(-0/RT)$ Ref. 96

Step 8

$k_{CH_2FCl} \sim 10^{7} \exp(-6400/RT)$

$k_{CH_2Cl_2} = 1.6 \times 10^{7} \exp(-6400/RT)$ Ref. 55

$k_{CHCl_2F} \sim 10^{8} \exp(-7500/RT)$

Step 9

$k_{RH} = 2.3 \times 10^{9} \exp(-9330/RT)$ Ref. 76

Step 10

$k_{RH} \sim 0.3 \times 10^{10}$

Step 11

$k_{RH} \sim 0.3 \times 10^{10}$

When choice of the rate parameters remains, the reasons for deciding on the above values are as follows.
For Step 2 the values listed are close to those in Table M as these values are expected to be a reasonable initial guess.
The low activation energy for step 3 comes from the argument that in going from methane to chloroform there is a decrease in the activation energy for hydrogen abstraction by trifluoromethyl radicals of about 5 Kcals/mole (Table K). If a similar decrease is observed for bromine abstraction by $CF_3\cdot$ radicals in going from methyl bromide to bromotrichloromethane, the activation energy obtained for bromine abstraction from bromotrichloromethane would be about 3 Kcal/mole. (E_{Br} for $CH_3Br + CF_3^{\cdot}$ = 8.3 Kcal/mole)[41]. The activation energy for bromine abstraction from bromotrichloromethane by R· radicals will therefore be about 4 Kcal/mole with a normal pre-exponential term. Step 5 must be similar in values to, if not less than, the rate parameters for the reaction ($CF_3\cdot$ + HBr)[39,40] and thus the values listed will provide a reasonable accurate starting point.
For step 6, the value is intermediate to the values obtained by Tedder and Walton ($10^{10.9}$ l $m^{-1}s^{-1}$)[70] and Huybrechts and De Maré ($10^{9.7}$ l $m^{-1}s^{-1}$)[45]. The cross termination reactions 10 and 11 are both likely to have similar values and $10^{10.5}$ l $m^{-1}s^{-1}$ should

be a reasonable initial value for both steps.

Except for dichloromethane, there is generally a small excess of RBr formed over the amount of chloroform produced. With dichloromethane the formed bromodichloromethane reacts further and hence there is less bromodichloromethane than chloroform. The decomposition of bromodichloromethane is not allowed for in this computer treatment.

Straight forward integration using the values for step 1-11 yields, in general, the fact that the model successfully predicts a slight surplus of bromo compound over chloroform. This is in contrast to the results obtained for integration of steps 1,2,3,6 and 7 which is the simple mechanism with termination in hexachloroethane and bromine only. Here the model yields identical amounts of chloroform and bromohalomethane.

Integration of the bromine chain mechanism, yields the slight surplus of RBr over chloroform, and this in itself is an indication that the proposed mechanism must include reactions due to bromine atoms.

Integration of the initial values for steps 1-9 give calculated ratios which directly parallel the observed results. (Table 1, 2, 3). The few meaningful optimization runs, obtained with these initial parameters, yielded the following results of note.

1) The activation energy for step 2 always decreases from the initial value. For CH_2FCl and CH_2Cl_2 the value reached the lower limit and was held there. For these compounds the pre-exponential term A_j decreased within the bounds, over the initial value. With $CHCl_2F$ the value of E decreased but that for A_j increased to

the upper limit.

2) Step 6 increases to or towards the upper limit while Step 7 generally decreases within the bounds.

3) Step 8 makes little difference to the results and is machine frozen at the initial values.

It ought to be pointed out that, at the most, only one quarter of the total number of data sets were used for optimization, as inclusion of more data sets drastically increased the amount of time between iterations.

It appears that inclusion of steps 10 and 11 are necessary, for extremely good fits between the calculated and observed values of $[C_2Cl_6]_f/[CCl_3Br]_f$ are obtained when these steps are included with the 'final' results obtained from optimization runs. Unfortunately optimization with these terms included were not possible for dichloromethane and dichlorofluoromethane as program interrupts of the type n/O occurred which terminated the job. The best that could be obtained was the inclusion of these steps in the final integration for all the data sets. This loses some of the good correspondence obtained for the calculated and observed values for chloroform and RBr (Tables 4,5,5',6,6'). The cross termination reactions 10 and 11 are likely to occur as the reaction of bromotrichloromethane with these halomethanes is close to or in the non-chain region where radical-radical reactions will occur. It appears that the overall mechanism, 1-11, is capable of reproducing the trends observed with the experimental results. Furthermore, reasonable correspondence is obtained with the calculated and observed values. Further work would be necessary to obtain meaningful Arrhenius parameters for all the unknown values. Work must be carried out to confirm that the initial values chosen give the best initial start. In particular the values used for steps 3 and 5 could be considerably in error, in that the values of the activation energies could be too low by several kilocalories. This would have the effect of reducing the rate for step 3 until it was comparable to that for step 2. Meaningful results will be obtained when none of the parameters for the major chain steps reaches the boundary values upon optimization. At the moment it suffices to point out that the reaction mechanism predictions, can closely follow the observed experimental results. Furthermore these preliminary results tend to confirm that the hydrogen abstraction reactions from halomethanes by trichloromethyl radicals do indeed have low activation energies, similar to those encountered and expected for abstraction from halomethanes by either trifluoromethyl or methyl radicals. The results also tend to confirm that the high rate of recombination of trichloromethyl radicals is more appropriate.

The program could profitably be rewritten for more efficient working on the IBM 360/44, and to remove minor faults. At present large amounts of computing time are necessary. Furthermore, minor program modifications are required before the results for difluoromethane can be treated without assuming the amount of bromodifluoromethane formed is identical to the amount chloroform.

In conclusion, the computer treatment of the overall mechanism further confirms that bromine atoms, as well as trichloromethyl radicals, must play a significant part in the overall kinetics of the reaction of bromotrichloromethane with these halomethanes.

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CHROMATOGRAMS

FIG 11

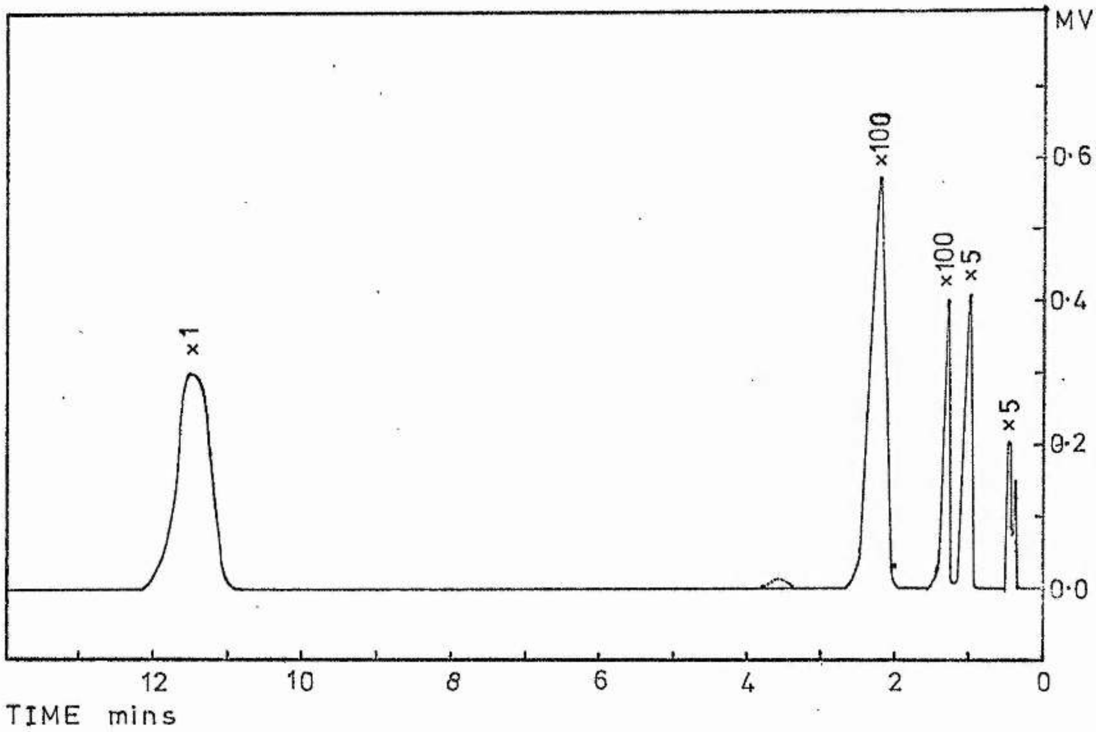

(a) $CCl_3Br + CH_2F_2$

FIG 12

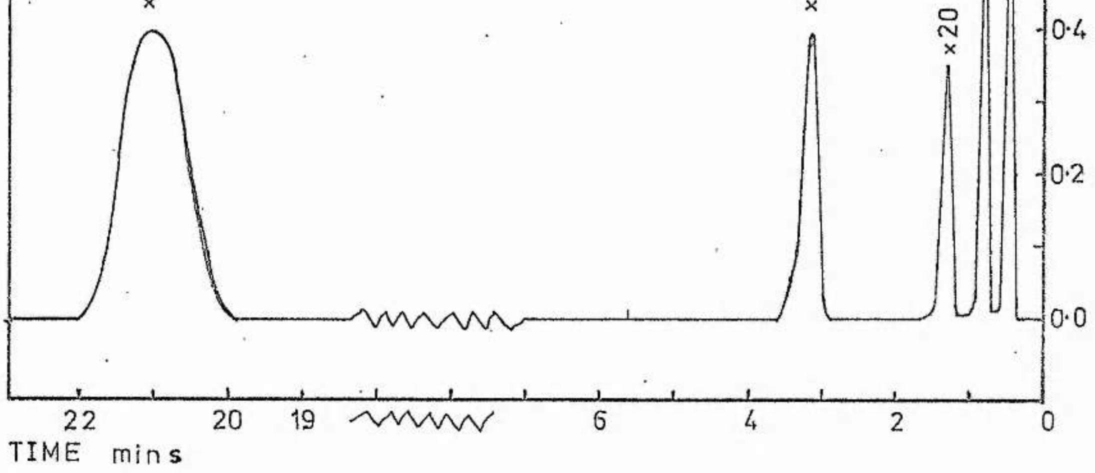

(b) $CCl_3Br + CH_2ClF$

FIG 13

(c) $CCl_3Br + CH_2Cl_2$

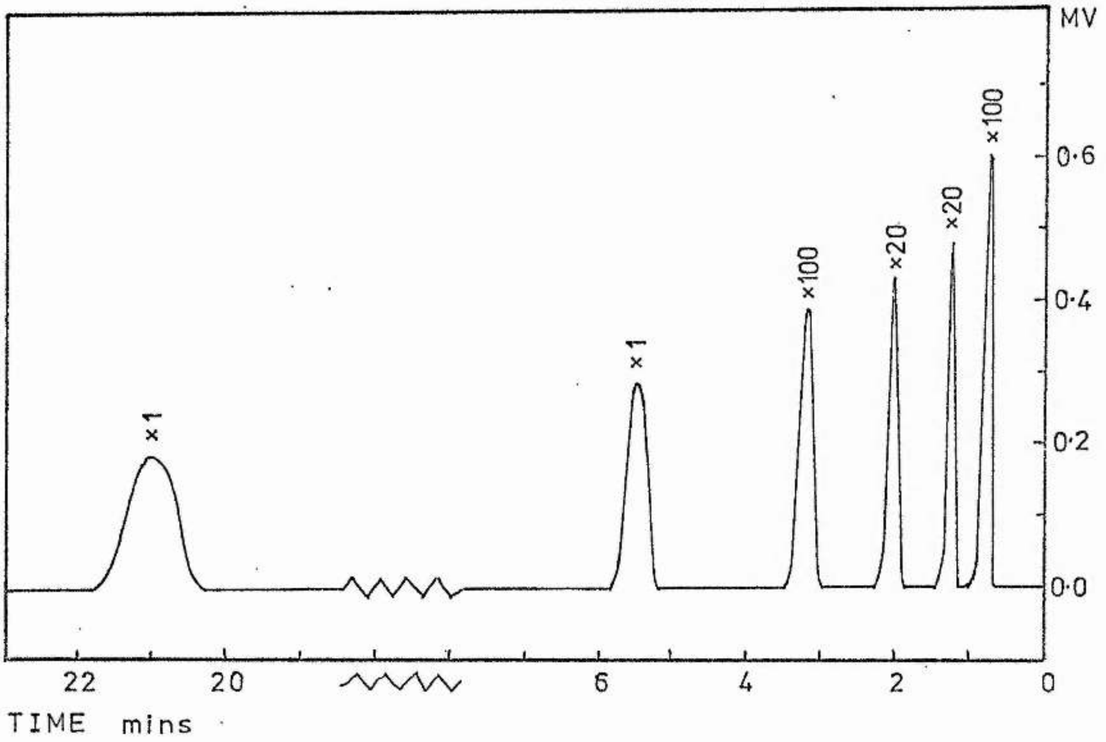


FIG 14

(d) $CCl_3Br + CHCl_2F$

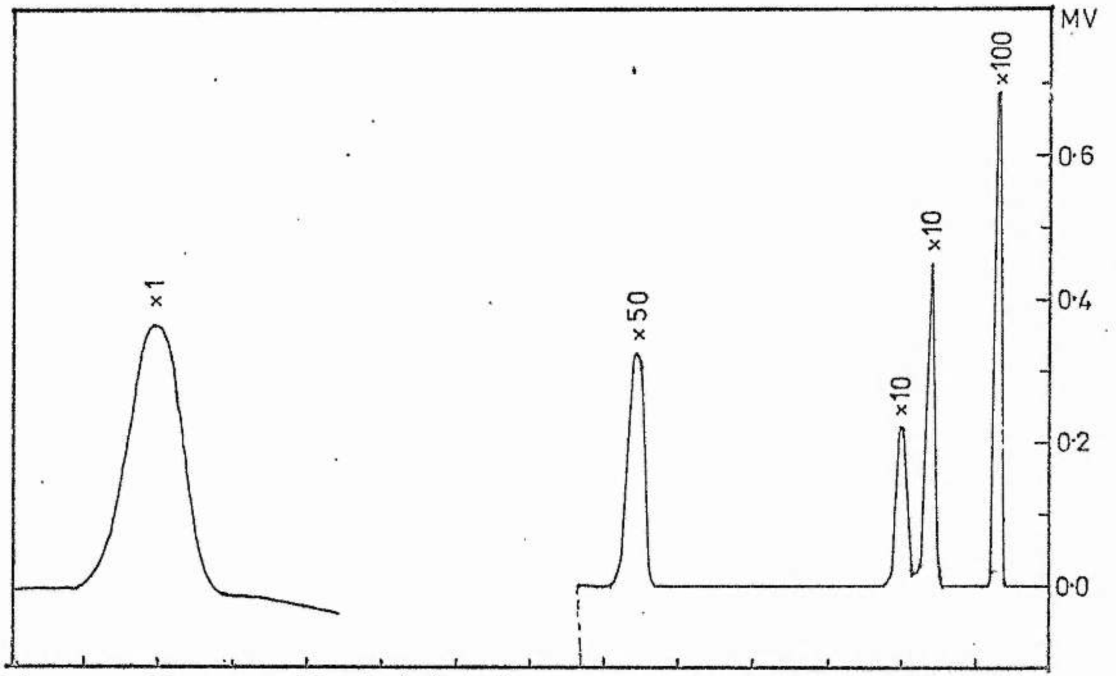
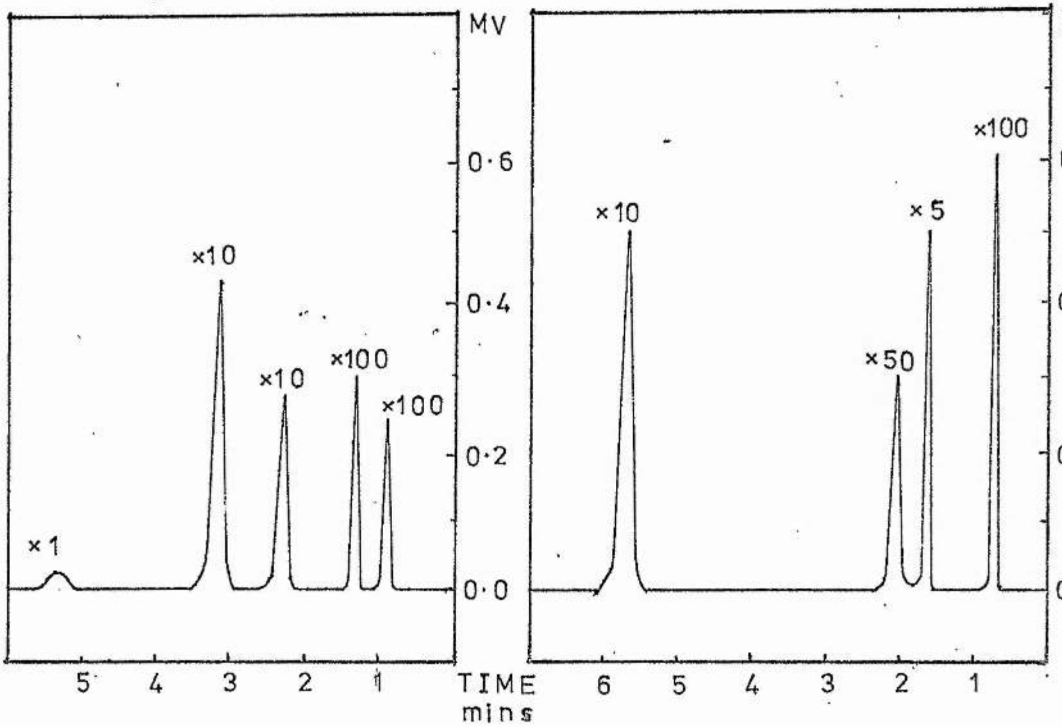


FIG 15

BROMINATION OF:-

(a) $CHCl_3$ + CH_2Cl_2

(b) $CHCl_3$ + $CHCl_2F$



(c) $CHCl_3$ + CH_2ClF

(d) CH_2FCl + $CHCl_2F$

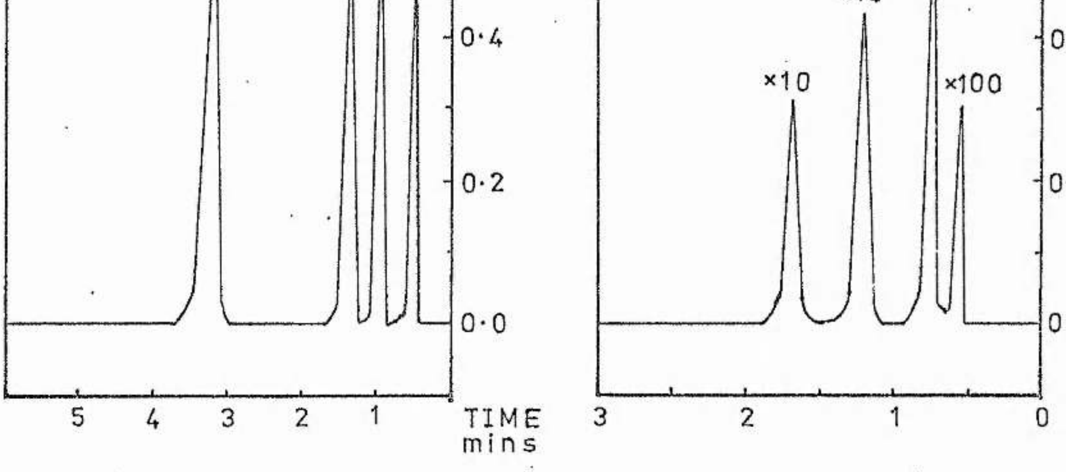
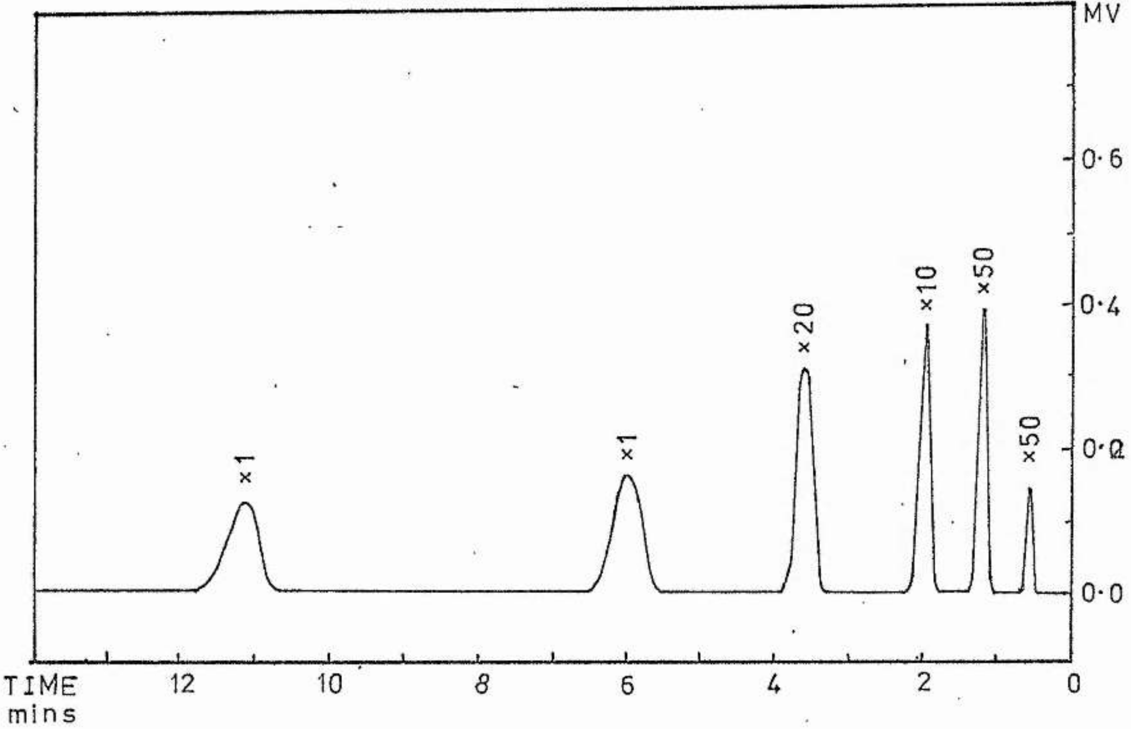


FIG 16

BROMINATION OF $CH_3Cl + CH_2Cl_2$



COMPUTER OUTPUT

```
                         TABLE 1     CH2FCL


      (RBR)/(CCL3BR)                 (C2CL6)/(CCL3BR)

   CALC      OBS      DIFF        CALC      OBS      DIFF

  14.701   16.090   -1.389       4.289     5.270    -0.981
  11.844   12.330   -0.486       3.446     4.540    -1.094
  10.483    9.560    0.923       3.045     3.460    -0.415
   9.169    8.420    0.749       2.660     3.240    -0.580
   6.666    4.430    2.236       1.930     2.420    -0.490
   4.315    2.390    1.925       1.249     1.790    -0.541
   2.101    0.660    1.441       0.611     0.980    -0.369
   7.715    5.210    2.505       1.721     2.260    -0.539
   6.718    3.520    3.198       1.324     1.650    -0.326
   5.609    2.420    3.189       0.938     1.230    -0.292
  21.029   14.820    6.209       4.309     5.000    -0.691
  10.010    9.410    0.600       2.979     3.750    -0.771
   6.004    5.900    0.104       2.356     3.070    -0.714
   3.394    3.090    0.304       1.832     2.360    -0.528
   1.878    2.090   -0.212       1.423     1.680    -0.257
   0.959    0.880    0.079       1.073     1.420    -0.347
   2.637    3.450   -0.813       3.617     5.070    -1.453
   5.913    5.590    0.323       3.727     4.950    -1.223
  11.306    9.680    1.626       3.910     4.800    -0.890
  20.064   13.230    6.834       4.204     4.430    -0.226
  29.412   18.560   10.852       4.516     4.610    -0.094
  43.139   21.470   21.669       4.971     4.830     0.141
   1.477    2.300   -0.823       2.810     3.910    -1.100
   3.268    4.200   -0.932       2.857     3.810    -0.953
   6.112    6.420   -0.308       2.931     3.640    -0.709
  10.483    9.740    0.743       3.045     3.590    -0.545
  14.839   12.330    2.509       3.159     3.580    -0.421
  20.726   14.850    5.876       3.311     4.160    -0.849
   0.876    0.950   -0.074       2.249     2.820    -0.571
   1.924    2.090   -0.166       2.271     3.040    -0.769
   3.559    3.070    0.489       2.305     2.680    -0.375
   6.004    5.020    0.984       2.356     2.850    -0.494
   8.365    5.580    2.785       2.405     2.480    -0.075
  11.440    7.500    3.940       2.469     2.870    -0.401
   0.529    0.810   -0.281       1.820     2.490    -0.670
   1.158    1.170   -0.012       1.831     2.430    -0.599
   2.130    1.790    0.340       1.847     2.110    -0.263
   3.562    2.760    0.802       1.871     2.450    -0.579
   4.920    3.250    1.670       1.894     2.080    -0.186
   6.655    4.600    2.055       1.923     2.290    -0.367


    C(I)

  0.2566E-04
  0.1030E 11
  0.1010E 09
  0.7816E 11
  0.9557E 09
  0.3000E 11
  0.4000E 11
  0.1610E 08
  0.2310E 10
  0.3000E 11
  0.3000E 11
```

TABLE 1

```
                                                                      ***  RESULTS  ***

                         INITIAL  VALUES                                (CHCL3)/(CCL3BR)

NO   RLI    TIME    TEMP    (CCL3BR)    (CH2FCL)       CALC      OBS      DIFF

 1   1.00  7200.0  436.2  0.124E-02  0.373E-02     14.649   17.040   -2.391
 2   1.00  6000.0  436.2  0.124E-02  0.373E-02     11.797   11.820   -0.023
 3   1.00  5400.0  436.2  0.124E-02  0.373E-02     10.438    9.780    0.658
 4   1.00  4800.0  436.2  0.124E-02  0.373E-02      9.127    7.880    1.247
 5   1.00  3600.0  436.2  0.124E-02  0.373E-02      6.629    4.200    2.429
 6   1.00  2400.0  436.2  0.124E-02  0.373E-02      4.281    2.010    2.271
 7   1.00  1200.0  436.2  0.124E-02  0.373E-02      2.071    0.470    1.601
 8   0.59  5400.0  436.2  0.124E-02  0.373E-02      7.676    5.080    2.596
 9   0.46  5400.0  436.2  0.124E-02  0.373E-02      6.680    3.700    2.980
10   0.33  5400.0  436.2  0.124E-02  0.373E-02      5.573    2.320    3.253
16   1.00  5400.0  451.2  0.124E-02  0.373E-02     20.940   15.240    5.700
17   1.00  5400.0  435.2  0.124E-02  0.373E-02      9.967    8.610    1.357
18   1.00  5400.0  424.2  0.124E-02  0.373E-02      5.978    5.540    0.438
19   1.00  5400.0  412.2  0.124E-02  0.373E-02      3.378    2.790    0.588
20   1.00  5400.0  400.2  0.124E-02  0.373E-02      1.869    1.750    0.119
21   1.00  5400.0  387.2  0.124E-02  0.373E-02      0.954    0.960   -0.006
22   1.00  5400.0  450.2  0.124E-02  0.570E-03      2.626    3.190   -0.564
23   1.00  5400.0  450.2  0.124E-02  0.124E-02      5.888    5.430    0.458
24   1.00  5400.0  450.2  0.124E-02  0.226E-02     11.259    9.450    1.809
25   1.00  5400.0  450.2  0.124E-02  0.373E-02     19.980   12.900    7.080
26   1.00  5400.0  450.2  0.124E-02  0.509E-02     29.288   18.620   10.668
27   1.00  5400.0  450.2  0.124E-02  0.678E-02     42.958   21.350   21.608
28   1.00  5400.0  436.2  0.124E-02  0.570E-03      1.471    2.450   -0.979
29   1.00  5400.0  436.2  0.124E-02  0.124E-02      3.254    4.170   -0.916
30   1.00  5400.0  436.2  0.124E-02  0.226E-02      6.086    6.100   -0.014
31   1.00  5400.0  436.2  0.124E-02  0.373E-02     10.438    9.140    1.298
32   1.00  5400.0  436.2  0.124E-02  0.509E-02     14.776   11.350    3.426
33   1.00  5400.0  436.2  0.124E-02  0.678E-02     20.638   13.610    7.028
34   1.00  5400.0  424.2  0.124E-02  0.570E-03      0.872    1.340   -0.468
35   1.00  5400.0  424.2  0.124E-02  0.124E-02      1.915    2.560   -0.645
36   1.00  5400.0  424.2  0.124E-02  0.226E-02      3.543    3.290    0.253
37   1.00  5400.0  424.2  0.124E-02  0.373E-02      5.978    4.680    1.298
38   1.00  5400.0  424.2  0.124E-02  0.509E-02      8.328    5.370    2.958
39   1.00  5400.0  424.2  0.124E-02  0.678E-02     11.390    7.940    3.450
40   1.00  5400.0  413.2  0.124E-02  0.570E-03      0.527    0.720   -0.193
41   1.00  5400.0  413.2  0.124E-02  0.124E-02      1.153    1.210   -0.057
42   1.00  5400.0  413.2  0.124E-02  0.226E-02      2.121    1.960    0.161
43   1.00  5400.0  413.2  0.124E-02  0.373E-02      3.546    2.800    0.746
44   1.00  5400.0  413.2  0.124E-02  0.509E-02      4.897    3.260    1.637
45   1.00  5400.0  413.2  0.124E-02  0.678E-02      6.624    4.610    2.014



                                                  I          A%I<            E%I<

                                                  1     0.1728E-07      0.6330E 04
                                                  2     0.1000E 05      0.1200E 05
                                                  3     0.1000E 07      0.4000E 04
                                                  4     0.3000E 04      0.1480E 05
                                                  5     0.3000E 08      0.3000E 04
                                                  6     0.3000E 11      0.0
                                                  7     0.4000E 11      0.0
                                                  8     0.1000E 05      0.6400E 04
                                                  9     0.5055E 05      0.9300E 04
                                                 10     0.3000E 11      0.0
                                                 11     0.3000E 11      0.0
```

TABLE 2 CH2CL2

```
    (RBR)/(CCL3BR)                  (C2CL6)/(CCL3BR)

 CALC      OBS     DIFF         CALC      OBS     DIFF

 8.413   16.760   -8.347        2.716    2.140    0.576
 6.073   12.520   -6.447        1.968    1.870    0.098
 4.450    7.540   -3.090        1.451    1.390    0.061
 3.664    5.350   -1.686        1.202    1.330   -0.128
 2.896    3.620   -0.724        0.959    0.930    0.029
 1.407    1.240    0.167        0.489    0.620   -0.131
 4.399    6.410   -2.011        1.087    1.220   -0.133
 3.300    3.070    0.230        0.646    0.620    0.026
 2.376    1.630    0.746        0.367    0.410   -0.043
12.117   21.770   -9.653        2.899    2.420    0.479
 7.308   12.630   -5.322        2.179    1.960    0.219
 3.801    8.920   -5.119        1.524    1.590   -0.066
 1.931    4.870   -2.939        1.058    1.230   -0.172
 1.167    2.550   -1.383        0.808    0.900   -0.092
 0.656    1.740   -1.084        0.592    0.730   -0.138
17.241   22.930   -5.689        3.062    2.280    0.782
12.117   18.820   -6.703        2.899    2.230    0.669
 7.025   14.580   -7.555        2.740    2.450    0.290
 3.742    9.710   -5.968        2.637    2.460    0.177
25.618   24.530    1.088        2.676    1.790    0.886
22.611   23.440   -0.829        2.594    1.760    0.834
19.582   22.640   -3.058        2.512    1.780    0.732
17.021   21.100   -4.079        2.444    1.870    0.574
14.057   19.030   -4.973        2.362    1.900    0.462
11.467   17.800   -6.333        2.292    1.970    0.322
 8.984   14.940   -5.956        2.225    1.790    0.435
 7.308   14.050   -6.742        2.179    1.880    0.299
 5.455   10.910   -5.455        2.129    1.800    0.329
 4.312   10.050   -5.738        2.099    1.700    0.399
 3.212    8.540   -5.328        2.069    1.790    0.279
 2.323    6.960   -4.637        2.045    1.670    0.375
 1.056    4.290   -3.234        2.011    1.680    0.331
 5.781   11.010   -5.229        1.642    1.460    0.182
 4.178    8.840   -4.662        1.604    1.410    0.194
 2.494    6.230   -3.736        1.564    1.520    0.044
 1.354    4.330   -2.976        1.538    1.610   -0.072
 3.077    6.100   -3.023        1.164    1.190   -0.026
 2.238    5.340   -3.102        1.146    1.100    0.046
 1.345    4.210   -2.865        1.127    1.120    0.007
 0.734    2.930   -2.196        1.113    1.180   -0.067


   C(I)

0.2566E-04
0.3217E 08
0.1010E 09
0.9815E 10
0.9557E 09
0.3000E 11
0.4000E 11
0.1610E 08
0.2310E 10
0.0
0.0
```

TABLE 2

```
                                                              ***  RESULTS  ***

                INITIAL  VALUES                                (CHCL3)/(CCL3BR)

NO  RLI    TIME    TEMP    (CCL3BR)    (CH2CL2)      CALC      OBS     DIFF

 1  1.00  9660.0  381.2  0.124E-02  0.373E-02     8.316   18.670  -10.354
 2  1.00  7200.0  381.2  0.124E-02  0.373E-02     5.980   13.790   -7.810
 3  1.00  5400.0  381.2  0.124E-02  0.373E-02     4.360    8.620   -4.260
 4  1.00  4500.0  381.2  0.124E-02  0.373E-02     3.575    5.850   -2.275
 5  1.00  3600.0  381.2  0.124E-02  0.373E-02     2.808    4.340   -1.532
 6  1.00  1800.0  381.2  0.124E-02  0.373E-02     1.322    1.610   -0.288
 7  0.56  7200.0  381.2  0.124E-02  0.373E-02     4.309    7.640   -3.331
 8  0.33  7200.0  381.2  0.124E-02  0.373E-02     3.213    4.040   -0.827
 9  0.18  7200.0  381.2  0.124E-02  0.373E-02     2.290    2.340   -0.050
15  1.00  7200.0  396.2  0.124E-02  0.373E-02    11.968   24.230  -12.262
16  1.00  7200.0  385.2  0.124E-02  0.373E-02     7.203   13.340   -6.137
17  1.00  7200.0  371.2  0.124E-02  0.373E-02     3.733   10.570   -6.837
18  1.00  7200.0  357.2  0.124E-02  0.373E-02     1.888    5.830   -3.942
19  1.00  7200.0  347.2  0.124E-02  0.373E-02     1.136    3.430   -2.294
20  1.00  7200.0  336.2  0.124E-02  0.373E-02     0.635    2.490   -1.855
21  1.00  7200.0  396.2  0.124E-02  0.509E-02    17.029   26.600   -9.571
22  1.00  7200.0  396.2  0.124E-02  0.373E-02    11.968   22.120  -10.152
23  1.00  7200.0  396.2  0.124E-02  0.226E-02     6.939   17.220  -10.281
24  1.00  7200.0  396.2  0.124E-02  0.124E-02     3.696   12.020   -8.324
25  1.00  7200.0  385.2  0.124E-02  0.113E-01    25.246   30.230   -4.984
26  1.00  7200.0  385.2  0.124E-02  0.102E-01    22.283   28.280   -5.997
27  1.00  7200.0  385.2  0.124E-02  0.904E-02    19.298   27.600   -8.302
28  1.00  7200.0  385.2  0.124E-02  0.802E-02    16.775   25.800   -9.025
29  1.00  7200.0  385.2  0.124E-02  0.678E-02    13.854   21.750   -7.896
30  1.00  7200.0  385.2  0.124E-02  0.565E-02    11.302   20.470   -9.168
31  1.00  7200.0  385.2  0.124E-02  0.452E-02     8.855   16.980   -8.125
32  1.00  7200.0  385.2  0.124E-02  0.373E-02     7.203   15.720   -8.517
33  1.00  7200.0  385.2  0.124E-02  0.283E-02     5.377   11.760   -6.383
34  1.00  7200.0  385.2  0.124E-02  0.226E-02     4.250   11.240   -6.990
35  1.00  7200.0  385.2  0.124E-02  0.170E-02     3.165    9.320   -6.155
36  1.00  7200.0  385.2  0.124E-02  0.124E-02     2.290    7.380   -5.090
37  1.00  7200.0  385.2  0.124E-02  0.570E-03     1.040    4.870   -3.830
38  1.00  7200.0  373.2  0.124E-02  0.509E-02     5.681   14.650   -8.969
39  1.00  7200.0  373.2  0.124E-02  0.373E-02     4.106   11.630   -7.524
40  1.00  7200.0  373.2  0.124E-02  0.226E-02     2.450    7.820   -5.370
41  1.00  7200.0  373.2  0.124E-02  0.124E-02     1.331    5.650   -4.319
42  1.00  7200.0  360.2  0.124E-02  0.509E-02     3.011    8.850   -5.839
43  1.00  7200.0  360.2  0.124E-02  0.373E-02     2.190    8.010   -5.820
44  1.00  7200.0  360.2  0.124E-02  0.226E-02     1.316    5.700   -4.384
45  1.00  7200.0  360.2  0.124E-02  0.124E-02     0.718    3.900   -3.182


                                          I        A%I<            E%I<

                                          1     0.1728E-07      0.6330E 04
                                          2     0.1000E 05      0.7000E 04
                                          3     0.1000E 07      0.4000E 04
                                          4     0.3550E 05      0.1086E 05
                                          5     0.3000E 08      0.3000E 04
                                          6     0.3000E 11      0.0
                                          7     0.4000E 11      0.0
                                          8     0.1000E 05      0.6400E 04
                                          9     0.5055E 05      0.9300E 04
                                         10     0.0             0.0
                                         11     0.0             0.0
```

TABLE 3 CHCl2F

```
   (RBR)/(CCL3BR)                     (C2CL6)/(CCL3BR)

  CALC       OBS      DIFF       CALC       OBS      DIFF

 11.789    18.100   -6.311      7.096     5.500     1.596
  9.014    11.720   -2.706      5.425     3.990     1.435
  6.478     6.510   -0.032      3.907     3.120     0.787
  4.152     3.240    0.912      2.521     2.240     0.281
  2.008     0.930    1.078      1.246     1.130     0.116
  9.014    10.330   -1.316      5.425     4.320     1.105
  6.994     5.600    1.394      3.446     3.010     0.436
  6.552     5.500    1.052      3.061     2.780     0.281
  5.689     3.400    2.289      2.366     2.130     0.236
  4.742     2.250    2.492      1.694     1.620     0.074
 15.867    18.250   -2.383      7.582     6.140     1.442
  7.914    10.330   -2.416      5.036     4.320     0.716
  5.116     8.360   -3.244      3.947     3.650     0.297
  3.000     4.370   -1.370      2.954     2.720     0.234
  1.649     2.700   -1.051      2.151     2.050     0.101
  0.926     1.490   -0.564      1.590     1.560     0.030
 23.027    25.920   -2.893      8.164     5.660     2.504
 15.867    18.600   -2.733      7.582     4.990     2.592
  9.029    12.490   -3.461      7.025     5.550     1.475
  4.752     8.630   -3.878      6.676     6.110     0.566
 17.769    21.500   -3.731      6.009     4.920     1.089
 11.148    13.110   -1.962      5.567     4.090     1.477
  9.014    10.260   -1.246      5.425     3.820     1.605
  5.262     6.840   -1.578      5.173     4.340     0.833
  2.816     3.860   -1.044      5.009     4.240     0.769
  1.274     2.250   -0.976      4.905     4.280     0.625
  7.129    10.500   -3.371      4.059     3.200     0.859
  5.116     7.480   -2.364      3.947     2.910     1.037
  3.032     5.400   -2.368      3.829     3.350     0.479
  1.639     2.920   -1.281      3.751     3.690     0.061
  4.147     5.200   -1.053      3.010     2.150     0.860
  3.000     4.640   -1.640      2.954     2.450     0.504
  1.793     2.970   -1.177      2.895     2.770     0.125
  0.974     1.990   -1.016      2.855     2.800     0.055


    C(I)

 0.5927E-04
 0.5125E 09
 0.1010E 09
 0.1056E 11
 0.9557E 08
 0.3000E 11
 0.4000E 11
 0.1146E 09
 0.2310E 10
 0.0
 0.0
```

TABLE 3

```
                                                                        ***  RESULTS  ***

                      INITIAL  VALUES                                   (CHCL3)/(CCL3BR)

NO   RLI     TIME     TEMP     (CCL3BR)      (CHCL2F)         CALC       OBS       DIFF

 1   1.00   9000.0   436.2   0.124E-02    0.373E-02        11.398    16.200    -4.802
 2   1.00   7200.0   436.2   0.124E-02    0.373E-02         8.671    11.100    -2.429
 3   1.00   5400.0   436.2   0.124E-02    0.373E-02         6.181     6.120     0.061
 4   1.00   3600.0   436.2   0.124E-02    0.373E-02         3.898     3.000     0.898
 5   1.00   1800.0   436.2   0.124E-02    0.373E-02         1.809     1.050     0.759
 6   1.00   7200.0   436.2   0.124E-02    0.373E-02         8.671     9.040    -0.369
 7   0.66   7200.0   436.2   0.124E-02    0.373E-02         6.691     5.350     1.341
 8   0.59   7200.0   436.2   0.124E-02    0.373E-02         6.257     5.350     0.907
 9   0.46   7200.0   436.2   0.124E-02    0.373E-02         5.411     3.490     1.921
10   0.33   7200.0   436.2   0.124E-02    0.373E-02         4.484     2.420     2.064
16   1.00   7200.0   449.2   0.124E-02    0.373E-02        15.271    16.520    -1.249
17   1.00   7200.0   433.2   0.124E-02    0.373E-02         7.611     9.040    -1.429
18   1.00   7200.0   423.2   0.124E-02    0.373E-02         4.914     6.840    -1.926
19   1.00   7200.0   411.2   0.124E-02    0.373E-02         2.874     3.870    -0.996
20   1.00   7200.0   398.2   0.124E-02    0.373E-02         1.573     2.440    -0.867
21   1.00   7200.0   386.2   0.124E-02    0.373E-02         0.879     1.580    -0.701
22   1.00   7200.0   449.2   0.124E-02    0.509E-02        22.168    23.680    -1.512
23   1.00   7200.0   449.2   0.124E-02    0.373E-02        15.271    17.380    -2.109
24   1.00   7200.0   449.2   0.124E-02    0.226E-02         8.687    11.930    -3.243
25   1.00   7200.0   449.2   0.124E-02    0.124E-02         4.571     8.090    -3.519
26   1.00   7200.0   436.2   0.124E-02    0.678E-02        17.102    19.250    -2.148
27   1.00   7200.0   436.2   0.124E-02    0.452E-02        10.726    11.830    -1.104
28   1.00   7200.0   436.2   0.124E-02    0.373E-02         8.671     8.900    -0.229
29   1.00   7200.0   436.2   0.124E-02    0.226E-02         5.061     5.960    -0.899
30   1.00   7200.0   436.2   0.124E-02    0.124E-02         2.708     3.680    -0.972
31   1.00   7200.0   436.2   0.124E-02    0.570E-03         1.225     2.220    -0.995
32   1.00   7200.0   423.2   0.124E-02    0.509E-02         6.848     9.970    -3.122
33   1.00   7200.0   423.2   0.124E-02    0.373E-02         4.914     6.730    -1.816
34   1.00   7200.0   423.2   0.124E-02    0.226E-02         2.912     5.100    -2.188
35   1.00   7200.0   423.2   0.124E-02    0.124E-02         1.573     2.850    -1.277
36   1.00   7200.0   411.2   0.124E-02    0.509E-02         3.973     4.900    -0.927
37   1.00   7200.0   411.2   0.124E-02    0.373E-02         2.874     4.440    -1.566
38   1.00   7200.0   411.2   0.124E-02    0.226E-02         1.717     3.150    -1.433
39   1.00   7200.0   411.2   0.124E-02    0.124E-02         0.933     2.300    -1.367


                                                 I         A%I<             E%I<

                                                 1      0.1514E-07       0.7170E 04
                                                 2      0.5000E 04       0.1000E 05
                                                 3      0.1000E 07       0.4000E 04
                                                 4      0.2287E 04       0.1330E 05
                                                 5      0.3000E 07       0.3000E 04
                                                 6      0.3000E 11       0.0
                                                 7      0.4000E 11       0.0
                                                 8      0.2000E 05       0.7500E 04
                                                 9      0.5055E 05       0.9300E 04
                                                10      0.0              0.0
                                                11      0.0              0.0
```

TABLE 4 CH2FCL

(RBR)/(CCL3BR) CALC	OBS	DIFF	(C2CL6)/(CCL3BR) CALC	OBS	DIFF
12.762	16.090	-3.328	2.905	5.270	-2.365
10.142	12.330	-2.188	2.464	4.540	-2.076
8.780	9.560	-0.780	2.258	3.460	-1.202
7.595	8.420	-0.825	2.039	3.240	-1.201
5.352	4.430	0.922	1.600	2.420	-0.820
3.314	2.390	0.924	1.142	1.790	-0.648
1.508	0.660	0.848	0.636	0.980	-0.344
5.912	5.210	0.702	1.541	2.260	-0.719
4.915	3.520	1.395	1.290	1.650	-0.360
3.862	2.420	1.442	1.015	1.230	-0.215
16.582	14.820	1.762	3.545	5.000	-1.455
8.418	9.410	-0.992	2.191	3.750	-1.559
5.258	5.900	-0.642	1.571	3.070	-1.499
3.086	3.090	-0.004	1.082	2.360	-1.278
1.768	2.090	-0.322	0.730	1.680	-0.950
0.932	0.880	0.052	0.465	1.420	-0.955
3.311	3.450	-0.139	1.378	5.070	-3.692
6.262	5.590	0.672	1.973	4.950	-2.977
10.270	9.680	0.590	2.657	4.800	-2.143
15.912	13.230	2.682	3.438	4.430	-0.992
20.974	18.560	2.414	4.075	4.610	-0.535
27.379	21.470	5.909	4.805	4.830	-0.025
1.891	2.300	-0.409	0.945	3.910	-2.965
3.576	4.200	-0.624	1.326	3.810	-2.484
5.821	6.420	-0.599	1.764	3.640	-1.876
8.780	9.740	-0.960	2.258	3.590	-1.332
11.568	12.330	-0.762	2.629	3.580	-0.951
14.834	14.850	-0.016	3.049	4.160	-1.111
1.130	0.950	0.180	0.680	2.820	-2.140
2.150	2.090	0.060	0.936	3.040	-2.104
3.498	3.070	0.428	1.236	2.680	-1.444
5.258	5.020	0.238	1.571	2.850	-1.279
6.789	5.580	1.209	1.827	2.480	-0.653
8.783	7.500	1.283	2.090	2.870	-0.780
0.682	0.810	-0.128	0.501	2.490	-1.989
1.315	1.170	0.145	0.673	2.430	-1.757
2.149	1.790	0.359	0.880	2.110	-1.230
3.228	2.760	0.468	1.117	2.450	-1.333
4.163	3.250	0.913	1.298	2.080	-0.782
5.281	4.600	0.681	1.489	2.290	-0.801

C(I)

0.2566E-04
0.1118E 09
0.1938E 08
0.7816E 11
0.9557E 08
0.4522E 11
0.1004E 09
0.1610E 08
0.2310E 10
0.3000E 11
0.3000E 11

TABLE 4

```
                                                                        ***  RESULTS  ***

                INITIAL  VALUES                                         (CHCL3)/(CCL3BR)

 NO  RLI    TIME    TEMP    (CCL3BR)     (CH2FCL)        CALC      OBS      DIFF

  1  1.00  7200.0  436.2  0.124E-02   0.373E-02     10.013   17.040   -7.027
  2  1.00  6000.0  436.2  0.124E-02   0.373E-02      7.796   11.820   -4.024
  3  1.00  5400.0  436.2  0.124E-02   0.373E-02      6.690    9.780   -3.090
  4  1.00  4800.0  436.2  0.124E-02   0.373E-02      5.700    7.880   -2.180
  5  1.00  3600.0  436.2  0.124E-02   0.373E-02      3.856    4.200   -0.344
  6  1.00  2400.0  436.2  0.124E-02   0.373E-02      2.233    2.010    0.223
  7  1.00  1200.0  436.2  0.124E-02   0.373E-02      0.892    0.470    0.422
  8  0.59  5400.0  436.2  0.124E-02   0.373E-02      4.473    5.080   -0.607
  9  0.46  5400.0  436.2  0.124E-02   0.373E-02      3.709    3.700    0.009
 10  0.33  5400.0  436.2  0.124E-02   0.373E-02      2.908    2.320    0.588
 16  1.00  5400.0  451.2  0.124E-02   0.373E-02     13.155   15.240   -2.085
 17  1.00  5400.0  435.2  0.124E-02   0.373E-02      6.393    8.610   -2.217
 18  1.00  5400.0  424.2  0.124E-02   0.373E-02      3.829    5.540   -1.711
 19  1.00  5400.0  412.2  0.124E-02   0.373E-02      2.123    2.790   -0.667
 20  1.00  5400.0  400.2  0.124E-02   0.373E-02      1.134    1.750   -0.616
 21  1.00  5400.0  387.2  0.124E-02   0.373E-02      0.545    0.960   -0.415
 22  1.00  5400.0  450.2  0.124E-02   0.570E-03      2.210    3.190   -0.980
 23  1.00  5400.0  450.2  0.124E-02   0.124E-02      4.505    5.430   -0.925
 24  1.00  5400.0  450.2  0.124E-02   0.226E-02      7.811    9.450   -1.639
 25  1.00  5400.0  450.2  0.124E-02   0.373E-02     12.592   12.900   -0.308
 26  1.00  5400.0  450.2  0.124E-02   0.509E-02     17.010   18.620   -1.610
 27  1.00  5400.0  450.2  0.124E-02   0.678E-02     22.685   21.350    1.335
 28  1.00  5400.0  436.2  0.124E-02   0.570E-03      1.197    2.450   -1.253
 29  1.00  5400.0  436.2  0.124E-02   0.124E-02      2.444    4.170   -1.726
 30  1.00  5400.0  436.2  0.124E-02   0.226E-02      4.226    6.100   -1.874
 31  1.00  5400.0  436.2  0.124E-02   0.373E-02      6.690    9.140   -2.450
 32  1.00  5400.0  436.2  0.124E-02   0.509E-02      9.029   11.350   -2.321
 33  1.00  5400.0  436.2  0.124E-02   0.678E-02     11.871   13.610   -1.739
 34  1.00  5400.0  424.2  0.124E-02   0.570E-03      0.675    1.340   -0.665
 35  1.00  5400.0  424.2  0.124E-02   0.124E-02      1.389    2.560   -1.171
 36  1.00  5400.0  424.2  0.124E-02   0.226E-02      2.413    3.290   -0.877
 37  1.00  5400.0  424.2  0.124E-02   0.373E-02      3.829    4.680   -0.851
 38  1.00  5400.0  424.2  0.124E-02   0.509E-02      5.108    5.370   -0.262
 39  1.00  5400.0  424.2  0.124E-02   0.678E-02      6.765    7.940   -1.175
 40  1.00  5400.0  413.2  0.124E-02   0.570E-03      0.382    0.720   -0.338
 41  1.00  5400.0  413.2  0.124E-02   0.124E-02      0.797    1.210   -0.413
 42  1.00  5400.0  413.2  0.124E-02   0.226E-02      1.398    1.960   -0.562
 43  1.00  5400.0  413.2  0.124E-02   0.373E-02      2.233    2.800   -0.567
 44  1.00  5400.0  413.2  0.124E-02   0.509E-02      2.989    3.260   -0.271
 45  1.00  5400.0  413.2  0.124E-02   0.678E-02      3.921    4.610   -0.689


                                                  I        A%I<              E%I<

                                                  1     0.1728E-07        0.6330E 04
                                                  2     0.3459E 04        0.9000E 04
                                                  3     0.1928E 07        0.2000E 04
                                                  4     0.3000E 04        0.1480E 05
                                                  5     0.3000E 07        0.3000E 04
                                                  6     0.4522E 11        0.0
                                                  7     0.1004E 09        0.0
                                                  8     0.1000E 05        0.6400E 04
                                                  9     0.5055E 05        0.9300E 04
                                                 10     0.3000E 11        0.0
                                                 11     0.3000E 11        0.0
```

TABLE 5 CH2CL2

```
     (RBR)/(CCL3BR)                  (C2CL6)/(CCL3BR)

  CALC      OBS       DIFF       CALC      OBS       DIFF

 22.925   16.760     6.165      5.006     2.140     2.866
 15.109   12.520     2.589      3.589     1.870     1.719
 10.264    7.540     2.724      2.635     1.390     1.245
  8.105    5.350     2.755      2.178     1.330     0.848
  6.128    3.620     2.508      1.731     0.930     0.801
  2.697    1.240     1.457      0.858     0.620     0.238
  9.155    6.410     2.745      2.010     1.220     0.790
  5.936    3.070     2.866      1.184     0.620     0.564
  3.747    1.630     2.117      0.644     0.410     0.234
 29.006   21.770     7.236      5.750     2.420     3.330
 17.950   12.630     5.320      4.057     1.960     2.097
  9.806    8.920     0.886      2.652     1.590     1.062
  5.283    4.870     0.413      1.729     1.230     0.499
  3.332    2.550     0.782      1.259     0.900     0.359
  1.956    1.740     0.216      0.872     0.730     0.142
 37.708   22.930    14.778      6.406     2.280     4.126
 29.006   18.820    10.186      5.750     2.230     3.520
 18.968   14.580     4.388      4.835     2.450     2.385
 11.112    9.710     1.402      3.971     2.460     1.511
 46.601   24.530    22.071      5.652     1.790     3.862
 42.150   23.440    18.710      5.452     1.760     3.692
 37.673   22.640    15.033      5.245     1.780     3.465
 33.852   21.100    12.752      5.059     1.870     3.189
 29.302   19.030    10.272      4.817     1.900     2.917
 25.175   17.800     7.375      4.573     1.970     2.603
 20.985   14.940     6.045      4.290     1.790     2.500
 17.950   14.050     3.900      4.057     1.880     2.177
 14.299   10.910     3.389      3.736     1.800     1.936
 11.827   10.050     1.777      3.491     1.700     1.791
  9.232    8.540     0.692      3.209     1.790     1.419
  6.950    6.960    -0.010      2.938     1.670     1.268
  3.345    4.290    -0.945      2.466     1.680     0.786
 13.766   11.010     2.756      3.050     1.460     1.590
 10.696    8.840     1.856      2.817     1.410     1.407
  7.013    6.230     0.783      2.460     1.520     0.940
  4.093    4.330    -0.237      2.110     1.610     0.500
  7.835    6.100     1.735      2.044     1.190     0.854
  6.044    5.340     0.704      1.897     1.100     0.797
  3.905    4.210    -0.305      1.673     1.120     0.553
  2.248    2.930    -0.682      1.458     1.180     0.278


    C(I)

 0.2566E-04
 0.2541E 08
 0.1010E 08
 0.9815E 10
 0.9557E 08
 0.6724E 11
 0.2211E 10
 0.1610E 08
 0.2310E 10
 0.0
 0.0
```

TABLE 5

```
                                                              *** RESULTS ***

                    INITIAL  VALUES                            (CHCL3)/(CCL3BR)

NO   RLI    TIME     TEMP    (CCL3BR)     (CH2CL2)       CALC      OBS      DIFF

 1   1.00   9660.0   381.2   0.124E-02    0.373E-02     18.964    18.670     0.294
 2   1.00   7200.0   381.2   0.124E-02    0.373E-02     12.102    13.790    -1.688
 3   1.00   5400.0   381.2   0.124E-02    0.373E-02      7.964     8.620    -0.656
 4   1.00   4500.0   381.2   0.124E-02    0.373E-02      6.165     5.850     0.315
 5   1.00   3600.0   381.2   0.124E-02    0.373E-02      4.555     4.340     0.215
 6   1.00   1800.0   381.2   0.124E-02    0.373E-02      1.888     1.610     0.278
 7   0.56   7200.0   381.2   0.124E-02    0.373E-02      7.317     7.640    -0.323
 8   0.33   7200.0   381.2   0.124E-02    0.373E-02      4.805     4.040     0.765
 9   0.18   7200.0   381.2   0.124E-02    0.373E-02      3.117     2.340     0.777
15   1.00   7200.0   396.2   0.124E-02    0.373E-02     24.010    24.230    -0.220
16   1.00   7200.0   385.2   0.124E-02    0.373E-02     14.514    13.340     1.174
17   1.00   7200.0   371.2   0.124E-02    0.373E-02      7.657    10.570    -2.913
18   1.00   7200.0   357.2   0.124E-02    0.373E-02      3.967     5.830    -1.863
19   1.00   7200.0   347.2   0.124E-02    0.373E-02      2.434     3.430    -0.996
20   1.00   7200.0   336.2   0.124E-02    0.373E-02      1.390     2.490    -1.100
21   1.00   7200.0   396.2   0.124E-02    0.509E-02     31.839    26.600     5.239
22   1.00   7200.0   396.2   0.124E-02    0.373E-02     24.010    22.120     1.890
23   1.00   7200.0   396.2   0.124E-02    0.226E-02     15.295    17.220    -1.925
24   1.00   7200.0   396.2   0.124E-02    0.124E-02      8.771    12.020    -3.249
25   1.00   7200.0   385.2   0.124E-02    0.113E-01     41.112    30.230    10.882
26   1.00   7200.0   385.2   0.124E-02    0.102E-01     36.883    28.280     8.603
27   1.00   7200.0   385.2   0.124E-02    0.904E-02     32.642    27.600     5.042
28   1.00   7200.0   385.2   0.124E-02    0.802E-02     29.043    25.800     3.243
29   1.00   7200.0   385.2   0.124E-02    0.678E-02     24.796    21.750     3.046
30   1.00   7200.0   385.2   0.124E-02    0.565E-02     20.993    20.470     0.523
31   1.00   7200.0   385.2   0.124E-02    0.452E-02     17.202    16.980     0.222
32   1.00   7200.0   385.2   0.124E-02    0.373E-02     14.514    15.720    -1.206
33   1.00   7200.0   385.2   0.124E-02    0.283E-02     11.360    11.760    -0.400
34   1.00   7200.0   385.2   0.124E-02    0.226E-02      9.278    11.240    -1.962
35   1.00   7200.0   385.2   0.124E-02    0.170E-02      7.146     9.320    -2.174
36   1.00   7200.0   385.2   0.124E-02    0.124E-02      5.316     7.380    -2.064
37   1.00   7200.0   385.2   0.124E-02    0.570E-03      2.511     4.870    -2.359
38   1.00   7200.0   373.2   0.124E-02    0.509E-02     11.093    14.650    -3.557
39   1.00   7200.0   373.2   0.124E-02    0.373E-02      8.396    11.630    -3.234
40   1.00   7200.0   373.2   0.124E-02    0.226E-02      5.314     7.820    -2.506
41   1.00   7200.0   373.2   0.124E-02    0.124E-02      3.008     5.650    -2.642
42   1.00   7200.0   360.2   0.124E-02    0.509E-02      6.115     8.850    -2.735
43   1.00   7200.0   360.2   0.124E-02    0.373E-02      4.578     8.010    -3.432
44   1.00   7200.0   360.2   0.124E-02    0.226E-02      2.840     5.700    -2.860
45   1.00   7200.0   360.2   0.124E-02    0.124E-02      1.576     3.900    -2.324


                                                   I        A%I<             E%I<

                                                   1     0.1728E-07       0.6330E 04
                                                   2     0.2504E 05       0.6000E 04
                                                   3     0.1000E 06       0.4000E 04
                                                   4     0.3550E 05       0.1086E 05
                                                   5     0.3000E 07       0.3000E 04
                                                   6     0.6724E 11       0.0
                                                   7     0.2211E 10       0.0
                                                   8     0.1000E 05       0.6400E 04
                                                   9     0.5055E 05       0.9300E 04
                                                  10     0.0              0.0
                                                  11     0.0              0.0
```

TABLE 5'   CH2CL2

```
      (RBR)/(CCL3BR)                 (C2CL6)/(CCL3BR)

  CALC      OBS      DIFF       CALC      OBS      DIFF

 11.301   16.760   -5.459      2.202     2.140    0.062
  8.085   12.520   -4.435      1.714     1.870   -0.156
  5.873    7.540   -1.667      1.341     1.390   -0.049
  4.812    5.350   -0.538      1.146     1.330   -0.184
  3.782    3.620   -0.162      0.943     0.930    0.013
  1.818    1.240    0.578      0.505     0.620   -0.115
  5.684    6.410   -0.726      1.112     1.220   -0.108
  4.160    3.070    1.090      0.740     0.620    0.120
  2.935    1.630    1.305      0.453     0.410    0.043
 14.361   21.770   -7.409      2.597     2.420    0.177
  9.441   12.630   -3.189      1.918     1.960   -0.042
  5.442    8.920   -3.478      1.285     1.590   -0.305
  3.045    4.870   -1.825      0.838     1.230   -0.392
  1.963    2.550   -0.587      0.603     0.900   -0.297
  1.177    1.740   -0.563      0.410     0.730   -0.320
 18.816   22.930   -4.114      2.880     2.280    0.600
 14.361   18.820   -4.459      2.597     2.230    0.367
  9.493   14.580   -5.087      2.205     2.450   -0.245
  5.845    9.710   -3.865      1.824     2.460   -0.636
 26.122   24.530    1.592      2.699     1.790    0.909
 23.529   23.440    0.089      2.610     1.760    0.850
 20.879   22.640   -1.761      2.511     1.780    0.731
 18.608   21.100   -2.492      2.420     1.870    0.550
 15.912   19.030   -3.118      2.298     1.900    0.398
 13.501   17.800   -4.299      2.175     1.970    0.205
 11.113   14.940   -3.827      2.033     1.790    0.243
  9.441   14.050   -4.609      1.918     1.880    0.038
  7.505   10.910   -3.405      1.763     1.800   -0.037
  6.243   10.050   -3.807      1.645     1.700   -0.055
  4.948    8.540   -3.592      1.509     1.790   -0.281
  3.819    6.960   -3.141      1.376     1.670   -0.294
  1.972    4.290   -2.318      1.133     1.680   -0.547
  7.690   11.010   -3.320      1.489     1.460    0.029
  5.897    8.840   -2.943      1.363     1.410   -0.047
  3.879    6.230   -2.351      1.178     1.520   -0.342
  2.344    4.330   -1.986      0.996     1.610   -0.614
  4.526    6.100   -1.574      1.003     1.190   -0.187
  3.459    5.340   -1.881      0.921     1.100   -0.179
  2.252    4.210   -1.958      0.801     1.120   -0.319
  1.338    2.930   -1.592      0.686     1.180   -0.494


    C(I)

 0.2566E-04
 0.2541E 08
 0.1010E 08
 0.9815E 10
 0.9557E 08
 0.6724E 11
 0.2211E 10
 0.1610E 08
 0.2310E 10
 0.3000E 11
 0.3000E 11
```

TABLE 5'

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                                                                        *** RESULTS ***

                          INITIAL  VALUES                               (CHCL3)/(CCL3BR)

 NO   RLI     TIME     TEMP     (CCL3BR)      (CH2CL2)        CALC       OBS      DIFF

  1   1.00   9660.0   381.2   0.124E-02    0.373E-02        9.283    18.670    -9.387
  2   1.00   7200.0   381.2   0.124E-02    0.373E-02        6.487    13.790    -7.303
  3   1.00   5400.0   381.2   0.124E-02    0.373E-02        4.607     8.620    -4.013
  4   1.00   4500.0   381.2   0.124E-02    0.373E-02        3.723     5.850    -2.127
  5   1.00   3600.0   381.2   0.124E-02    0.373E-02        2.879     4.340    -1.461
  6   1.00   1800.0   381.2   0.124E-02    0.373E-02        1.328     1.610    -0.282
  7   0.56   7200.0   381.2   0.124E-02    0.373E-02        4.615     7.640    -3.025
  8   0.33   7200.0   381.2   0.124E-02    0.373E-02        3.438     4.040    -0.602
  9   0.18   7200.0   381.2   0.124E-02    0.373E-02        2.488     2.340     0.148
 15   1.00   7200.0   396.2   0.124E-02    0.373E-02       11.899    24.230   -12.331
 16   1.00   7200.0   385.2   0.124E-02    0.373E-02        7.643    13.340    -5.697
 17   1.00   7200.0   371.2   0.124E-02    0.373E-02        4.263    10.570    -6.307
 18   1.00   7200.0   357.2   0.124E-02    0.373E-02        2.301     5.830    -3.529
 19   1.00   7200.0   347.2   0.124E-02    0.373E-02        1.447     3.430    -1.983
 20   1.00   7200.0   336.2   0.124E-02    0.373E-02        0.848     2.490    -1.642
 21   1.00   7200.0   396.2   0.124E-02    0.509E-02       16.034    26.600   -10.566
 22   1.00   7200.0   396.2   0.124E-02    0.373E-02       11.899    22.120   -10.221
 23   1.00   7200.0   396.2   0.124E-02    0.226E-02        7.513    17.220    -9.707
 24   1.00   7200.0   396.2   0.124E-02    0.124E-02        4.398    12.020    -7.622
 25   1.00   7200.0   385.2   0.124E-02    0.113E-01       23.459    30.230    -6.771
 26   1.00   7200.0   385.2   0.124E-02    0.102E-01       20.961    28.280    -7.319
 27   1.00   7200.0   385.2   0.124E-02    0.904E-02       18.414    27.600    -9.186
 28   1.00   7200.0   385.2   0.124E-02    0.802E-02       16.242    25.800    -9.558
 29   1.00   7200.0   385.2   0.124E-02    0.678E-02       13.677    21.750    -8.073
 30   1.00   7200.0   385.2   0.124E-02    0.565E-02       11.403    20.470    -9.067
 31   1.00   7200.0   385.2   0.124E-02    0.452E-02        9.178    16.980    -7.802
 32   1.00   7200.0   385.2   0.124E-02    0.373E-02        7.643    15.720    -8.077
 33   1.00   7200.0   385.2   0.124E-02    0.283E-02        5.903    11.760    -5.857
 34   1.00   7200.0   385.2   0.124E-02    0.226E-02        4.797    11.240    -6.443
 35   1.00   7200.0   385.2   0.124E-02    0.170E-02        3.697     9.320    -5.623
 36   1.00   7200.0   385.2   0.124E-02    0.124E-02        2.772     7.380    -4.608
 37   1.00   7200.0   385.2   0.124E-02    0.570E-03        1.357     4.870    -3.513
 38   1.00   7200.0   373.2   0.124E-02    0.509E-02        6.278    14.650    -8.372
 39   1.00   7200.0   373.2   0.124E-02    0.373E-02        4.642    11.630    -6.988
 40   1.00   7200.0   373.2   0.124E-02    0.226E-02        2.878     7.820    -4.942
 41   1.00   7200.0   373.2   0.124E-02    0.124E-02        1.631     5.650    -4.019
 42   1.00   7200.0   360.2   0.124E-02    0.509E-02        3.592     8.850    -5.258
 43   1.00   7200.0   360.2   0.124E-02    0.373E-02        2.635     8.010    -5.375
 44   1.00   7200.0   360.2   0.124E-02    0.226E-02        1.605     5.700    -4.095
 45   1.00   7200.0   360.2   0.124E-02    0.124E-02        0.889     3.900    -3.011


                                                 I         A%I<             E%I<

                                                 1     0.1728E-07       0.6330E 04
                                                 2     0.2504E 05       0.6000E 04
                                                 3     0.1000E 06       0.4000E 04
                                                 4     0.3550E 05       0.1086E 05
                                                 5     0.3000E 07       0.3000E 04
                                                 6     0.6724E 11       0.0
                                                 7     0.2211E 10       0.0
                                                 8     0.1000E 05       0.6400E 04
                                                 9     0.5055E 05       0.9300E 04
                                                10     0.3000E 11       0.0
                                                11     0.3000E 11       0.0
```

TABLE 6 CHCL2F

```
      (RBR)/(CCL3BR)                    (C2CL6)/(CCL3BR)

  CALC      OBS      DIFF          CALC      OBS      DIFF

 13.552   18.100   -4.548          7.020    5.500    1.520
 10.316   11.720   -1.404          5.325    3.990    1.335
  7.380    6.510    0.870          3.797    3.120    0.677
  4.704    3.240    1.464          2.413    2.240    0.173
  2.255    0.930    1.325          1.154    1.130    0.024
 10.316   10.330   -0.014          5.325    4.320    1.005
  7.964    5.600    2.364          3.333    3.010    0.323
  7.450    5.500    1.950          2.947    2.780    0.167
  6.449    3.400    3.049          2.250    2.130    0.120
  5.351    2.250    3.101          1.580    1.620   -0.040
 16.805   18.250   -1.445          7.359    6.140    1.219
  9.228   10.330   -1.102          4.952    4.320    0.632
  6.369    8.360   -1.991          3.897    3.650    0.247
  4.068    4.370   -0.302          2.924    2.720    0.204
  2.477    2.700   -0.223          2.132    2.050    0.082
  1.544    1.490    0.054          1.578    1.560    0.018
 24.430   25.920   -1.490          7.845    5.660    2.185
 16.805   18.600   -1.795          7.359    4.990    2.369
  9.548   12.490   -2.942          6.896    5.550    1.346
  5.021    8.630   -3.609          6.608    6.110    0.498
 20.484   21.500   -1.016          5.823    4.920    0.903
 12.779   13.110   -0.331          5.446    4.090    1.356
 10.316   10.260    0.056          5.325    3.820    1.505
  6.005    6.840   -0.835          5.114    4.340    0.774
  3.207    3.860   -0.653          4.976    4.240    0.736
  1.449    2.250   -0.801          4.890    4.280    0.610
  8.899   10.500   -1.601          3.992    3.200    0.792
  6.369    7.480   -1.111          3.897    2.910    0.987
  3.764    5.400   -1.636          3.800    3.350    0.450
  2.030    2.920   -0.890          3.734    3.690    0.044
  5.635    5.200    0.435          2.971    2.150    0.821
  4.068    4.640   -0.572          2.924    2.450    0.474
  2.425    2.970   -0.545          2.877    2.770    0.107
  1.316    1.990   -0.674          2.845    2.800    0.045


    C(I)

 0.5927E-04
 0.4444E 08
 0.7120E 09
 0.1056E 11
 0.1303E 11
 0.7900E 11
 0.4917E 11
 0.3437E 08
 0.2310E 10
 0.0
 0.0
```

TABLE 6

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                                                                      ***  RESULTS  ***

                          INITIAL  VALUES                              (CHCL3)/(CCL3BR)

NO  RLI    TIME    TEMP   (CCL3BR)    (CHCL2F)         CALC      OBS       DIFF

 1  1.00  9000.0  436.2  0.124E-02   0.373E-02        13.532    16.200    -2.668
 2  1.00  7200.0  436.2  0.124E-02   0.373E-02        10.299    11.100    -0.801
 3  1.00  5400.0  436.2  0.124E-02   0.373E-02         7.366     6.120     1.246
 4  1.00  3600.0  436.2  0.124E-02   0.373E-02         4.692     3.000     1.692
 5  1.00  1800.0  436.2  0.124E-02   0.373E-02         2.244     1.050     1.194
 6  1.00  7200.0  436.2  0.124E-02   0.373E-02        10.299     9.040     1.259
 7  0.66  7200.0  436.2  0.124E-02   0.373E-02         7.949     5.350     2.599
 8  0.59  7200.0  436.2  0.124E-02   0.373E-02         7.436     5.350     2.086
 9  0.46  7200.0  436.2  0.124E-02   0.373E-02         6.435     3.490     2.945
10  0.33  7200.0  436.2  0.124E-02   0.373E-02         5.338     2.420     2.918
16  1.00  7200.0  449.2  0.124E-02   0.373E-02        16.778    16.520     0.258
17  1.00  7200.0  433.2  0.124E-02   0.373E-02         9.213     9.040     0.173
18  1.00  7200.0  423.2  0.124E-02   0.373E-02         6.359     6.840    -0.481
19  1.00  7200.0  411.2  0.124E-02   0.373E-02         4.061     3.870     0.191
20  1.00  7200.0  398.2  0.124E-02   0.373E-02         2.473     2.440     0.033
21  1.00  7200.0  386.2  0.124E-02   0.373E-02         1.542     1.580    -0.038
22  1.00  7200.0  449.2  0.124E-02   0.509E-02        24.390    23.680     0.710
23  1.00  7200.0  449.2  0.124E-02   0.373E-02        16.778    17.380    -0.602
24  1.00  7200.0  449.2  0.124E-02   0.226E-02         9.532    11.930    -2.398
25  1.00  7200.0  449.2  0.124E-02   0.124E-02         5.013     8.090    -3.077
26  1.00  7200.0  436.2  0.124E-02   0.678E-02        20.450    19.250     1.200
27  1.00  7200.0  436.2  0.124E-02   0.452E-02        12.758    11.830     0.928
28  1.00  7200.0  436.2  0.124E-02   0.373E-02        10.299     8.900     1.399
29  1.00  7200.0  436.2  0.124E-02   0.226E-02         5.995     5.960     0.035
30  1.00  7200.0  436.2  0.124E-02   0.124E-02         3.202     3.680    -0.478
31  1.00  7200.0  436.2  0.124E-02   0.570E-03         1.446     2.220    -0.774
32  1.00  7200.0  423.2  0.124E-02   0.509E-02         8.885     9.970    -1.085
33  1.00  7200.0  423.2  0.124E-02   0.373E-02         6.359     6.730    -0.371
34  1.00  7200.0  423.2  0.124E-02   0.226E-02         3.758     5.100    -1.342
35  1.00  7200.0  423.2  0.124E-02   0.124E-02         2.027     2.850    -0.823
36  1.00  7200.0  411.2  0.124E-02   0.509E-02         5.626     4.900     0.726
37  1.00  7200.0  411.2  0.124E-02   0.373E-02         4.061     4.440    -0.379
38  1.00  7200.0  411.2  0.124E-02   0.226E-02         2.421     3.150    -0.729
39  1.00  7200.0  411.2  0.124E-02   0.124E-02         1.314     2.300    -0.986


                                                  I        A%I<            E%I<

                                                  1     0.1514E-07      0.7170E 04
                                                  2     0.1000E 05      0.7280E 04
                                                  3     0.7050E 07      0.4000E 04
                                                  4     0.2287E 04      0.1330E 05
                                                  5     0.1000E 09      0.4221E 04
                                                  6     0.7900E 11      0.0
                                                  7     0.4917E 11      0.0
                                                  8     0.6000E 04      0.7500E 04
                                                  9     0.5055E 05      0.9300E 04
                                                 10     0.0             0.0
                                                 11     0.0             0.0
```

TABLE 6' CHCL2F

(RBR)/(CCL3BR)			(C2CL6)/(CCL3BR)		
CALC	OBS	DIFF	CALC	OBS	DIFF
11.703	18.100	-6.397	5.430	5.500	-0.070
8.990	11.720	-2.730	4.159	3.990	0.169
6.486	6.510	-0.024	2.992	3.120	-0.128
4.165	3.240	0.925	1.916	2.240	-0.324
2.011	0.930	1.081	0.924	1.130	-0.206
8.990	10.330	-1.340	4.159	4.320	-0.161
7.008	5.600	1.408	2.629	3.010	-0.381
6.569	5.500	1.069	2.329	2.780	-0.451
5.705	3.400	2.305	1.785	2.130	-0.345
4.751	2.250	2.501	1.258	1.620	-0.362
14.453	18.250	-3.797	5.667	6.140	-0.473
8.061	10.330	-2.269	3.878	4.320	-0.442
5.600	8.360	-2.760	3.073	3.650	-0.577
3.597	4.370	-0.773	2.320	2.720	-0.400
2.200	2.700	-0.500	1.699	2.050	-0.351
1.376	1.490	-0.114	1.261	1.560	-0.299
20.813	25.920	-5.107	5.983	5.660	0.323
14.453	18.600	-4.147	5.667	4.990	0.677
8.286	12.490	-4.204	5.360	5.550	-0.190
4.382	8.630	-4.248	5.166	6.110	-0.944
17.633	21.500	-3.867	4.491	4.920	-0.429
11.104	13.110	-2.006	4.241	4.090	0.151
8.990	10.260	-1.270	4.159	3.820	0.339
5.261	6.840	-1.579	4.016	4.340	-0.324
2.819	3.860	-1.041	3.921	4.240	-0.319
1.276	2.250	-0.974	3.862	4.280	-0.418
7.800	10.500	-2.700	3.137	3.200	-0.063
5.600	7.480	-1.880	3.073	2.910	0.163
3.319	5.400	-2.081	3.005	3.350	-0.345
1.794	2.920	-1.126	2.960	3.690	-0.730
4.974	5.200	-0.226	2.351	2.150	0.201
3.597	4.640	-1.043	2.320	2.450	-0.130
2.149	2.970	-0.821	2.287	2.770	-0.483
1.168	1.990	-0.822	2.264	2.800	-0.536

C(I)
0.5927E-04
0.4444E 08
0.7120E 09
0.1056E 11
0.1303E 11
0.7900E 11
0.4917E 11
0.3437E 08
0.2310E 10
0.3000E 11
0.3000E 11

TABLE 6'

```
                                                                        *** RESULTS ***

                         INITIAL  VALUES                                (CHCL3)/(CCL3BR)

 NO   RLI     TIME    TEMP     (CCL3BR)      (CHCL2F)         CALC       OBS      DIFF

  1   1.00   9000.0   436.2   0.124E-02    0.373E-02       11.685    16.200    -4.515
  2   1.00   7200.0   436.2   0.124E-02    0.373E-02        8.974    11.100    -2.126
  3   1.00   5400.0   436.2   0.124E-02    0.373E-02        6.472     6.120     0.352
  4   1.00   3600.0   436.2   0.124E-02    0.373E-02        4.154     3.000     1.154
  5   1.00   1800.0   436.2   0.124E-02    0.373E-02        2.000     1.050     0.950
  6   1.00   7200.0   436.2   0.124E-02    0.373E-02        8.974     9.040    -0.066
  7   0.66   7200.0   436.2   0.124E-02    0.373E-02        6.994     5.350     1.644
  8   0.59   7200.0   436.2   0.124E-02    0.373E-02        6.555     5.350     1.205
  9   0.46   7200.0   436.2   0.124E-02    0.373E-02        5.692     3.490     2.202
 10   0.33   7200.0   436.2   0.124E-02    0.373E-02        4.739     2.420     2.319
 16   1.00   7200.0   449.2   0.124E-02    0.373E-02       14.428    16.520    -2.092
 17   1.00   7200.0   433.2   0.124E-02    0.373E-02        8.047     9.040    -0.993
 18   1.00   7200.0   423.2   0.124E-02    0.373E-02        5.590     6.840    -1.250
 19   1.00   7200.0   411.2   0.124E-02    0.373E-02        3.591     3.870    -0.279
 20   1.00   7200.0   398.2   0.124E-02    0.373E-02        2.196     2.440    -0.244
 21   1.00   7200.0   386.2   0.124E-02    0.373E-02        1.373     1.580    -0.207
 22   1.00   7200.0   449.2   0.124E-02    0.509E-02       20.776    23.680    -2.904
 23   1.00   7200.0   449.2   0.124E-02    0.373E-02       14.428    17.380    -2.952
 24   1.00   7200.0   449.2   0.124E-02    0.226E-02        8.272    11.930    -3.658
 25   1.00   7200.0   449.2   0.124E-02    0.124E-02        4.375     8.090    -3.715
 26   1.00   7200.0   436.2   0.124E-02    0.678E-02       17.602    19.250    -1.648
 27   1.00   7200.0   436.2   0.124E-02    0.452E-02       11.085    11.830    -0.745
 28   1.00   7200.0   436.2   0.124E-02    0.373E-02        8.974     8.900     0.074
 29   1.00   7200.0   436.2   0.124E-02    0.226E-02        5.252     5.960    -0.708
 30   1.00   7200.0   436.2   0.124E-02    0.124E-02        2.814     3.680    -0.866
 31   1.00   7200.0   436.2   0.124E-02    0.570E-03        1.274     2.220    -0.946
 32   1.00   7200.0   423.2   0.124E-02    0.509E-02        7.787     9.970    -2.183
 33   1.00   7200.0   423.2   0.124E-02    0.373E-02        5.590     6.730    -1.140
 34   1.00   7200.0   423.2   0.124E-02    0.226E-02        3.314     5.100    -1.786
 35   1.00   7200.0   423.2   0.124E-02    0.124E-02        1.791     2.850    -1.059
 36   1.00   7200.0   411.2   0.124E-02    0.509E-02        4.965     4.900     0.065
 37   1.00   7200.0   411.2   0.124E-02    0.373E-02        3.591     4.440    -0.849
 38   1.00   7200.0   411.2   0.124E-02    0.226E-02        2.145     3.150    -1.005
 39   1.00   7200.0   411.2   0.124E-02    0.124E-02        1.166     2.300    -1.134


                                                    I         A%I<           E%I<

                                                    1     0.1514E-07     0.7170E 04
                                                    2     0.1000E 05     0.7280E 04
                                                    3     0.7050E 07     0.4000E 04
                                                    4     0.2287E 04     0.1330E 05
                                                    5     0.1000E 09     0.4221E 04
                                                    6     0.7900E 11     0.0
                                                    7     0.4917E 11     0.0
                                                    8     0.6000E 04     0.7500E 04
                                                    9     0.5055E 05     0.9300E 04
                                                   10     0.3000E 11     0.0
                                                   11     0.3000E 11     0.0
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