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**A STUDY OF THE HALOGENATION OF ALIPHATIC
HYDROCARBONS AND DERIVATIVES THEREOF**

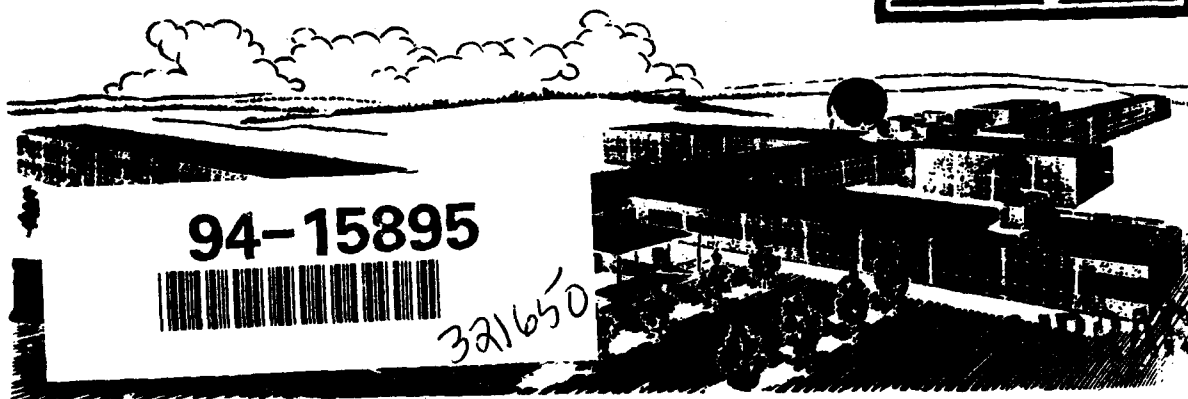
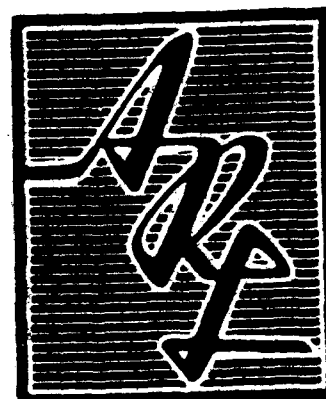
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**THE UNIVERSITY OF SHEFFIELD
SHEFFIELD, ENGLAND**

AUGUST 1961

**AERONAUTICAL RESEARCH LABORATORY
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE**

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P. S. FREDRICKS

THE UNIVERSITY OF SHEFFIELD
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AERONAUTICAL RESEARCH LABORATORY
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This final technical report was prepared by the University of Sheffield, Sheffield, England, under contract AF 61(052)-63 on Task 70317, "Carbon Heteroatom Systems" of Project 7023, "Research on New Chemical Systems and Methods of Synthesis", during the period 1 March 1958 to 31 March 1961. The original contract was established 1 March 1958.

Dr. Leonard Spialter of the Chemistry Research Branch, Aeronautical Research Laboratory of the Office of Aerospace Research, United States Air Force, was the task scientist.

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ABSTRACT

Fluorination, chlorination and bromination of the 1- and 2- haloalkanes and some related compounds have been investigated in the gas phase. Fluorination proved to be the least selective process, bromination the most. A substituent halogen accelerates bromination at the carbon atom to which substituent is attached, but chlorination is slightly and fluorination strongly retarded at this position. All three modes of halogenation are retarded at adjacent sites; fluorination being relatively most affected, bromination the least. Experiments have been carried out over a range of temperatures and indicate that changes in reactivity observed are due principally to changes in activation energy for hydrogen abstraction. These results throw light on the factors controlling hydrogen abstraction by free radicals.

It was also found that radicals of the type $\text{-CHX}\dot{\text{C}}\text{H-}$ where X is a halogen atom are relatively unstable. This is of some importance in allylic substitution. Another unexpected observation was that $\text{RCHX}\dot{\text{C}}\text{HR}$ radicals are stereospecific in their reactions.

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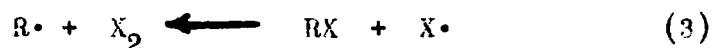
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INTRODUCTION

(a) General Background

In spite of the intense technical interest in the preparation of organic fluorine compounds, the investigation of the reaction between elementary fluorine and organic compounds has been largely qualitative. This qualitative work, which was begun by Moissan himself¹, has been most extensively developed by Bigelow². However, little attention has been paid to quantitative studies, and practically no information is available about the influence different substituents have on the course of fluorination. The mechanism of fluorination is beyond doubt identical to that of chlorination³. Chlorination is easier to study and a considerable body of



data is available about the mechanism and kinetics of chlorination.³ For this reason it seemed suitable to attempt to study fluorination by comparing it with chlorination under similar conditions. Work on these lines had already been undertaken in these laboratories, and the fluorination and chlorination of n-butane and iso-butane had been compared in both the gas and liquid phases^{4,5}. As the work proceeded it became clear that similar experiments with bromination would greatly assist the theoretical interpretation of the results. Thus a complete study of the halogenation (fluorination,

chlorination and bromination) of the monohalobutanes was undertaken.

(b) Objectives of the Present Investigation

The work described in the present report was intended to be a direct continuation of the halogenation studies already undertaken in this laboratory. Substituted aliphatic compounds were to be fluorinated, chlorinated and brominated in order to obtain a picture of the effect different substituents have on these reactions. The easiest and most interesting substituents to commence this work are the halogens. There has been considerable previous study of the halogenation of the alkyl halides^{6,7,8,9,10,11,12,13}, usually involving the same halogen as reagent and substituent. The early workers made the generalisation that the halogen atom already in the molecule directs attack away from itself⁶ and this has been accepted¹³ in spite of the fact that the results already available show that this is a poor approximation of the truth. The present work described below involves the fluorine both as a substituent and reagent for the first time, it also provides far more precise data for chlorination and bromination than available previously.

E X P E R I M E N T A L

(a) General Procedure

Two gaseous streams, one of the halogen and nitrogen and the other of the alkyl halide in nitrogen, were preheated separately to the intended

reaction temperature and then brought together in a mixing vessel. Reaction occurred in this mixing vessel and a subsequent reaction spiral, both of which were maintained at the same temperature. After passing through the reactor the gas stream continued through a packed column to remove unchanged halogen and a second column to remove the halogen halide formed and finally through a trap maintained at -70° in which the reaction products and unchanged alkyl halide condensed. Samples of liquid were then withdrawn from the trap for injection into a gas phase chromatography column which was used for both the separation and estimation of the components of the product.

By far the greatest problem in the present work has been the correct identification of the various isomer formed during each halogenation. When dihalides of known structure were available the procedure was to chromatograph the product and then add the individual dihalides one at a time to the reaction product and see which peak had been enlarged. By this means the peaks on the original chromatogram could be identified unequivocally. However, in many cases synthesis of the dihalides would have been tedious in the extreme, for instance no satisfactory synthesis of unsymmetrical 1:2 dihalides is known. Another method was to halogenate a 2-halobutane and compare the retention times of the products, e.g. chlorination of n-butyl fluoride yielded four dihalide peaks, fluorination of 2-chlorobutane likewise yielded four dihalide peaks, two of which had identical retention times to two peaks from the former. These must therefore

be 1-fluoro-2-chlorobutane and 1-fluoro-3-chlorobutane. It was possible in some cases to identify peaks by analogy, e.g. chlorination of n-butyl fluoride and n-butyl chloride yielded chromatograms of identical shape, differing only slightly in their relative areas. All peaks from the chlorination of butyl chloride had been identified by addition of known compounds. The final peak from butyl fluoride which corresponded to the 1:4-dichlorobutane peak was identified as 1-fluoro-4-chlorobutane by the same means. The reasonable assumption was therefore that the other peaks from butyl fluoride corresponded with those from butyl chloride similarly.

(b) Preparation and Synthesis of Authentic Dihalides for Identification

1:1-Dichlorobutane¹⁴: n-Butyraldehyde (62 cc.) was added drop by drop to phosphorus pentachloride (100 g.); in some preparations the phosphorus pentachloride was dissolved in carbon disulphide. The mixture was stirred overnight and then heated to 100° for a short while. The cooled mixture was poured on to ice and steam distilled. The upper layer of the distillate was separated, washed with sodium hydrogen carbonate, dried and then distilled. The fraction boiling at 114-115° was collected; yield 20-25%.

1:2-Dichlorobutane: n-Butyl iodide was prepared from m-butyl bromide by treatment with sodium iodide in acetone¹⁵. The iodide (b.p. 126-8°) was added drop by drop to a saturated solution of potassium hydroxide in alcohol which was under reflux¹⁶. Gaseous butene-1 was passed through a calcium chloride tube and collected in a trap at -70°. When the evolution of

butene-1 ceased, the trap was disconnected and joined instead to a chlorine cylinder. A deficiency of chlorine was added and the trap was allowed to warm up to room temperature so that unchanged butene-1 distilled out. The residue was nearly pure 1:2-dichlorobutane.

1:3-Dichlorobutane: 1:3-butandiol was saturated with hydrogen chloride. The solution was heated at 100° in a sealed tube for two days. The tube was then opened and the solution resaturated with hydrogen chloride and the process repeated¹⁷. The final product consisted of two layers. The upper layer was separated, washed with water and then with sodium hydrogen carbonate solution. The final product was dried and distilled.

1:4-Dichlorobutane: Eastman Kodak material was found by chromatography to be quite pure and was used without further purification.

1:1-Difluorobutane: Hydrogen fluoride (15 cc.) was added to a mixture of 1:1-dichlorobutane (32 g.) and red mercuric oxide (60 g.) in a copper reactor, cooled to -70°¹⁸. The reaction mixture was stirred vigorously and slowly allowed to warm to 0°. After half an hour the reactor was opened and the contents poured on to crushed ice. The organic layer was separated and gas phase chromatography indicated the presence of three components apart from traces of low boiling products. These were 1:1-difluorobutane, 1-chloro-1-fluorobutane and unchanged 1:1-dichlorobutane. The pure 1:1-difluorobutane was isolated by collecting the eluted material from several runs of the gas phase chromatogram, b.p. 43-49°; Found: C, 51.4;

H, 8.5; $C_4H_8F_2$ requires C, 51.1; H, 8.6%. 1:1-Difluorobutane was also prepared by using mercuric fluoride prepared using elementary fluorine as for the 1:3-difluoride, see below.

1:3-Difluorobutane: Mercuric chloride (158 g.) was placed in a "Monel" metal autoclave. The mercuric chloride was stirred and heated while fluorine was passed through the bomb. The passage of fluorine was continued until no chlorine could be detected in the outflowing gas. 1:3-Dibromobutane (54 g.), which had been prepared from 1:3-butanediol by treatment with concentrated hydrobromic acid and sulphuric acid, was added to the bomb and there was an immediate evolution of heat. The autoclave was heated and over a period of three hours 15 cc. of crude material was distilled. Gas phase chromatography indicated that this consisted mainly of the desired 1:3-difluorobutane, b.p. 63-68°. (Found: C, 50.7; H, 8.6; $C_4H_8F_2$ requires C, 51.1; H, 8.6%.)

1:4-Difluorobutane: 1:4-Butanediol di-p-toluene sulphonate was treated with potassium fluoride in ethylene glycol¹⁹. The 1:4-difluorobutane had b.p. 78°. 1:4-Difluorobutane was also prepared from 1:4-dichlorobutane by treatment with potassium fluoride in ethylene glycol according to the method of Heffman²⁰.

1, Fluore-4-chlorobutane²¹: 1:4-Dichlorobutane (254 g.) was added to a mixture of potassium fluoride (175 g.) and ethylene glycol (250 cc.). The mixture was refluxed at 110° for twenty hours and then poured into water

(1,000 cc.). The organic layer was extracted with ether and the extract dried over sodium sulphate. The ether was evaporated and the residue fractionated, the fraction boiling at 115° (47.3 g., i.e. 21%) was collected.

1-Chloro-1-fluorobutane²³: The preparation was carried out exactly as previously reported for 1,1-difluorobutane but using a decreased proportion of hydrogen fluoride and mercuric oxide to that of the 1,1-dichlorobutane. The product was isolated by gas phase chromatography.

1,2-Dibromobutane: The commercial material was found by chromatography to be quite pure and was used without further purification.

1,3-Dibromobutane²⁴: Concentrated hydrobromic acid (D_4 ²⁵ 1.46) (833 g.) and sulphuric acid (250 g.) was mixed and 1,3-butandiol (180 g.) was added. The mixture was heated slowly under reflux as sulphuric acid (400 g.) was run in dropwise. The mixture was refluxed for an hour and then distilled until no water insoluble product appeared in the distillate. The water insoluble layer was separated, washed with water, followed by 36 ml. of concentrated sulphuric acid and then sodium bicarbonate solution. The product was dried over sodium sulphate and distilled at reduced pressure. The fraction boiling at $69-73^{\circ}$ at 40 mm. pressure was collected.

1,4-Dibromobutane²⁵: Dry hydrogen bromide was passed into tetrahydrofuran at 90°C . The mixture was then distilled under reduced pressure. The fraction boiling at $106-110^{\circ}/30$ mm.Hg was collected.

1-Bromo-3-chlorobutane: Dry hydrogen bromide (1 mole) was passed into 1,3-dihydroxybutane (1 mole) at 0°C and the solution was heated on a steam bath for half an hour. After cooling chloroform and ice were added and the mixture made neutral. The chloroform layer was separated and the aqueous layer extracted twice with chloroform. The combined extracts were dried over sodium sulphate and the chloroform removed under reduced pressure. The 1-bromo-3-hydroxybutane²⁶ distilled at 66-68°C at 15 mm. Hg pressure. 1-Bromo-3-hydroxybutane (14 g.) was refluxed for one hour with thionyl chloride (14 g.), poured into water and the mixture made neutral. The mixture was extracted with ether and the combined extract was dried over sodium sulphate. The ether was evaporated and the residue fractionated. The 1-bromo-3-chlorobutane boiled at 34-36.3°C/15 mm. Hg. (Found: C, 28.3; H, 4.8. C_4H_8ClBr requires C, 28.0; H, 4.7%.)

1-Bromo-4-chlorobutane²⁷: Dry hydrogen chloride was passed into tetrahydrofuran at room temperature. The saturated solution was allowed to stand at room temperature for 12 hours and then distilled in vacuo. The crude product boiling between 80-90°C at 15 mm. Hg was redistilled and the pure 4-chlorobutan-1-ol collected at 84-5°C/15 mm. Hg. 4-Chlorobutan-1-ol (109 g.) was added to a mixture of concentrated hydrobromic acid (D_4^{25} 1.46) (209 g.) and sulphuric acid (63 g.). A further 50 g. of sulphuric acid was run in slowly and the mixture refluxed for two hours. The 1-bromo-4-chlorobutane was isolated as described for 1,3-dibromobutane and boiled at

69-72°C/15 mm. Hg.

2,2-Dichlorobutane²⁸: To dry, stirred methyl ethyl ketone (200 ml.) was added in portions phosphorus pentachloride (500 g.). Stirring was continued for a further 2-3 hours and then the mixture was poured on to ice and stirred for one hour. The organic layer was separated, washed with sodium carbonate solution, dried over sodium sulphate and fractionated. This yielded about 100 g. of olefinic material and 61 g. of the desired dichloride boiling at 100-101°C.

2,3-Dichlorobutanes²⁹: Sec-butanol (200 ml.) was refluxed over stirred syrupy phosphoric acid (300 ml.) at 120°C. The butene-2 evolved was collected in a trap at -78°C. A calculated quantity of chlorine diluted with an equal volume of nitrogen was metered into the butene-2 at -78°C. The product was fractionated and the dichlorobutanes (156 g.) collected at 114-116°C.

2-Chloro-2-fluorobutane³⁰ and 2,2-difluorobutane²⁸: 2,2-Dichlorobutane (20 g.) was run on to antimony trifluoride (40 g.) containing about 5% of bromine. The mixture was warmed slowly on a water bath and when the reaction started a further 40 g. of 2,2-dichlorobutane was added and heating continued at 60-80°C. The product distilled between 65 and 70°C and hydrogen fluoride was evolved. After the addition of a little sodium fluoride to absorb the hydrogen fluoride the product was fractionated. The fraction boiling at 40-65°C was shown to contain a large proportion of 2,2-difluorobutane and the fraction boiling at 65-66°C contained the 2-chloro-2-fluorobutane. Bromine was added to remove chlorobutenes and the products isolated by gas phase

chromatography.

2-Chloro-3-fluorobutanes: The 2,3-dichlorobutanes were reacted with mercuric oxide and hydrogen fluoride exactly as for the preparation of 1-chloro-1-fluorobutane. The products were isolated by gas phase chromatography.

2,3-Difluorobutanes: The 2,3-dichlorobutanes were reacted with mercuric oxide and hydrogen fluoride exactly as for the preparation of 1,1-difluorobutane. The products were isolated by gas phase chromatography. Besides the meso- and d,1,2,3-difluorobutanes, a third product was isolated which was identified by its infra-red spectrum as 2,2-difluorobutane. A rearrangement must have taken place, probably by loss of hydrogen fluoride, to give a 2-fluorobutene and subsequent Markownikoff readdition.

Attempted preparation of 1-chloro-2-fluorobutane: 1,2-Dichlorobutane (20 g.) was reacted with mercuric oxide (45 g.) and hydrogen fluoride (10 ml.). Two products were expected, 1-chloro-2-fluoro- and 2-chloro-1-fluorobutane. The chromatogram of the product contained only one chloro-fluorobutane peak, the retention time of which corresponded to that of the peak containing both 1-chloro-2-fluoro- and 1-chloro-3-fluorobutane from the fluorination of n-butyl chloride, and the chlorination of sec-butyl fluoride. No product was present with a retention time corresponding to that of 2-chloro-1-fluorobutane from the chlorination of n-butyl fluoride. The infra-red spectrum of the compound isolated from the reaction surprisingly was almost identical to that of the final peak in the chlorination of sec-butyl

fluoride, which would be expected to contain mostly 1-chloro-1-fluorobutane and a little of the 1-chloro-2-fluorobutane. Thus the evidence seems to indicate that there had been a rearrangement to form 1-chloro-3-fluorobutane. If, as suggested before, this takes place by loss of hydrogen fluoride and readdition, the expected direction of addition of hydrogen fluoride to 1-chlorobut-2-ene would give 1-chloro-3-fluorobutane.

(c) Apparatus and Procedure for the Halogenations

Two identical reactors were constructed, one made of glass which fitted into a vapour jacket (see Fig. 1), the other made of copper which fitted into an electric furnace. They consisted of two pre-heating spirals made from 6 m.m. O.D. tubing (total volume 25 cc. each) which entered a mixing vessel with their jets opposed. The mixing vessel (75 cc.) ended in a reactor spiral of similar tubing (total volume 100 cc.).

The butyl halide was introduced into the reactor by passing a stream of nitrogen through a trap containing the compound. The trap was surrounded by a constant temperature bath. The concentration of butyl halide in the gas stream was controlled by the temperature of this bath and actual concentration determined from a vapour pressure curve which was measured in the conventional way beforehand. The concentration of the halogen used was so low that it was impractical to metre the gas at the flow rates requires. The halogen was therefore mixed with nitrogen in a large

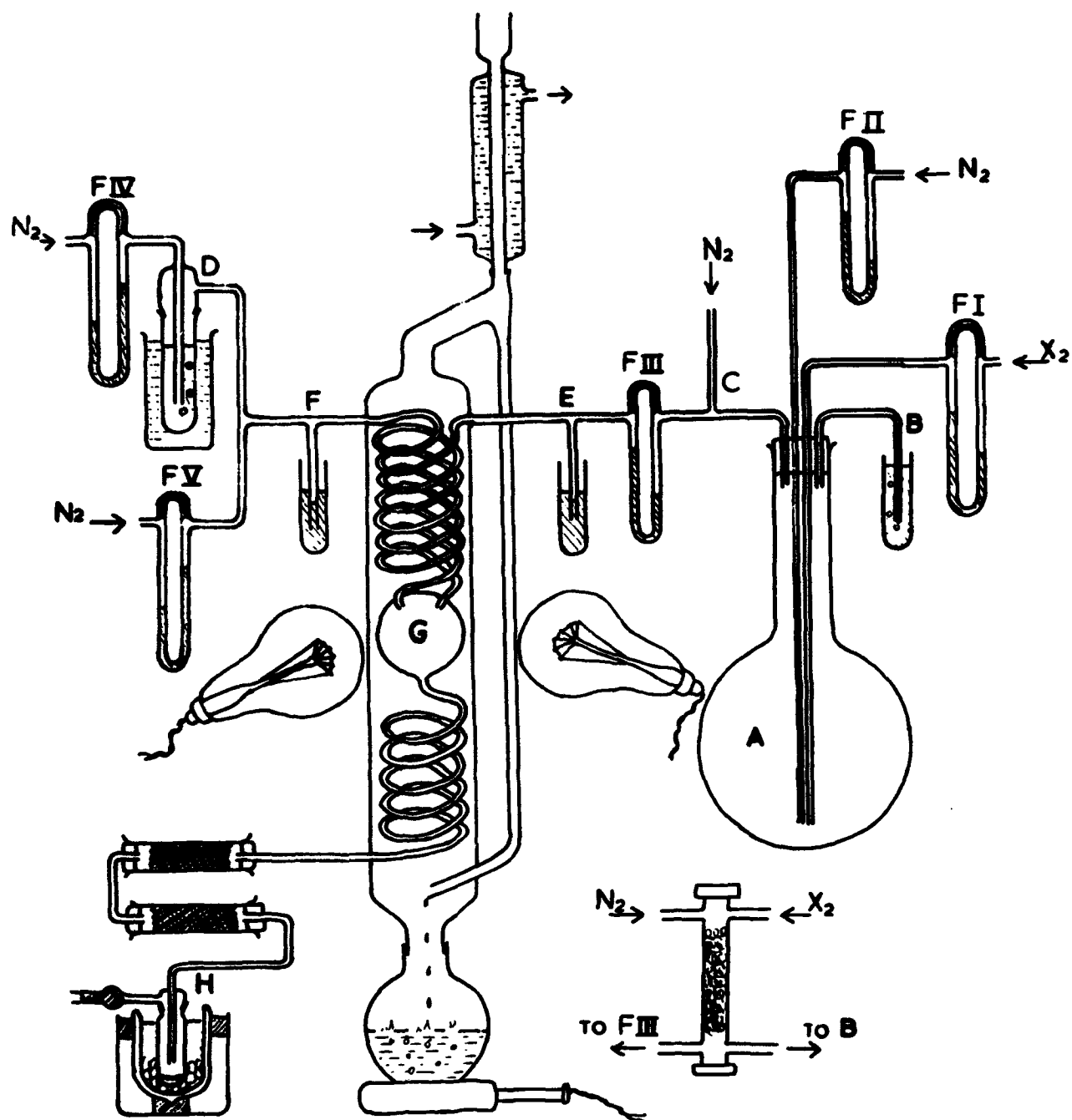


Figure 1. Apparatus for Halogenations

mixing vessel to the correct relative concentration, but only part of the mixed gases were fed into the reactor, the remainder escaped to waste. By this means accurately measured flows of halogen could be used.

The controlling factors for total concentration of reactants were the exothermic nature of the reactions and the volatility of the products. The former problem has been discussed previously⁶. When the products had very low volatility the total concentration of the reactants had to be kept low to prevent condensation of the products either in the reactor or in the subsequent parts of the apparatus. This would have required very lengthy reaction times in order to get sufficient material for analysis, so long as the apparatus was used at atmospheric pressure. However, by coupling the apparatus to a high-speed vacuum pump, much greater flow rates could be obtained, while keeping the relative concentrations of the reactants the same but lowering the total concentration in the reactor by reducing the pressure. The rates of flow were now controlled by a series of capillaries.

(d) Gas Phase Chromatography

The apparatus has been described previously¹. The analysis depends on the assumption that the thermal conductivity of the isomeric dihalobutanes is very similar. All the data at present available indicate that any variation in the thermal conductivity of isomers of this type would be extremely small. In the chlorination of butyl chloride the validity of this assumption was checked by analysing identical runs on both our chromatography column and on a Pye Chromatograph. The results were the same within experimental error.

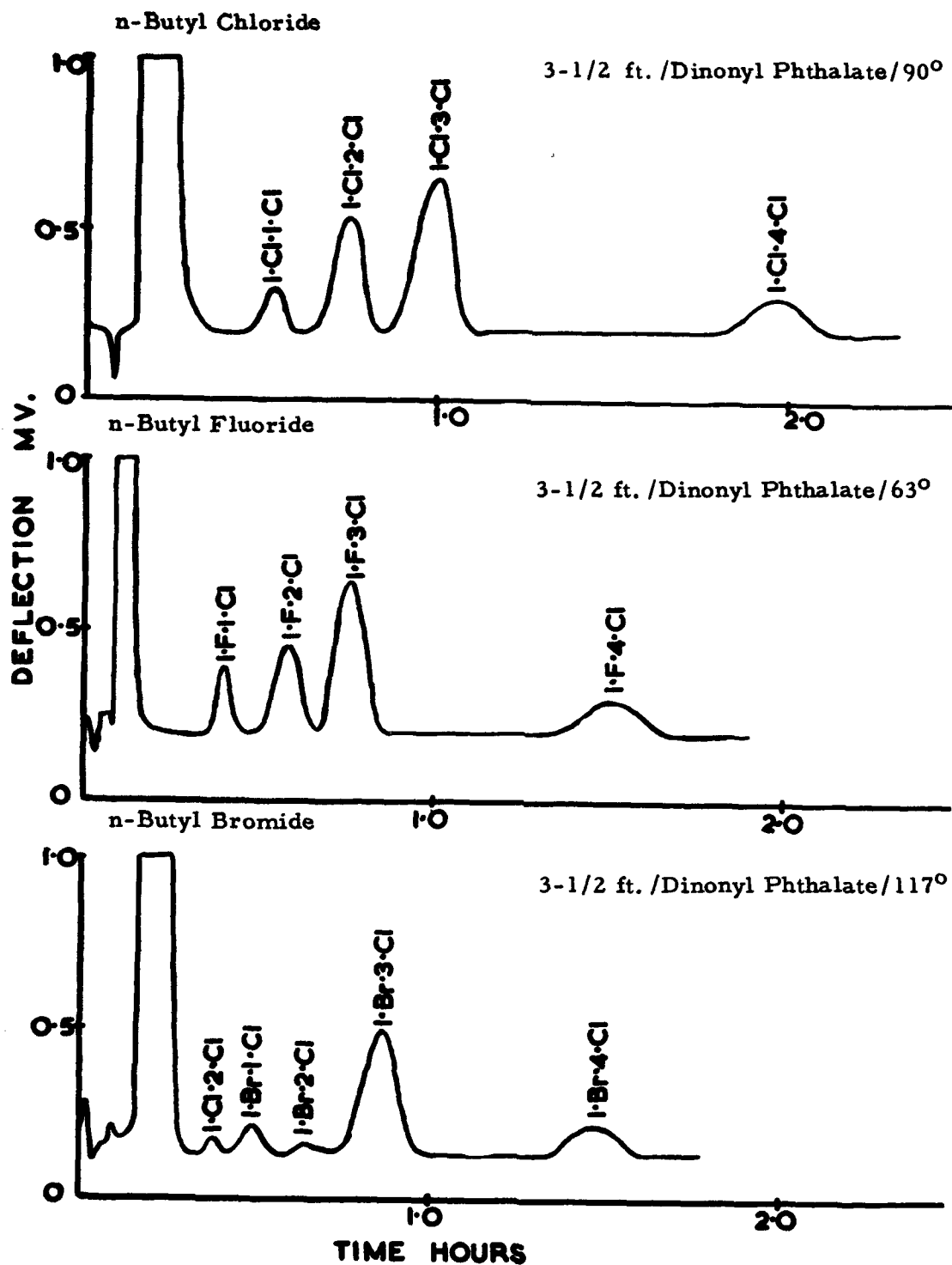


Figure 2. Chromatograms of Chlorinated n-Butyl Halides

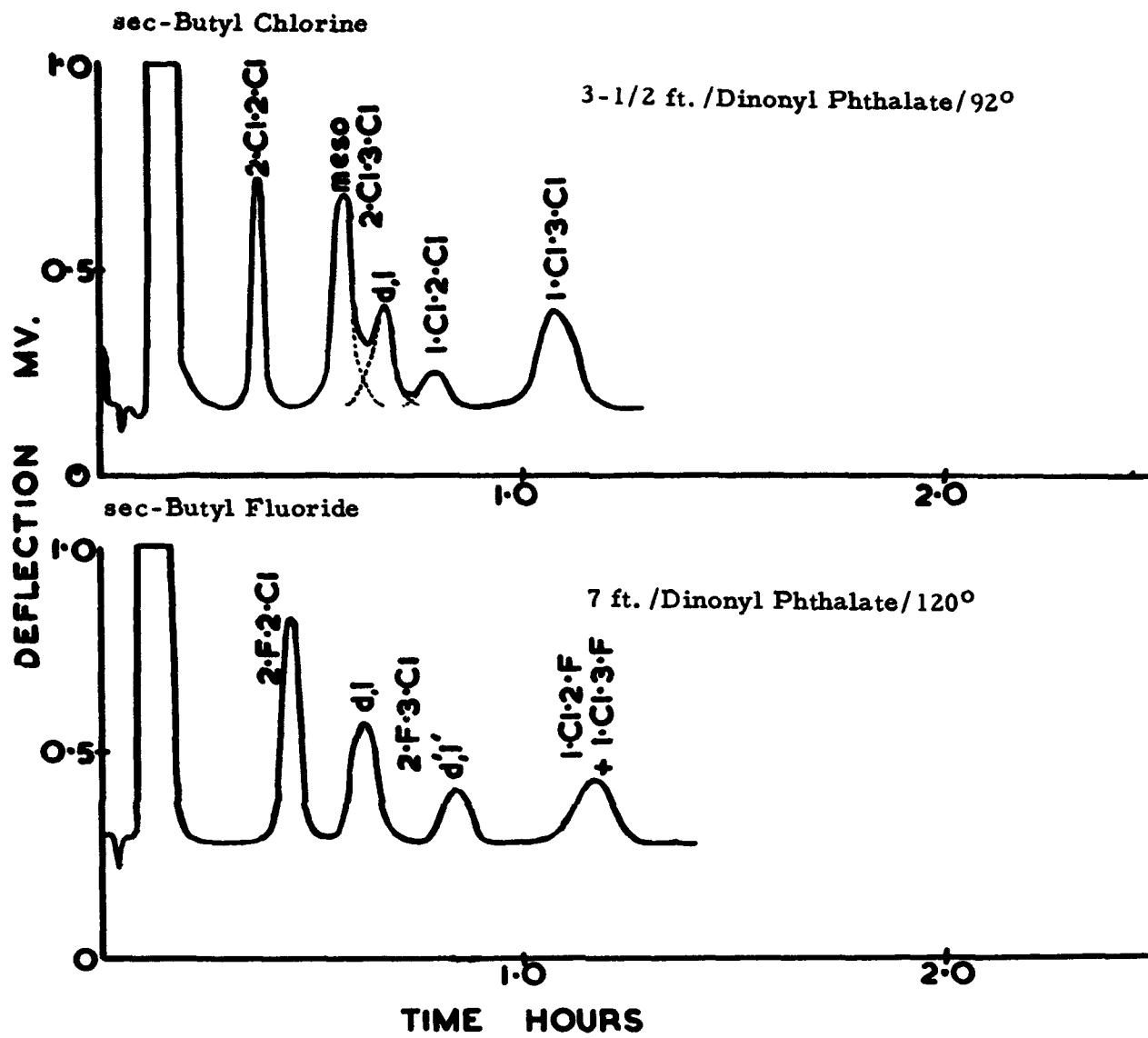


Figure 3. Chromatograms of Fluorinated n-Butyl Halides

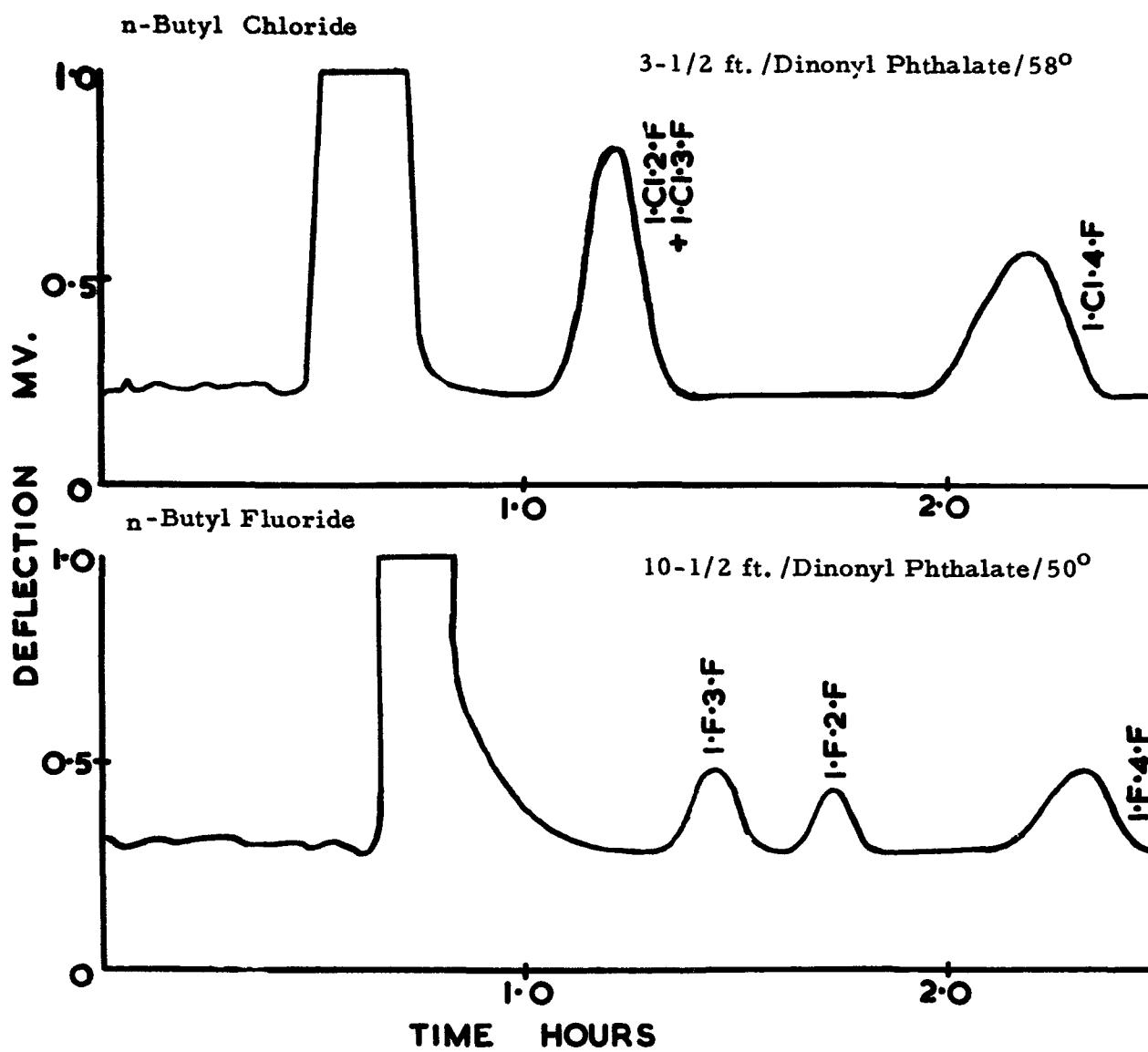


Figure 4. Chromatograms of Fluorinated n-Butyl Halides

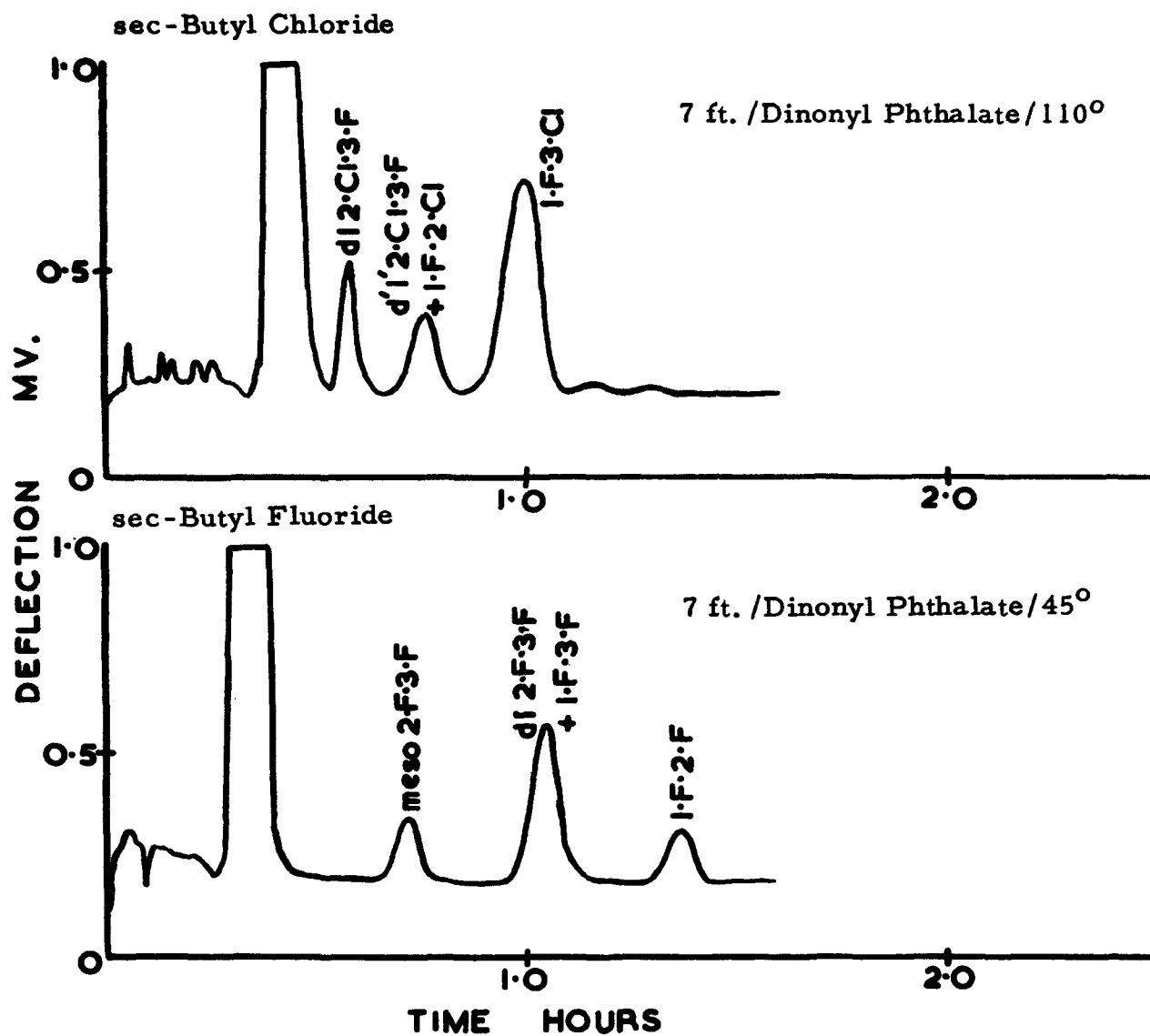


Figure 5. Chromatograms of Fluorinated sec-Butyl Halides

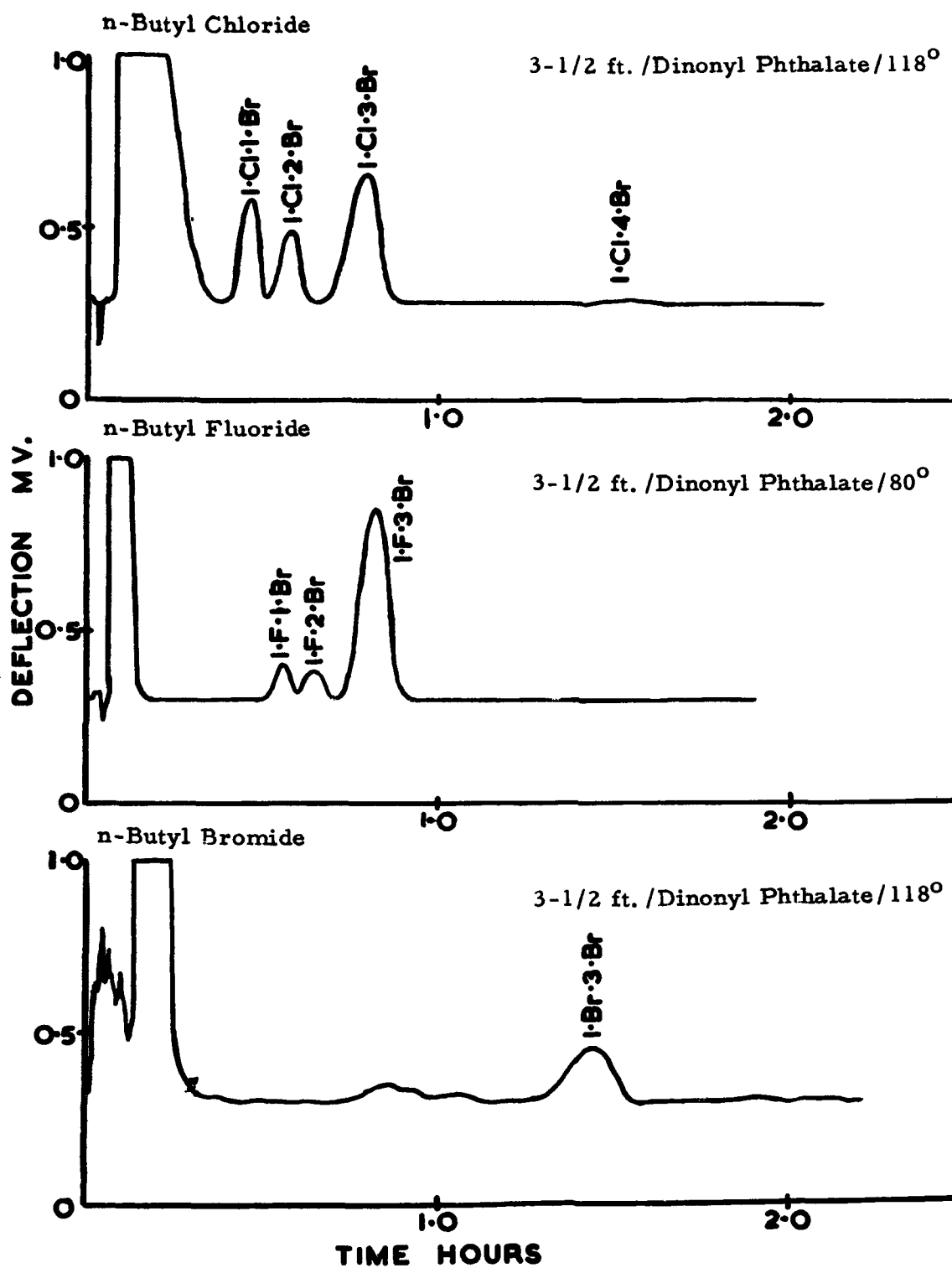


Figure 6. Chromatograms of Brominated n-Butyl Halides

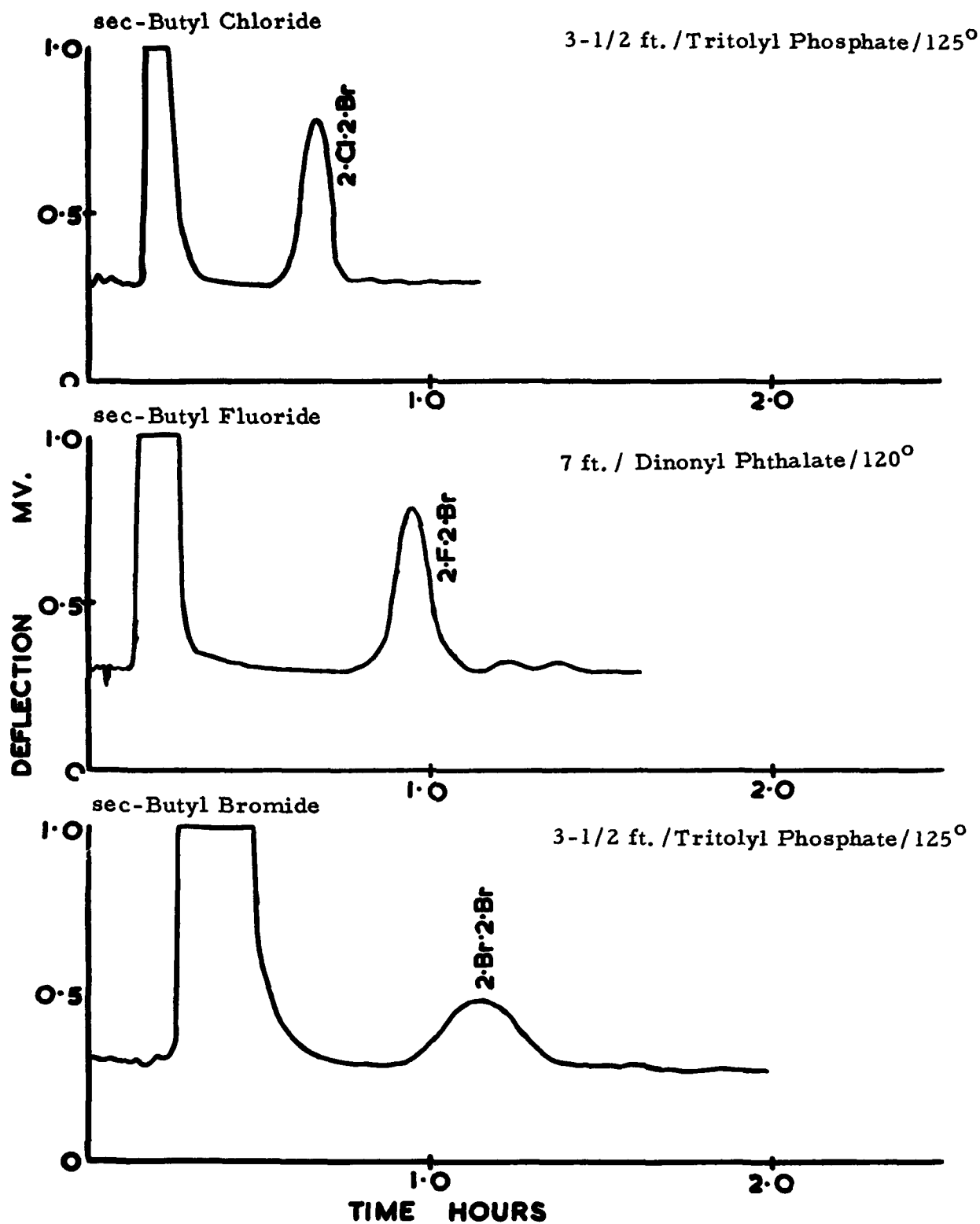


Figure 7. Chromatograms of Brominated sec-Butyl Halides

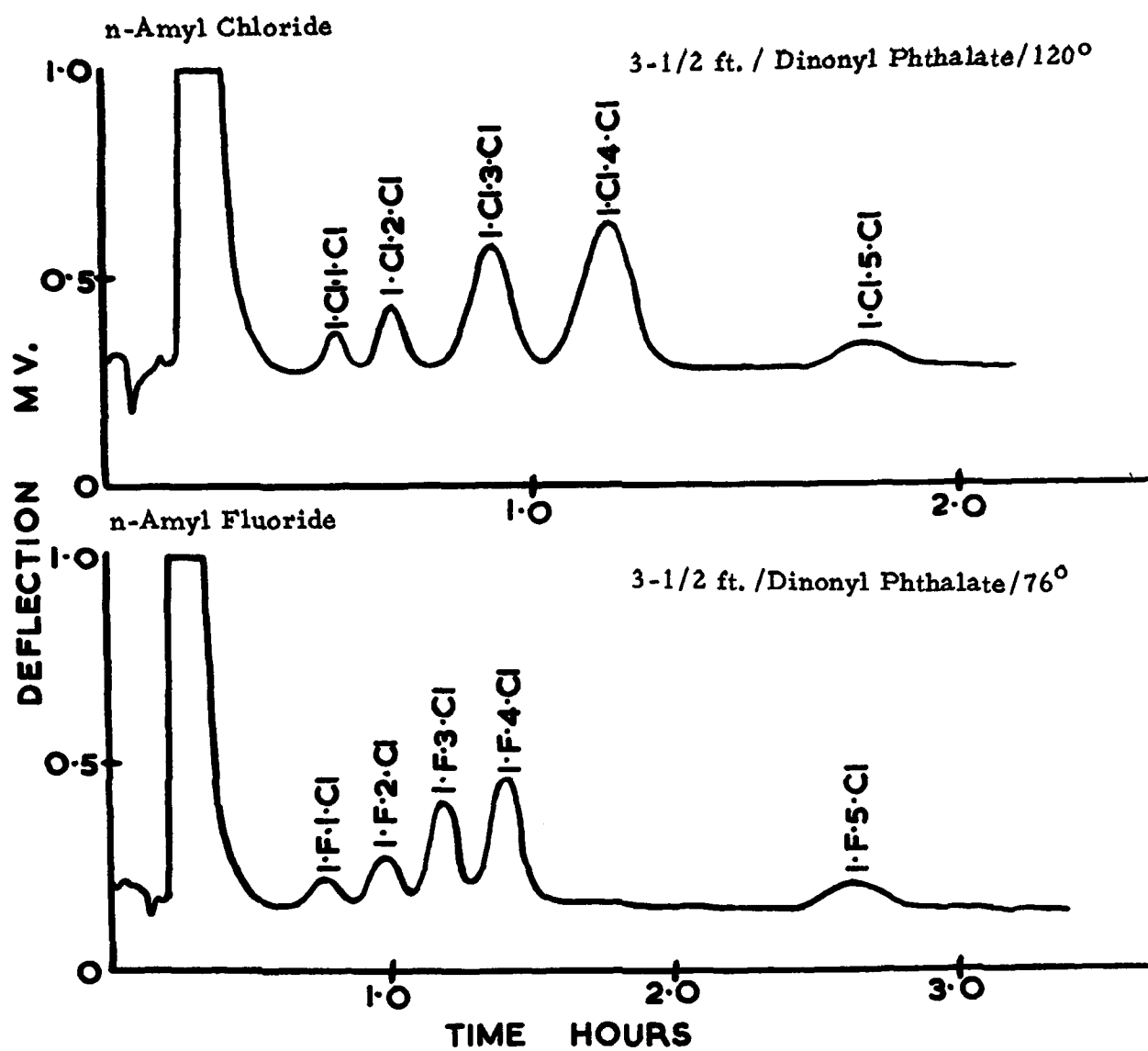


Figure 8. Chromatograms of Chlorinated n-Amyl Halides

(e) Chlorination of n-Butyl Chloride

n-Butyl chloride (10 parts) + chlorine (1 part) + nitrogen (400 parts)

Temperature	No. runs	CH_2Cl ——— CH_2 ——— CH_2 ——— CH_3				
35°	10	8.5 ± 0.3	27.0 ± 1.4	49.5 ± 1.4	15.0 ± 1.6	%
35°	10	8.1 ± 0.6	25.8 ± 0.6	48.6 ± 1.1	17.5 ± 1.2	%
78°	10	9.6 ± 0.8	26.1 ± 1.1	45.7 ± 1.0	18.6 ± 1.0	%
146°	8	9.6 ± 1.1	22.5 ± 1.2	47.1 ± 0.8	20.8 ± 2.0	%
146°	5	8.2 ± 0.7	22.1 ± 1.6	47.5 ± 1.8	22.2 ± 3.1	%

≡ Nitrogen (200 parts)

⌘ Analysed on a Pye Argon Chromatograph Cat. 12,000.

The products were identified by the individual addition of the authentic dihalide to the reaction products.

(f) Chlorination of n-Butyl Fluoride

n-Butyl fluoride (10 parts) + chlorine (1 part) + nitrogen (100 parts)

Temperature	No. runs	CH_2F ——— CH_2 ——— CH_2 ——— CH_3				
0°	10	9.7 ± 0.6	20.8 ± 0.6	52.5 ± 0.6	17.0 ± 1.5	%
35°	10	10.7 ± 0.8	20.8 ± 0.5	48.6 ± 0.7	19.9 ± 0.9	%
78°	7	11.4 ± 0.4	21.8 ± 0.4	47.4 ± 0.4	19.4 ± 1.0	%
146°	7	12.7 ± 0.8	21.5 ± 0.8	45.4 ± 0.5	20.4 ± 1.4	%

≡ Nitrogen 400 parts.

Identification of products: 1-fluoro-4-chlorobutane was identified by the addition of authentic material. The shape of the chromatogram was identical to the shape from chlorinated butyl chloride. Fluorination of sec-butyl chloride yielded a mixture, the chromatogram of which had two peaks which coincided with the chromatogram from the above results, these were therefore 1-fluoro-2-chloro- and 1-fluoro-3-chlorobutane. The remaining peak was therefore 1-fluoro-1-chlorobutane.

(g) Chlorination of n-Butyl Bromide

n-Butyl bromide (4 parts) + chlorine (4 parts) + nitrogen (200 parts)

The experiments were performed at 252 mm. of Hg.

Temperature	No. runs	CH ₂ Br ————— CH ₂ ————— CH ₂ ————— CH ₃	
35°	4	8.0 ± 0.8	Trace 66.8 ± 1.5 25.2 ± 1.9 %
78°	6	7.8 ± 0.5	" 64.9 ± 1.7 27.3 ± 2.0 %

Identification of products: there were five peaks on the chromatogram.

The first in order of elution proved to be 1:2-dichlorobutane. The fifth peak was identified as 1-bromo-4-chlorobutane by the addition of authentic material, and the fourth peak was identified as 1-bromo-3-chlorobutane similarly. The second peak was established as 1-bromo-1-chlorobutane by comparison with the products from the bromination of butyl chloride. The third and smallest peak was therefore 1-bromo-2-chlorobutane.

(h) Fluorination of n-Butyl Fluoride

Temperature	No. runs	CH_2F ————— CH_2 ————— CH_2 ————— CH_3
21°	10	? 23.8 ± 1.8 30.5 ± 1.4 45.7 ± 1.6

Identification of products: only three peaks appeared on the chromatogram. The first in order of elution was identified as 1:3-difluorobutane and the last to be eluted was 1:4-difluorobutane. Addition of authentic material showed that any 1:1-difluorobutane present in the product would have been masked by the unchanged butyl fluoride. Therefore the remaining peak was 1:2-difluorobutane. Because of the impossibility of separating the 1,1-difluorobutane from the unchanged butyl fluoride by gas phase chromatography, the reaction product was examined on the mass spectrometer. The calculation of results from the mass-spectra proved considerably more difficult than expected; the large excess of unchanged butyl fluoride again greatly complicated the problem. The products from two runs having identical conditions to those described previously were analysed and the results (%) were as follows:-

Unchanged $\text{C}_4\text{H}_9\text{F}$	1,1-	1,2-	1,3-	1,4- $\text{C}_4\text{H}_8\text{F}_2$
92.2	0.5	1.3	3.5	3.0
92.0	0.5	1.0	4.9	2.1

The agreement between the mass-spectra results and those obtained by gas chromatography is very good (the relative proportions of the 1,2- and the 1,4-isomer are identical by both methods, and the mass-spectra indicate the presence of slightly more of the 1,3-isomer). The mass-spectra clearly show the 1,1-isomer to be present in the smallest proportion.

(i) Fluorination of n-Butyl Chloride

n-Butyl chloride (5 parts) + fluorine (1 part) + nitrogen (100 parts)

Temperature	No. runs	$\text{CH}_2\text{Cl} \text{-----} \text{CH}_2 \text{-----} \text{CH}_2 \text{-----} \text{CH}_3$			
21°	5	-	52.3 ± 1.6	47.7 ± 1.6	

Identification of products: there were only two peaks on the chromatogram. The second was established as due to 1-chloro-4-fluorobutane by addition of authentic material. Comparison with the chromatogram of chlorinated n-butyl fluoride and addition of authentic material showed that 1-chloro-1-fluorobutane would not have been separated from the unchanged butyl chloride. In the chlorination of n-butyl fluoride, the chlorofluorobutanes were eluted in the order 1,1-, 1,2-, 1,3- and 1,4-. In the fluorination of n-butyl fluoride the elution order of the 1,2- and the 1,3-difluoride was inverted. This suggested that in the fluorination of butyl chloride the 1-chloro-2-fluoro- and 1-chloro-3-fluorobutane would have very similar retention times. The size of the first peak actually obtained indicated that the retention times of the two products were so similar that only one large peak appeared on the chromatogram. This was confirmed by careful comparison with the chromatogram from the chlorination of 2-fluorobutane.

(j) Bromination of n-Butyl Chloride

n-Butyl chloride (10 parts) + bromine (1 part) + nitrogen (400 parts)

Temperature	No. runs	$\text{CH}_2\text{Cl} \text{-----} \text{CH}_2 \text{-----} \text{CH}_2 \text{-----} \text{CH}_3$			
146°	9	23.0 ± 2.0	21.7 ± 0.9	55.3 ± 2.4	Trace

Identification of products: the very small peak which was the last to be eluted was identified as due to 1-bromo-4-chlorobutane by addition of authentic material. The first peak was identified as due to 1-bromo-1-chlorobutane by comparison with the chromatograms from the chlorination of n-butyl bromide. The remaining two peaks were therefore of 2-bromo-1-chlorobutane and 3-bromo-1-chlorobutane and were assumed to be eluted in this order by analogy with the dichlorobutanes.

(k) Bromination of n-Butyl Fluoride

n-Butyl fluoride (10 parts) + bromine (2 parts) + nitrogen (400 parts)

Temperature	No. runs	CH ₂ F	CH ₂	CH ₂	CH ₃
146°	5	10.0 ± 0.5	8.9 ± 0.5	81.1 ± 0.6	Not detected

Identification of products: there were only three peaks on the chromatogram and the third and largest was collected and submitted to nuclear magnetic spectroscopy. Both the ¹H and ¹⁹F spectra were examined. The proton spectrum clearly established the presence of a methyl group adjacent to a -CHX- group. This means that the peak must have been due to 3-bromo-1-fluorobutane and all the other details of the spectra confirmed this. The remaining peaks were assumed to be due to 1-bromo-1-fluorobutane and 2-bromo-1-fluorobutane eluted in this order by analogy with the results described above.

(l) Bromination of n-Butyl Bromide

Bromination of n-butyl bromide was strongly inhibited by some product

of the reaction, and when conditions similar to those described for the bromination of butyl chloride and butyl fluoride were employed a large proportion of the bromine failed to react and the sides of the vessel became coated with a brown film. We believe this to be due to the formation of olefinic material by loss of bromine from some of the intermediate radicals ($-\dot{\text{C}}\text{H}-\text{CHBr}- \longrightarrow -\text{CH}=\text{CH}-$). Runs were attempted at both 78° and 146° ; the chromatogram only showed one large peak which was found to be due to 1,3-dibromobutane by the addition of authentic material. There were other very small and badly defined peaks; two of these were identified as due to 1,2- and 1,4-dibromobutane, but there remained other low-boiling compounds which could not be identified.

(m) Chlorination of n-Hexane

n-Hexane (10 parts) + chlorine (1 part) + nitrogen (340 parts)

Temperature	No. runs	1-chlorohexane	2- and 3-chlorohexane
78°	7	$19.4 \pm 0.6\%$	$80.6 \pm 0.6\%$

Identification of products: there were two peaks on the chromatogram.

The boiling points of 2-chloro- and 3-chlorohexane are extremely close and the size of the first peak indicated that they were eluted together and that the second peak was the 1-chlorohexane.

(n) Chlorination of n-Amyl Chloride

n-Amyl chloride (1 part) + chlorine (1 part) + nitrogen (300 parts)

The experiments were performed at 252 mm. of Hg.

Temperature	No. runs	$\text{CH}_2\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$				
78°	7	5.9 ± 0.7	14.7 ± 1.1	27.7 ± 1.5	40.7 ± 1.6	$11.1 \pm 0.8\%$

Identification of products: by analogy with the chlorination of n-butyl chloride the isomers were assumed to be eluted in the order of increasing boiling point, i.e. 1,1-, 1,2-, 1,3-, 1,4-, 1,5-dichloropentane.

(e) Chlorination of n-Amyl Fluoride

n-Amyl fluoride (10 parts) + chlorine (1 part) + nitrogen (340 parts)

Temp.	No. runs	CH ₂ F	CH ₂	CH ₂	CH ₂	CH ₃
78°	5	7.1 ± 0.7	12.1 ± 1.4	27.6 ± 1.2	39.7 ± 2.4	13.5 ± 1.0%

Identification of products: the isomers were assumed to be eluted in the same order as the dichloropentanes.

(p) Chlorination of n-Hexyl Fluoride

The chlorination of n-hexyl fluoride was investigated at 78°C.

Difficulty was encountered in separating the products on the existing gas chromatography apparatus and no satisfactory results were obtained.

(q) Chlorination of sec-Butyl Chloride

sec-Butyl chloride (11 parts) + chlorine (1 part) + nitrogen (360 parts)

Temperature	No. runs	CH ₃	CHCl	CH ₂	CH ₃
			(meso)	(d,l)	
35°	7	4.1 ± 0.7	26.3 ± 0.7	36.4 ± 1.1 51.0 ± 0.5	14.6 ± 0.6 18.6 ± 0.9
78°	6	4.3 ± 0.9	26.2 ± 1.1	35.0 ± 1.2 49.8 ± 1.3	14.8 ± 0.6 19.7 ± 0.8

The products were identified by the individual addition of the authentic dihalide to the reaction products. The two 2,3-dichlorobutanes were assumed to be eluted in order of their boiling points.

(r) Chlorination of sec-Butyl Fluoride

sec-Butyl fluoride (10 parts) + chlorine (1 part) + nitrogen (400 parts)

Temp. No. runs (2-fluoro-2-chloro)(2-fluoro-3-chloro-)(1-chloro-2-fluorobutane
(1-chloro-3-fluorobutane)

			(d,1)	(d', 1')	
35°	10	35.6 ± 2.1	24.7 ± 0.9	16.9 ± 0.9	22.8 ± 1.5
			41.6 ± 1.3		
78°	11	33.0 ± 1.7	24.2 ± 1.8	16.4 ± 1.3	26.4 ± 3.1
			40.6 ± 2.2		

Identification of products: 2-chloro-2-fluoro-, d,l 2-chloro-3-fluoro-, and d', 1' 2-chloro-3-fluorobutane were each identified by the addition of authentic material. This was confirmed by comparison of infra-red spectra and in the case of the last two by analysis of their nuclear magnetic resonance spectra. The last peak on the chromatogram was shown to contain both 2-fluoro-1-chloro- and 3-fluoro-1-chlorobutane by comparison with the chromatogram of fluorinated n-butyl chloride.

(s) Fluorination of sec-Butyl Fluoride

sec-Butyl fluoride (10 parts) + fluorine (2 parts) + nitrogen (400 parts)

Temp.	No. runs	CH ₃ —	CHF—	CH ₂ —	CH ₃
			(meso)	(d,1)	
21°	7	23.9 ± 0.9	-	19.2 ± 1.9	44.2 ± 2.0
				12.7 ± 1.1	
				31.9 ± 2.2	

Identification of products: there were only three peaks on the chromatogram.

By addition of authentic material it was shown that 2,2-difluorobutane would elute with the unchanged butyl fluoride. The first peak was shown to be meso 2,3-difluorobutane by comparison of its infra-red spectrum with that of authentic material. The second peak was shown to contain both 1,3- and d,l 2,3-difluorobutane similarly by comparing with infra-red spectra of the authentic materials separately and of mixtures. The final peak was shown to be 1,2-difluorobutane by comparison with the chromatogram of fluorinated n-butyl fluoride. An attempt to obtain further information using mass spectra was unsuccessful, although considerable effort was devoted to it.

Identification by infra-red spectra

The proportions of 1,3-difluoro- and d,l 2,3-difluorobutane in the second peak on the chromatogram were determined by study of its infra-red spectrum. The spectra of the separate pure compounds showed that there was an absorption band at 848 cm^{-1} for 1,3-difluorobutane and no absorption occurred with d,l 2,3-difluorobutane at this wavelength. There were also bands at 1178 cm^{-1} and 933 cm^{-1} for d,l 2,3-difluorobutane where only a moderate absorption occurred for 1,3-difluorobutane. Four mixtures of varying proportions of these two isomers were made and their spectra obtained. From the optical density at these wavelengths it was possible to calculate the ratios of the two isomers in the reaction product. The method of calculation is indicated below.

I = transmission intensity at any wavelength.

I_0 = total transmission intensity.

ϵ_ω = extinction coefficient at any wave number $\omega\text{ cm}^{-1}$.

l = length of cell.

C = concentration of substance.

$$I = I_0 e^{-\epsilon cl}.$$

$$\log I_0 - \log I = \epsilon cl.$$

$D = \epsilon cl$ where D = Optical density.

Let suffix 1,3 refer to 1,3-difluorobutane

and " 2,3 " " d,l 2,3-difluorobutane

For pure 1,3-difluorobutane we can write:-

$$\text{at } 1178 \text{ cm.}^{-1} \quad D_{1178}^{1,3} = \epsilon_{1178}^{1,3} \times [1,3-] \times 1$$

$$\text{at } 848 \text{ cm.}^{-1} \quad D_{848}^{1,3} = \epsilon_{848}^{1,3} \times [1,3-] \times 1$$

$$\therefore \frac{D_{1178}^{1,3}}{D_{848}^{1,3}} = \frac{\epsilon_{1178}^{1,3}}{\epsilon_{848}^{1,3}}$$

For pure d,l 2,3-difluorobutane we can write:-

$$\text{at } 1178 \text{ cm.}^{-1} \quad D_{1178}^{2,3} = \epsilon_{1178}^{2,3} \times [2,3-] \times 1$$

$$\text{at } 848 \text{ cm.}^{-1} \quad D_{848}^{2,3} = \epsilon_{848}^{2,3} \times [2,3-] \times 1 = 0$$

For a mixture of the two we can write:-

$$\text{at } 1178 \text{ cm.}^{-1} \quad D_{1178}^{\text{Mixture}} = \epsilon_{1178}^{1,3} \times [1,3-]^{\text{Mixture}} \times 1 + \epsilon_{1178}^{2,3} \times [2,3-]^{\text{Mixture}} \times 1$$

$$\text{at } 848 \text{ cm.}^{-1} \quad D_{848}^{\text{Mixture}} = \epsilon_{848}^{1,3} \times [1,3-]^{\text{Mixture}} \times 1$$

which reduces to:-

$$\frac{[2,3-]^{\text{Mixture}}}{[1,3-]^{\text{Mixture}}} = \frac{D_{1178}^{\text{Mixture}} - D_{848}^{\text{Mixture}} \left(\frac{\epsilon_{1178}^{1,3}}{\epsilon_{848}^{1,3}} \right)}{D_{848}^{\text{Mixture}}} \times \left(\frac{\epsilon_{848}^{1,3}}{\epsilon_{1178}^{2,3}} \right)$$

Using values from the synthetic mixtures of known ($[2,3-]^{\text{Mixture}} / [1,3-]^{\text{Mixture}}$)

we can calculate the constant ($\epsilon_{848}^{1,3} / \epsilon_{1178}^{2,3}$) and thus find the ratio

$[2,3-]^{Mist.} / [1,3-]^{Mist.}$ for the reaction mixture. Calculations based on four synthetic mixtures, firstly absorption at 1178 cm^{-1} and 848 cm^{-1} and secondly at 933 cm^{-1} and 848 cm^{-1} yielded eight results, the average of which was taken.

$$\frac{[2,3-]^{Mist.}}{[1,3-]^{Mist.}} = \frac{1}{3,4_6 \pm 0.4}$$

t) Fluorination of sec-Butyl Chloride

sec-Butyl chloride (10 parts) + fluorine (5 parts) + nitrogen (400 parts)

Temp.	No. runs	CH ₃ ————— CHCl ————— CH ₂ ————— CH ₃	
		(d,1) (d'1')	
21°	4	7.9 ± 0.3 ? 17.0 ± 0.9 8.5 ± 0.3 66.6 ± 0.8	
			25.5 ± 1.0

Identification of products: there were only three chlorofluorobutane peaks on the chromatogram. Using the normal proportions of reactants, the first of these was not fully resolved from the unchanged sec-butyl chloride. An increase in the ratio of fluorine to sec-butyl chloride was made in order to increase the amount of fluorinated products so that smaller samples could be chromatographed. By this means the first chlorofluorobutane peak was resolved from the unchanged starting material and it was found to be 1,1 2-chloro-3-fluorobutane by the addition of authentic material. The first peak was shown to be 3-chloro-1-fluorobutane by comparison with the

chromatogram of chlorinated n-butyl fluoride. The centre peak was found to contain both d,l 2-chloro-3-fluorobutane and 2-chloro-1-fluorobutane. The presence of the former was established by the addition of authentic material and the latter by comparison with the chromatogram of chlorinated n-butyl fluoride. All these identifications were confirmed by observation of the infra-red spectra of the separate peaks, and in the case of the second peak which contained the two isomers an estimate of their relative concentrations was made. The method was analogous to that used for the two difluorobutanes in the previous experiment. The synthetic mixtures were made up with known ratios of these two isomers and their spectra obtained. The 2-chloro-1-fluorobutane was isolated from chlorinated n-butyl fluoride and the d,l' 2-chloro-3-fluorobutane was synthetic material. The calculation was simplified in this case because there was an absorption band in the spectrum of each of the chlorofluorobutanes in a region where the other did not absorb. The absorption band of 2-chloro-1-fluorobutane was at 845 cm^{-1} and that of d,l' 2-chloro-3-fluorobutane was at 895 cm^{-1} . Thus, using the same symbols as before:-

$$\frac{[2,1-]_{\text{Mixt.}}}{[2,3-]_{\text{Mixt.}}} = \frac{\epsilon_{895}^{2,3-}}{\epsilon_{845}^{2,1-}} \times \frac{D_{845}^{\text{Mixt.}}}{D_{895}^{\text{Mixt.}}}$$

The two synthetic mixtures had concentrations in the ratio:-

$$\frac{[2,1-]^{Mixture}}{[2,3-]^{Mixture}} = \frac{1.63}{1} , \frac{1.08}{1}$$

Measurement of the optical densities in the reaction mixture gave the following two ratios:-

$$\frac{[2,1-]^{Mixture}}{[2,3-]^{Mixture}} = \frac{0.94}{1} , \frac{0.90}{1}$$

These figures have been incorporated in the results recorded above.

(u) Bromination of sec-Butyl Chloride

sec-Butyl chloride (11 parts) + bromine (1 part) + nitrogen (400 parts)

The reaction was carried out at 146°. There was only one large peak on the chromatogram in addition to that of the unchanged sec-butyl bromide.

By analogy with the following two experiments this was identified as 2-bromo-2-chlorobutane. Two extremely small peaks could just be detected on the chromatogram after the large 2-bromo-2-chlorobutane peak. These were presumably due to the two 2-bromo-3-chlorobutanes, but they were present in too small a quantity to be measured accurately.

(v) Bromination of sec-Butyl Fluoride

sec-Butyl fluoride (10 parts) + bromine (1 part) + nitrogen (400 parts)

The reaction was carried out at 146°. There was only one large peak on the chromatograms in addition to that of the unchanged sec-butyl fluoride.

This major product was collected from several runs on the chromatography

column and its nuclear magnetic resonance spectrum examined. This clearly established it to be 2-bromo-3-fluorobutane. The H^1 spectrum had two prominent groups of peaks, a triplet due to the protons on carbon atom 4 and a doublet due to the protons on carbon atom 1. The methylene protons on carbon atom 3 should have given eight weak peaks due to doublet splitting by the F^{14} atom and quartet splitting from the protons on C_4 . These were partly obscured by the strong doublet already referred to. Two small peaks were also present on the chromatograms and were presumed to be d,l and d', l' 2-bromo-3-fluorobutane. They were eluted after the 2-bromo-2-fluorobutane and were assumed to be eluted in the order erythro before threo. Five analysis runs were made, giving a value of erythro : threo of 1.8:1.

(w) Bromination of sec-Butyl Bromide

sec-Butyl bromide (10 parts) + bromine (1 part) + nitrogen (400 parts)
The reaction was carried out at 146° . Unlike the bromination of 1-bromobutane the reaction proceeded smoothly. There was only one large peak on the chromatogram in addition to the unchanged sec-butyl bromide. This major product was collected from several runs and identified as 2,2-dibromobutane by examination of its nuclear magnetic resonance spectra. The presence of a strong singlet peak in the H^1 spectra, due to a non-interacting methyl group (C_1), together with a triplet due to hydrogen atoms on carbon atom 4, was sufficient to establish its identity.

Two small and badly defined peaks eluted after the 2,2-dibromobutane were assumed to be meso- and d,l 2,3-dibromobutane.

(x) Identification by Infra-red Spectra

In certain cases, especially with the more volatile chloro-, fluoro- and difluorobutanes, the identification of the isomers was confirmed by comparing the infra-red spectra in the gas phase of a particular peak from the chromatogram of a reaction product with that of a synthetic model compound.

The method of obtaining the spectrum was to collect the compound as it was eluted from the gas phase chromatography column in a trap at -78°C . After connecting the trap into a vacuum line and degassing, the trap was warmed up to room temperature and the vapour transferred into the vacuum line and the evacuated gas cell. The pressure was then adjusted to a suitable value by cooling the trap if necessary, recorded, and the total pressure made up to atmospheric by allowing nitrogen to enter the system. The gas cell, which was 10 cm. in length with rock salt end windows 3.5 cm. in diameter, was then transferred to a Grubb Parsons Double Beam Infra-red Spectrometer (Type S.3A) and the spectrum of the compound obtained. A "blank" run with nitrogen only in the cell showed that the spectrometer could be run with nothing in the reference beam.

Reproductions of the spectra of identified compounds are shown. The ordinates of the graphs represent the absorption approximately from 0-100%. All spectra obtained are tabulated on the following page.

<u>Compound</u>	<u>Reaction</u>	<u>Approx. Pressure</u> mm.
2-chloro-2-fluorobutane	$\text{SbF}_3 + 2,2\text{-dichlorobutane}$	29 ±
"	$\text{Cl}_2 + 2\text{-fluorobutane}$	44
d,l 2-chloro-3-fluorobutane	$\text{HgO} + \text{HF} + 2,3\text{-dichlorobutane}$	28
"	$\text{Cl}_2 + 2\text{-fluorobutane}$	33 ±
d,l' 2-chloro-3-fluorobutane	$\text{HgO} + \text{HF} + 2,3\text{-dichlorobutane}$	28
"	$\text{Cl}_2 + 2\text{-fluorobutane}$	29 ±
1-chloro-2-fluorobutane) 1-chloro-3-fluorobutane)	$\text{Cl}_2 + 2\text{-fluorobutane}$	22
1-chloro-2-fluorobutane) 1-chloro-3-fluorobutane)	$\text{F}_2 + 1\text{-chlorobutane}$	23
1-chloro-3-fluorobutane	$\text{HgO} + \text{HF} + 1,2\text{-dichlorobutane}$	19 ±
"	$\text{HgO} + \text{HF} + 1,3\text{-dichlorobutane}$	
2,2-difluorobutane	$\text{SbF}_3 + 2,2\text{-dichlorobutane}$	9 ±
meso 2,3-difluorobutane	$\text{HgO} + \text{HF} + 2,3\text{-dichlorobutane}$	11 ±
"	$\text{F}_2 + 2\text{-fluorobutane}$	10
1,2-difluorobutane	$\text{F}_2 + 2\text{-fluorobutane}$	13
"	$\text{F}_2 + 1\text{-fluorobutane}$	19 ±
1,3-difluorobutane	$\text{F}_2 + 1\text{-fluorobutane}$	21
1,3-difluorobutane	$\text{HgF}_2 + 1,3\text{-dibromobutane}$	26 ±
d,l 2,3-difluorobutane	$\text{HgO} + \text{HF} + 2,3\text{-dichlorobutane}$	18 ±
1,3-difluorobutane and d,l 2,3-difluorobutane)	$\text{F}_2 + 2\text{-fluorobutane}$	27.5 ±

<u>Compound</u>	<u>Reaction</u>	<u>Approx. Pressure</u> mm.
	Synthetic Mixture (1)	20
1,3-difluorobutane and	" " (2)	22 =
d,l 2,3-difluorobutane	" " (3)	29
	" " (4)	30
1-chloro-1-fluorobutane	HgO + HF + 1,1-dichlorobutane	18 =
2-chloro-1-fluorobutane	Cl ₂ + 1-fluorobutane	21 =
3-chloro-1-fluorobutane	Cl ₂ + 1-fluorobutane	21 =
4-chloro-1-fluorobutane	KF + 1,4-dichlorobutane	liquid film =
1,1-difluorobutane	HgO + HF + 1,1-dichlorobutane	22 =
1,4-difluorobutane	KF + 1,4-dichlorobutane	16
1,4-difluorobutane	F ₂ + 1-fluorobutane	24 =
d,l 2-chloro-3-fluorobutane	F ₂ + 2-chlorobutane	19
3-chloro-1-fluorobutane	F ₂ + 2-chlorobutane	26
2-chloro-1-fluorobutane and d'l'-2-chloro-3-fluorobutane)	F ₂ + 2-chlorobutane	27
2-chloro-1-fluorobutane and d'l'-2-chloro-3-fluorobutane)	Synthetic Mixture 1	15
	Synthetic Mixture 2	19

= Spectra reproduced.

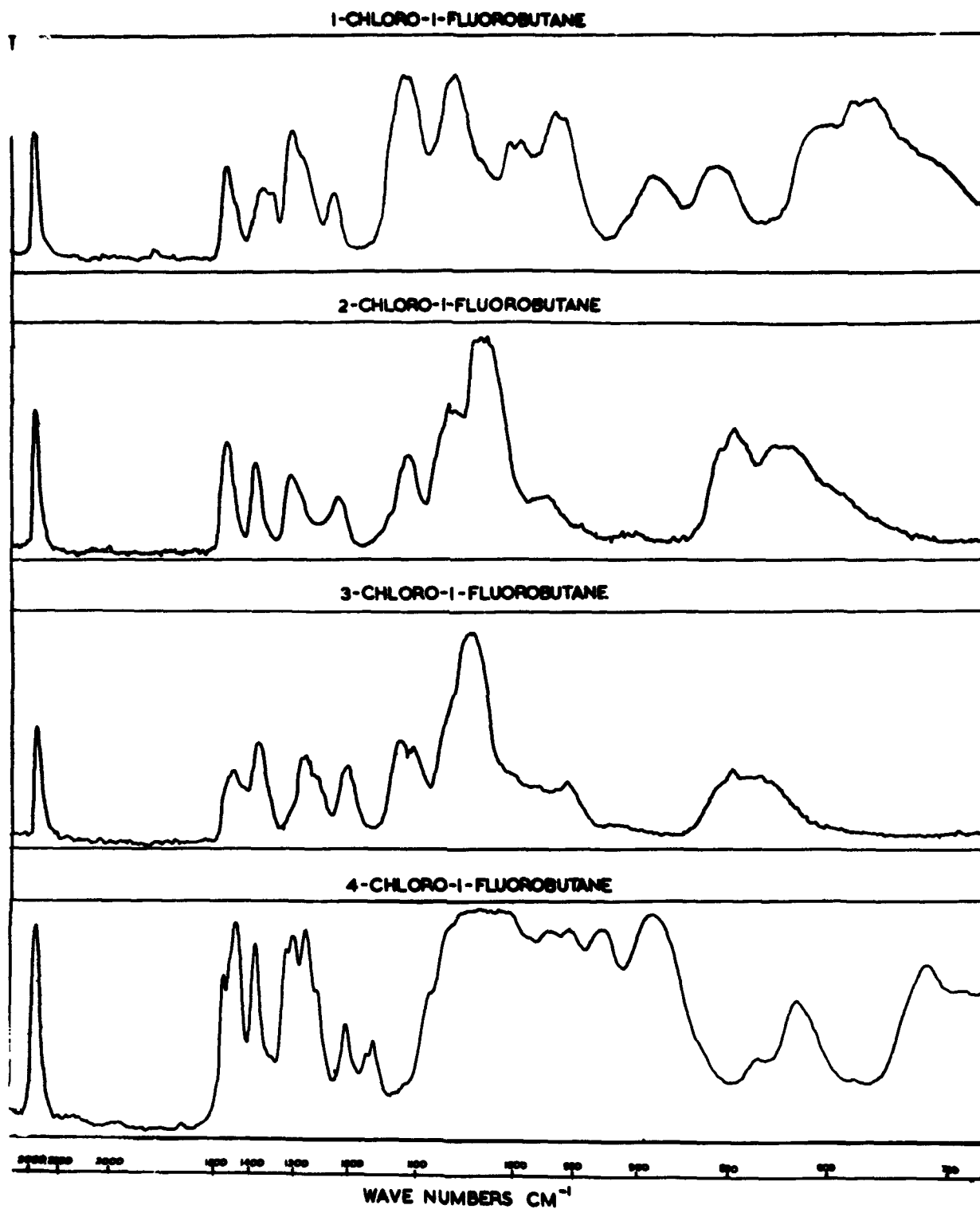


Figure 9a. Infra-Red Spectra

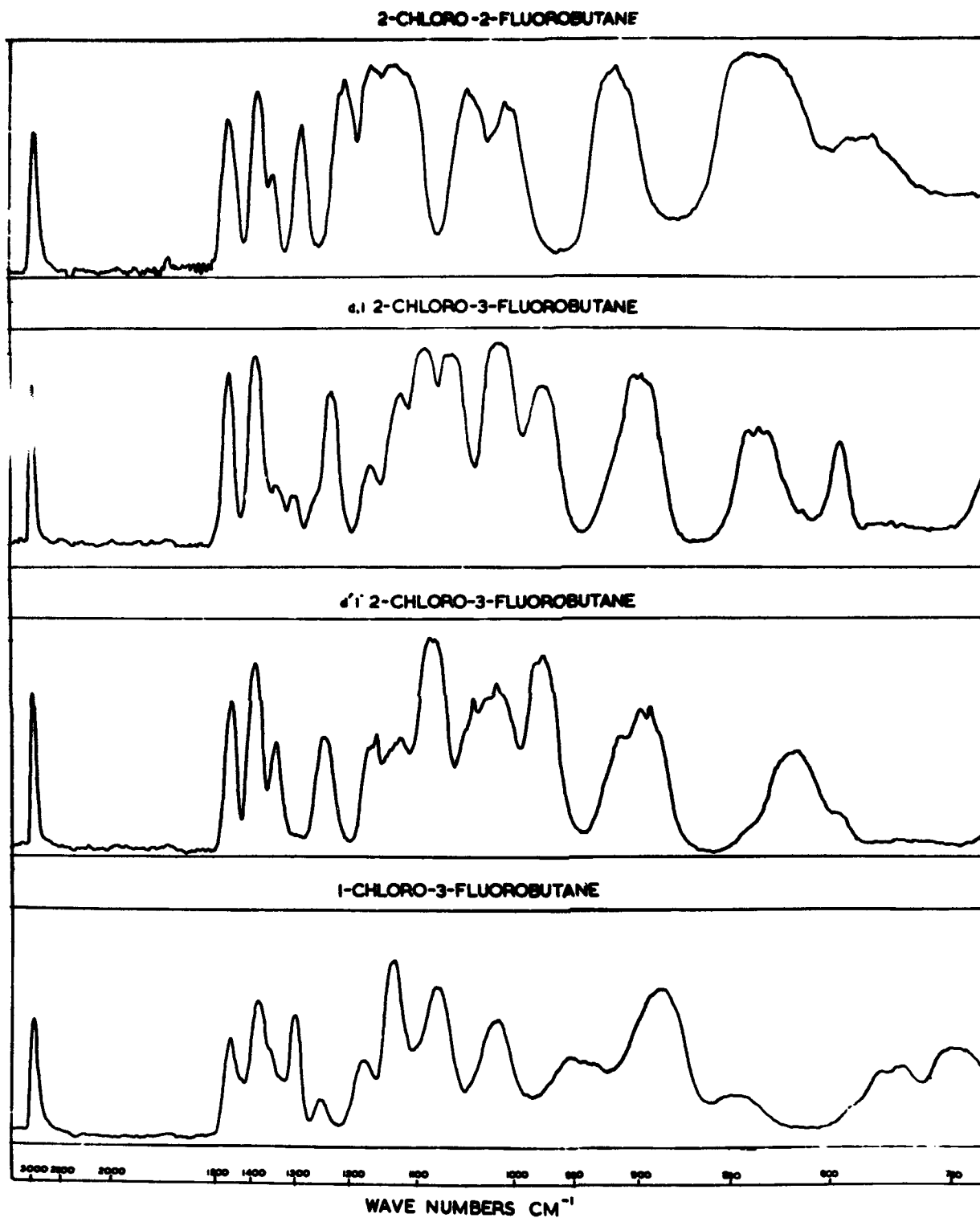


Figure 9b. Infra-Red Spectra

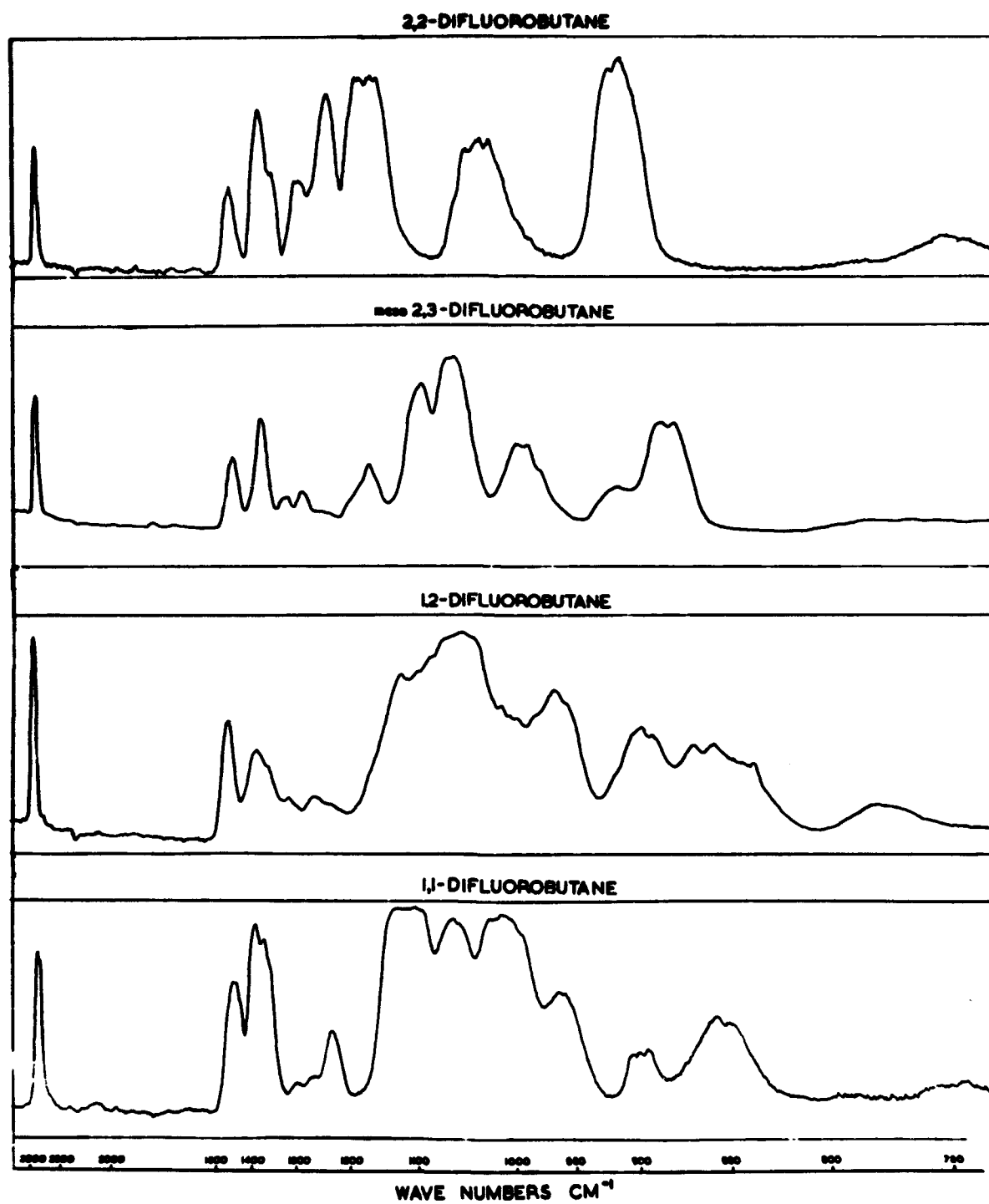


Figure 9c. Infra-Red Spectra

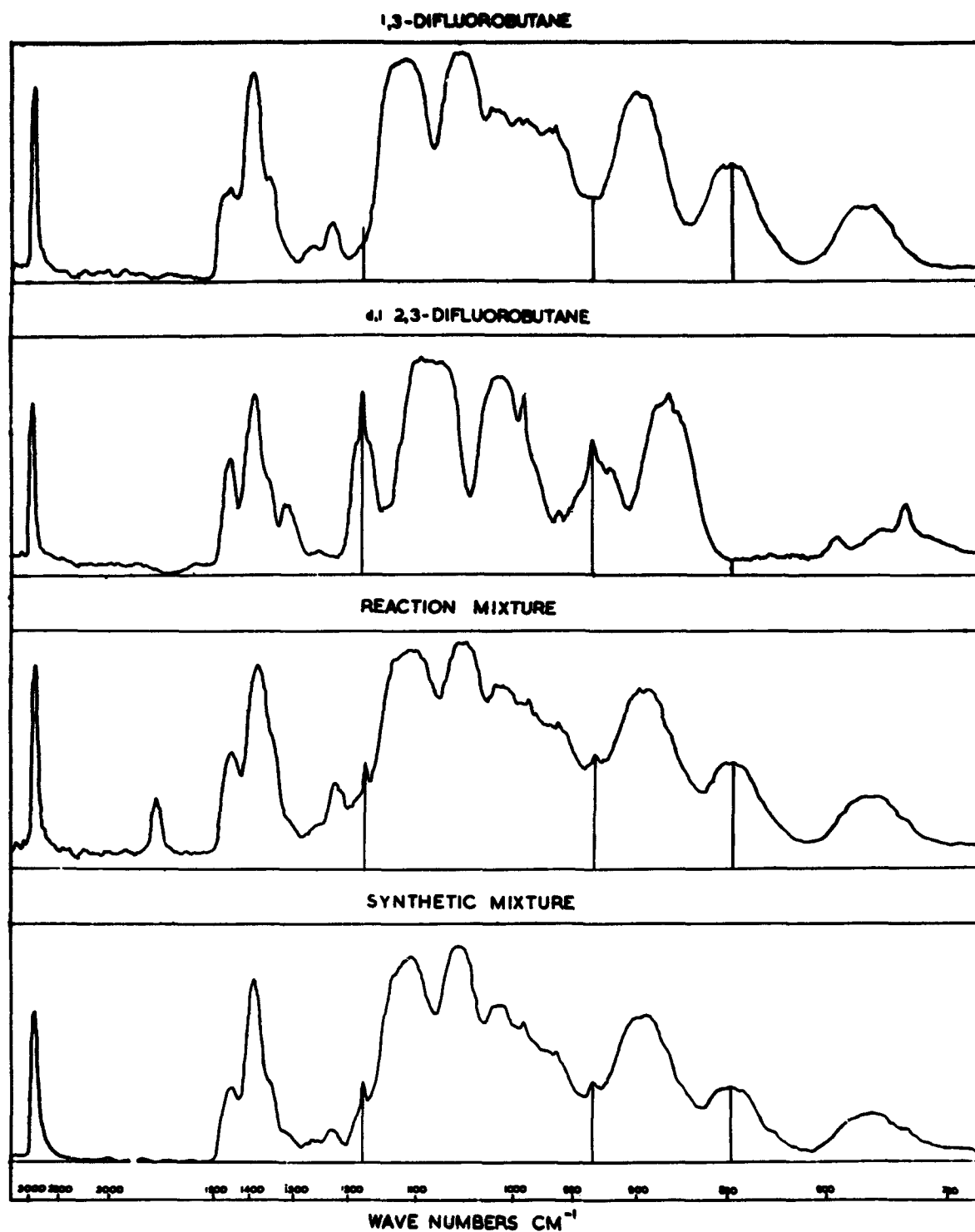


Figure 9d. Infra-Red Spectra

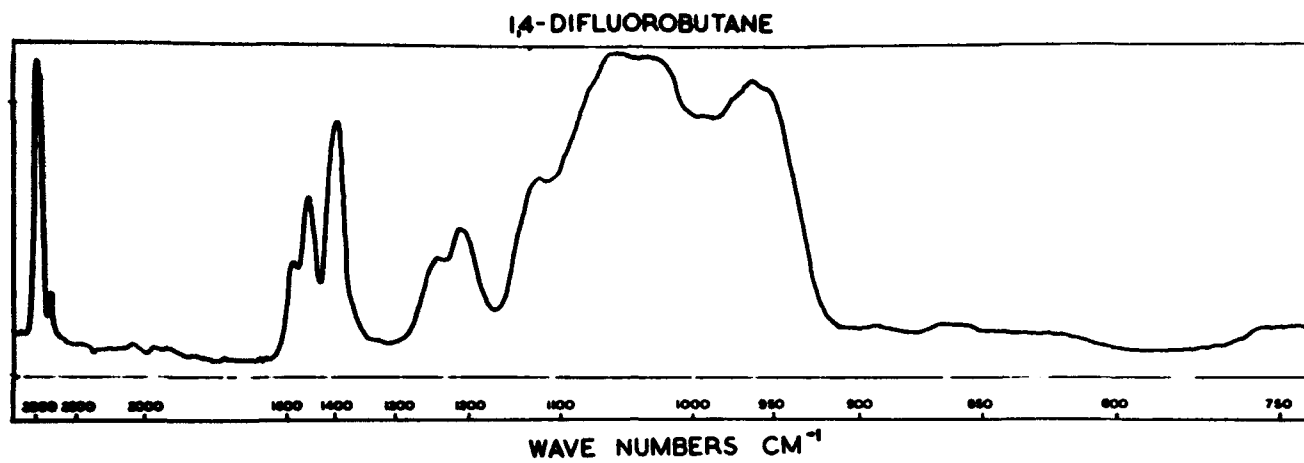


Figure 9e. Infra-Red Spectra

(y) Competitive Chlorination of n-Butane and n-Butyl Chloride using a Flow Apparatus

Approximately equal concentrations of butane (4.4 parts) and n-butyl chloride (2.0 parts) were reacted with chlorine (1 part) in the presence of nitrogen (200 parts). The reaction was carried out at 78° in the apparatus used for all the other studies. The rates that were compared were the chlorination of the secondary position in n-butane with the chlorination of position 3 in 1-chlorobutane. There was no reason to suppose that the thermal conductivities of 2-chlorobutane and 1,3-dichlorobutane are similar, so that the gas phase chromatography apparatus had to be calibrated with synthetic mixtures of known concentrations. These chromatograms of a mixture containing 0.6936 g. of 2-chlorobutane and 0.5038 g. of 1,3-dichlorobutane gave relative peaks areas (2-chlorobutane/1,3-dichlorobutane) of 1.48:1, 1.46:1 and 1.39:1. A single chromatogram of a mixture containing 0.2472 g. of 2-chlorobutane and 0.4334 g. of 1,3-dichlorobutane gave relative peak areas of 0.589:1, giving an average conversion factor (2-chlorobutane/1,3-dichlorobutane) of 1.32. Using this data the relative rate of chlorination of the secondary position in n-butane was estimated to be 1.13 ± 0.06 times the rate of chlorination of the 3-position in n-butyl chloride.

(s) Competitive Chlorination of n-Butane and n-Butyl Chloride using a Static Apparatus

The apparatus consisted of a conventional vacuum line with the butane and butyl chloride vapour stored in large glass bulbs. The chlorine was condensed into a trap, connected to the vacuum line and then degassed in the usual way. The trap was then surrounded by a solid CO_2 / acetone bath at which temperature the vapour pressure of chlorine is known to be 40 mm., so that a bulb of known volume could be filled at this pressure ready for subsequent transference to the reaction vessel. The butane and n-butyl chloride were transferred at known pressures into the reaction vessel in the usual way. The greatest problem was the accurate determination of the relative amounts of 2-chlorobutane (b.p. 68°) and 1,3-dichlorobutane. A different column from that used in the previous experiment was employed, which gave much more efficient separation, notably of the 2-chlorobutane formed from the unchanged n-butyl chloride. However, the 2-chlorobutane came through as a sharp narrow peak, while the 1,3-dichlorobutane came through as a broad flat peak. Extensive calibration was attempted but because of this difference in peak shape the scatter was large. Eight competitive runs were attempted.

<u>Reactants</u>		<u>Products</u>		<u>Relative Rate</u>
$(C_4H_{10})/(C_4H_9Cl)$		$(C_4H_9)/(C_4H_8Cl_2)$		
4.2	4.2	216	102	1.16
2.7	4.6	84	58	1.35
2.8	4.8	90	67	1.24
2.1	4.4	94.5	89	1.22
1.8	4.6	145.5	172	1.19
2.6	4.1	122.5	49	2.19
1.3	5.0	105	113	1.96
2.2	5.0	68	54.5	1.56

$$\frac{\text{Rate of chlorination of } C_2 \text{ in n-butane}}{\text{Rate of chlorination of } C_3 \text{ in n-Butyl Chloride}} = 1.48 \pm 0.29$$

(z') Competitive Chlorination of n-Butyl Chloride and sec-Butyl Chloride

A stream of nitrogen was entrained through a mixture of n-butyl and sec-butyl chlorides in a trap surrounded by an ice bath. The relative concentrations of two butyl chlorides in the vapour phase was determined by having a trap maintained at -78° , which was normally by-passed but through which the butyl chloride nitrogen mixture could be led prior to the reaction vessel. By this means it was possible to condense a small sample of the mixture at any stage of the halogenation run. Provided the

amount of liquid mixture in the initial trap was large the relative concentrations in the vapour did not vary significantly during a run.

Butyl chlorides (10 parts) + chlorine (1 part) + nitrogen (400 parts)

<u>Temp.</u>	<u>No. runs</u>	<u>Reactants</u>	<u>Products</u>
		(2-chloro)/(1-chloro)	(1,3-dichloro)/(1,4-dichloro)
35°	6	0.99 $\pm$ 0.04	77.8 $\pm$ 1.9 / 22.2 $\pm$ 1.9
78°	7	0.95 $\pm$ 0.05	76.3 $\pm$ 2.1 / 23.7 $\pm$ 2.1

The 1,3-dichlorobutane is derived from both the n-butyl chloride and the sec-butyl chloride. The proportion derived from the n-butyl chloride was calculated using the data previously obtained of the (1,3-dichloro)/(1,4-dichloro) ratio from the chlorination of n-butyl chloride. These gave values of the Relative Selection of carbon atom 4 in 2-chlorobutane to carbon atom 4 in 1-chlorobutane as 0.74 $\pm$ 0.32 at 35° and 0.80 $\pm$ 0.28 at 78°.

(x') Competitive Chlorination of n-Butyl Fluoride and sec-Butyl Fluoride

Exactly the same procedure as employed in the previous experiment was used for the competitive chlorination of n-butyl fluoride and sec-butyl fluoride. It was possible on the chromatogram to separate completely 1-chloro-4-fluorobutane and 2-chloro-2-fluorobutane so that relative rates could be compared directly and no calculation was necessary. However, the 2-chloro-2-fluorobutane peak was a small sharp peak while the 1-chloro-4-fluorobutane peak was very broad and flat, and the results show so large a scatter that their value is open to question. The butyl fluoride

mixture was not available in large amounts and so the ratio of the two compounds varied considerably during a run. Thus the results have to be computed individually.

Butyl fluorides (10 parts) + chlorine (1 part) + nitrogen (400 parts)

<u>Reactants</u>	<u>Products</u>	<u>Relative Rate</u>
(1-fluoro-)/(2-fluoro-)	(2-chloro-2-fluoro-)/ (1-chloro-1-fluoro-)	
0.60	0.63	3.1
0.57	0.70	3.7
0.53	1.83	10.3
0.53	1.43	8.0
1.39 →	2.61	5.6
1.39	3.19	6.9
1.26	2.73	6.5
1.26	3.01	7.2
1.31	1.62	3.7
1.13	2.67	7.1

(y') Comparison of the Chlorination of n-Hexane in the Gas and Solvent Phases

The chlorination of n-hexane in the gas phase was carried out exactly as before.

n-Hexane (10 parts) + chlorine (1 part) + nitrogen (350 parts)

Temp. °C.	No. of runs	RS_1^2
14	12	2.98 ± 0.06
40	9	2.74 ± 0.09
120	11	2.54 ± 0.07
160	10	2.44 ± 0.07

The experiments in the liquid phase were carried out in a reaction vessel with a long capillary through which the hydrogen chloride could escape. The vessel was filled completely so that there was no vapour present at the start of the reaction. Carbon tetrachloride was saturated with chlorine at room temperature and then cooled or heated to the desired reaction temperature. It was then added rapidly to the hexane already in the reaction vessel at the desired temperature in the dark. As soon as the reaction system was mixed the reaction vessel was illuminated by a 100 watt tungsten lamp for 20 minutes. The ratio of the two chlorohexanes was determined as before.

n-Hexane (10 parts) + chlorine (1 part) + carbon tetrachloride (5 parts)

Temp. °C	No. of runs	RS_1^2
80	2	2.03 ± 0.11
20	9	2.21 ± 0.07
0	11	2.31 ± 0.04
-35	11	2.82 ± 0.15
-78	9	3.23 ± 0.05

(w') Preliminary Studies of the Chlorination of n-Butyl Ether, n-Butyl Cyanide and 1,1-Dichlorobutane

Dibutyl ether (5 parts) was reacted with chlorine (2 parts) in the presence of nitrogen (200 parts) at 252 mm. pressure. The reaction was carried out in the usual flow apparatus at 78°. The chromatograms showed that there had been considerable decomposition. The largest reaction product peaks were the last two to be eluted. The very last was shown to be 4-chlorobutyl^{butyl}/ether by addition of authentic material synthesised from 1,4-dichlorobutane and sodium butoxide. It seems probable that the other large peak was 3-chlorobutyl butyl ether.

Butyl cyanide (5 parts) was reacted with chlorine (4 parts) and nitrogen (200 parts) at 78° and 252 mm. The reaction was carried out in the usual reaction vessel, using very high flow rates at 78°. Only a small part of the chlorine was consumed. The chromatograms showed only two peaks of any size, which were probably the 3 and 4 chloro-derivatives.

1,1-Chlorobutane (10 parts) was reacted with chlorine (1 part) in the presence of nitrogen (400 parts) at 220 mm. pressure. The reaction was carried out in the usual flow apparatus at 78°. The products were analysed on a chromatography apparatus using an Argon ionization detector, because the apparatus used for the previous work was not able to separate the mixture. The chromatograms were not very satisfactory and it seemed certain that the ionization detector does not give a linear response with

highly chlorinated compounds. In particular the 1,1,1-trichlorobutane seemed to give a particularly small and erratic signal. The very approximate results listed below are not in very good accord with previous work in the liquid phase.

Temp. °C.	CHCl_2	CH_2	CH_2	CH_3
78	0.7%	14.5%	56.2%	28.6%

DISCUSSION

(a) Halogenation of the n-Butyl Halides

The experimental results are summarised in Table I as Relative Selections (RS_p^X), i.e., relative selectivities per hydrogen atom at each carbon atom, the primary hydrogen atoms in n-butane being taken as unity.

$$RS_p^X = \frac{3}{2} [1,x\text{-Dihalogenobutane}] / [1,4\text{-Dihalogenobutane}]$$

TABLE I. HALOGENATION OF N-BUTYL HALIDES.

Temperature	X	CH ₂ X	CH ₂	CH ₂	CH ₃
(a) <u>Fluorination</u>					
20°	H	1	1.3	1.3	1
21°	F	<0.3	0.8	1.0	1
21°	Cl	?		1.7	1
(b) <u>Chlorination</u>					
0°	H	1	4.3	4.3	1
35°	"	1	3.9	3.9 ⁵	1
78°	"	1	3.6 ⁵	3.6 ⁵	1
146°	"	1	3.3	3.3	1
0°	F	0.9	1.8	(4.6)	1
35°	"	0.8	1.6	3.7	1
78°	"	0.9	1.7	3.7	1
146°	"	0.9	1.6	3.2	1
35°	Cl	0.7	2.2	4.2	1
78°	"	0.8	2.1	3.7	1
146°	C	0.7	1.6	3.4	1
35°	Br	0.5	-	4.0	1
78°	"	0.4	-	3.6	1
(c) <u>Bromination</u>					
146°	H	1	82	82	1
146°	F	10	9	82	1 *
146°	Cl	34	32	82	1 *

* RS_p^3 is assumed to be 82 and the RS_p^2 and RS_p^1 are calculated accordingly.

The results are presented together with the previous data from the halogenation of n-butane⁵ for the purposes of comparison. The similarity of the RS_p^3 values in all the chlorination experiments strongly suggests that this comparison is valid. The competitive experiments suggest that carbon atom 4 in the n-butyl halides is slightly less reactive than the primary carbon atoms in butane. However, the competitive experiments were so unprecise that although the butyl halides may be very slightly less reactive than indicated in the table, the error is likely to be small. The results presented are in good agreement with the limited and much less accurate data available previously. The only reaction which had been studied in any detail before was the chlorination of n-butyl chloride. These previous results are compared with the present work below.

TABLE II. THE CHLORINATION OF N-BUTYL CHLORIDE (PREVIOUS WORK)

<u>Reaction Conditions</u>	% isomers				Ref.
	CH ₂ Cl	CH ₂	CH ₂	CH ₃	
Cl ₂ in liquid phase 35-40°	3.2	17.9	52.6	26.3	7
Cl ₂ in gas phase 202°	11.6	10.7	46.4	31.3	8
SO ₂ Cl ₂ in liquid phase 80°	7	22	47	24	13
Cl ₂ in liquid phase 68°	7.8	23.5	49.2	19.5	31
Cl ₂ in liquid phase 80°	4.7	20.5	52.2	22.6	32
Cl ₂ in gas phase 78°	9.6	26.1	45.7	18.6	present work

Considering the variety of conditions the results are on the whole in good agreement, in particular the present work and that of Walling and Mayalis³¹ are very close, although it seems probable that the similarity is partly fortuitous. The only other part of this work which had received any previous work was the bromination of n-butyl chloride and n-butyl bromide in the gas phase¹². The whole study was far less accurate and considerable polybromination occurred, nonetheless the results obtained are qualitatively in agreement with the present work. Thus n-butyl chloride brominated at 100° yielded 1-bromo-1-chlorobutane, 2-bromo-1-chlorobutane and 3-bromo-1-chlorobutane in the ratios 1:1:2, while n-butyl bromide yielded 1,1-dibromobutane, 1,2-dibromobutane and 1,3-dibromobutane in the ratios 3:1:3 together with a large amount of tribromo- and some tetrabromobutanes.

The results listed in Table I can be summarised as follows. The effect of the substituent halogen in position 1 is to retard substitution at position 2 for all three halogenation processes, the effectiveness of the substituent halogens being in the order $F > Cl > (Br)$; a substituent fluorine atom only slightly deactivates the 3-position. The substituent halogen also affects substitution at carbon atom 1, but to an extent and manner which varies greatly with the nature of the attacking radical. The selectivity of the radicals is in the same order as found for unsubstituted alkanes⁵, $Br > Cl > F$, but the nature of the selectivity is no longer similar. At

carbon atom 2 bromination is relatively the least affected by the halogen present, fluorine the most. At carbon atom 1 fluorination is appreciably and chlorination slightly retarded by the substituent halogens in the order $\text{Br} > \text{Cl} \approx \text{F}$, but bromination is activated. The chlorination experiments done over a range of temperatures indicate that the changes in reactivity noted are mainly due to changes in the activation energy of the process.

(b) Halogenation of the sec-Butyl Halides

The chlorination results are summarised in Table III, as Relative Selections (RS_p^X), i.e. the relative selectivities per hydrogen atom at each site, the reactivity of the primary hydrogen atoms in n-butane being taken as unity.

TABLE III. THE CHLORINATION OF THE SEC-BUTYL HALIDES

Temperature	X	CH_3 —————	CHX —————	CH_2 —————	CH_3
35°	H	1	3.9	3.9	1
78°	"	1	3.6 ⁵	3.6 ⁵	1
35°	F	<0.1	3.6	2.1	0.7
78°	"	<0.1	3.2	2.0	0.7
35°	Cl	0.2	3.2	3.1	0.8
78°	"	0.2	3.0	2.9	0.8

The RS values in Table III were calculated by assuming that the rate of chlorination at carbon atom 2 would be affected to the same extent by the substituent halogen as the rate of chlorination at carbon atom 1 in the n-butyl halides. The correctness of this assumption was demonstrated by

the competitive chlorination of n- and sec-butyl chlorides. The rate of chlorination at 35° of carbon atom 4 in sec-butyl chloride was found to be 0.76 ± 0.4 times that at carbon atom 4 in n-butyl chloride (calculated 0.8 times, see Table III). At 78° the relative rate was 0.82 ± 0.38 (calculated 0.8 times, see Table III). The rate of chlorination at position 1 in sec-butyl fluoride is an assumed value. 1-Chloro-2-fluoro- and 1-chloro-3-fluorobutane were eluted together in the gas phase chromatography. Examination of the infra-red spectrum of the eluted material showed that the amount of 1-chloro-2-fluorobutane present was very small and on this observation the figure < 0.1 is based.

The fluorination results are very difficult to correlate. The actual percentages of the isomers obtained are given in Table IV. If it is assumed that carbon atom 3 is affected in the same way in sec-butyl

TABLE IV. FLUORINATION OF SEC-BUTYL HALIDES (% ISOMERS)

Temperature	X	CH ₃ ————— CHX ————— CH ₂ ————— CH ₃	
21°	F	23.9	31.9
21°	Cl	7.9	25.5

fluoride as carbon atom 2 is affected in n-butyl fluoride (this assumption would certainly not be valid for chlorination but may be for fluorination) then relative selectivities can be estimated and these are given in Table V.

TABLE V. FLUORINATION OF SEC-BUTYL HALIDES (APPROXIMATE SELECTIVITIES)

Temperature	X	CH ₃	CHX	CH ₂	CH ₃
21°	H	1	1.3	1.3	1
21°	F	0.4	?	0.8	0.7 ₄

The bromine results can be summarised simply by saying that the rate of attack at carbon atom 2, i.e. the carbon atom carrying the substituent halogen, is very much faster than attack at any of the other sites. The relative selection value for carbon atom 2 must be a factor of 10^2 greater than that for a normal primary hydrogen atom.

2-Chlorobutane had previously been chlorinated by Tischenko and Churbakov⁷ and by Rust and Vaughan⁸. Only the latter workers report results which can be compared, and considering the high temperature of their chlorination and the crudeness of their method of analysis, the agreement with the present results is very good. The reason for the comparatively low

TABLE VI. CHLORINATION OF 2-CHLOROBUTANE (% ISOMERS)

Conditions	CH ₃	CHCl	CH ₂	CH ₃	Reference
200° gas phase	0	23	38	39	7
78° gas phase	4	26	50	18	present work

value for 2,3-chlorobutane obtained by Rust and Vaughan will be discussed later. Kharasch and his co-workers brominated sec-butyl chloride at 100° and only obtained 2-bromo-2-chlorobutane, as in the present investigation. However, their results from the bromination of 2-bromobutane are very different.

They obtained 23.2% meso and 11% racemic 2,3-dibromobutane, only 10% 2,2-dibromobutane and 37.3% of a tribromobutane plus 6.6% of a tetrabromobutane. The apparatus provided for the separation of the brominated products by fractional distillation, the low boiling fraction being recycled. As any decomposition products which boiled at the same temperature or lower than the starting material would also be recycled, it seems probable that the high yields of polybromides and the presence of 2,3-dibromobutane in the reaction product was due to the recycling of olefinic material formed by radical dissociation reactions.

The results for the halogenation of the sec-butyl halides form a consistent picture when considered with those from the halogenation of the n-butyl halides. It was striking to observe that the most reactive site to chlorination and bromination was that to which the substituent halogen atom was attached. This is in accord with Rust and Vaughan's result, but in direct contradiction to the assertion that a substituent halogen directs attack away from itself.¹³

(c) Directive Effects in Hydrogen Abstraction Reactions

The ease of abstraction of hydrogen atoms from aliphatic hydrocarbons by free radicals is invariably in the order tertiary > secondary > primary. This can be explained either as due to resonance stabilisation of the incipient alkyl radical by hyperconjugation or as due to the inductive effect. Great emphasis has been laid on the importance of polar effects^{14,33}, and in the

chlorination of aliphatic compounds they have been regarded as all-important³³. To distinguish between the inductive effect and hyperconjugation in unsubstituted aliphatic compounds is difficult, since the two effects are complementary. In an attempt to assess the relative importance of the two effects the rate of chlorination of the secondary hydrogen atoms in n-butane and n-hexane were compared and the latter were found to be 0.86 times as reactive. The most obvious explanation of this result is reduced hyperconjugation at the two central carbon atoms in hexane. However, Ubbelohde had previously obtained similar results³⁴ and attributed the lower reactivity of the secondary hydrogen atoms in n-hexane to "crumpling" of the molecule. A second approach was made to the problem in which the chlorination of 1-chloropentane was re-investigated³⁵ and the chlorination of 1-fluoropentane and 1-fluorohexane investigated for the first time. The latter was unsuccessful but the chlorination of the two halopentanes was completed and compared with the corresponding butyl halide.

TABLE VII. CHLORINATION OF 1-HALOBUTANES AND 1-HALOPENTANES. RS_p^x at 78°.

CH ₂ Cl —————	CH ₂ —————	CH ₂ —————	CH ₃	
0.8	2.1	3.7	1	
CH ₂ Cl —————	CH ₂ —————	CH ₂ —————	CH ₂ —————	CH ₃
0.8	2.0	3.75	5.5	1
CH ₂ F —————	CH ₂ —————	CH ₂ —————	CH ₃	
0.9	1.7	3.7	1	
CH ₂ F —————	CH ₂ —————	CH ₂ —————	CH ₂ —————	CH ₃
0.8	1.35	3.1	4.4	1

It has previously been argued that the rate of chlorination on carbon atom 3 in 1-chlorobutane is close to that in n-butane, therefore the substituent chlorine atom in 1-chloropentane has little effect on carbon atom 3, yet the hydrogens at this position are markedly less reactive than those on carbon atom 4. The same argument applies with less certainty to 1-fluorobutane and 1-fluoropentane. Clearly the difference in reactivity in positions 3 and 4 in the 1-halopentanes can most readily be attributed to the greater possibilities of hyperconjugation at position 4. (The RS values of the pentyl halides do not fall quite in line with those from the butyl halide.)

It will be noticed that although there is certainly deactivation due to a polar effect, resonance stabilisation of the incipient radical is of predominant importance. Thus the hydrogen atoms on carbon atom 2 are less reactive (to abstraction by chlorine atoms) than those on carbon atom 3 by a factor 2, and yet the hydrogen atoms on carbon atom 1, although the least reactive, differ from that on the adjacent carbon atom 2 still only by a factor of 2 instead of nearly 10, as would be predicted by the inductive effect (c.f. the dissociation constants of the corresponding carboxylic acids $\text{CH}_2\text{ClCH}_2\text{CH}_2\text{COOH}$ $K_A = 3.0 \times 10^{-5}$, $\text{CH}_3\text{CHClCH}_2\text{COOH}$ $K_A = 8.9 \times 10^{-5}$, $\text{CH}_3\text{CH}_2\text{CHClCOOH}$ $K_A = 139 \times 10^{-5}$). In fact as the RS values show, carbon atom 1 is only very slightly deactivated to chlorination. Considering now the results as a whole we are therefore led to the conclusion that hydrogen atoms on the same carbon atom as the substituent halogen are comparatively

easily abstracted by chlorine and bromine atoms. The position is very slightly deactivated to chlorination but is actually activated to bromination. This is in very sharp contrast to the previously accepted generalisation that the halogen already in the molecule directs attack away from itself. With fluorination, however, position 1 in butyl fluoride is strongly deactivated and the evidence available suggests that it is also appreciably deactivated in butyl chloride, so that in fluorination further substitution really does occur preferentially at sites remote from the substituent halogen atom.

These conclusions have been based on results with n-alkyl halides. They are amply confirmed by the work with the 2-halobutanes. Attention has already been drawn to the fact that the most reactive site in these molecules to bromination or chlorination is the one bearing the substituent halogen. This emphasises even more vividly the incorrectness of the generalisation that the substituent halogen directs attack away from itself. The results from the chlorination of sec-butyl chloride demonstrate more clearly the importance of hyperconjugation in determining the reactivity of a particular hydrogen atom. Thus the hydrogen atoms on carbon atom 1 in sec-butyl chloride, on carbon atom 2 in n-butyl chloride and on carbon atom 3 in sec-butyl chloride are all the same distance from the substituent halogen and yet their reactivities relative to the corresponding sites in unsubstituted butane are approximately 0.2, 0.6 and 0.8. The extent of

deactivation due to the inductive effect must be the same for each site, but the extent of possible hyperconjugation is very different.

Perhaps the most striking result of the work so far is the very marked difference in the nature of the selectivity of the three different halogen atoms as hydrogen abstractors. The importance of resonance stabilisation of the incipient alkyl radical by conjugation or hyper conjugation has been stressed above, and this readily explains the high reactivity of the α -position in chlorination and bromination (c.f. IA and IB). The extent of the slight deactivation of the α -position to chlorination follows the order



$\text{Br} > \text{Cl} \approx \text{F}$ so often observed with the halogens when the mesomeric effect ($\text{M}+$) is in opposition to the inductive effect ($\text{I}-$)^{36,37}. In bromination and in hydrogen abstraction by methyl radicals³⁸ the resonance stabilisation ($\text{M}+$) overcomes the inductive effect and the hydrogen atoms on the same carbon atom as the substituent are activated. With methyl radicals the extent of this activation follows the mesomeric release of the halogens (i.e. $\text{F} > \text{Cl} > \text{Br}$). The low reactivity of position 2 relative to position 3 in all the halogenations must be partly due to the reduced possibilities for hyperconjugation and not solely to the inductive effect.

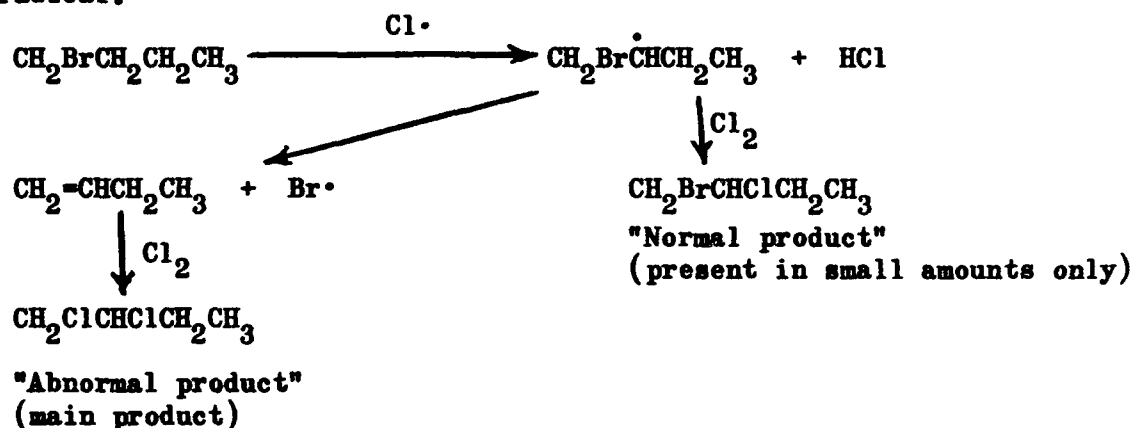
Several papers have discussed the difference in selectivity of different radicals^{39,40,41,42}, but they have all been based on very limited

data. The transition state in the hydrogen abstraction reactions must have some of the characteristics of both reactants and products. In general the smaller $D(C-H)$ and the larger $D(H-X)$ the lower the activation energy. The breaking of the $C-H$ bond will be greatly affected by the stability of the incipient alkyl radical, and the greater the resonance stabilisation of the alkyl radical the smaller $D(C-H)$ ⁴³. However, it is also essential to consider the bond being formed; unlike the $C-H$ bond, which is almost non-polar, the $H-X$ bond formed may be highly polar, usually in the direction $H \overset{+}{\longleftrightarrow} X$. The more polar HX , the more polar we may expect the transition state $C \overset{+}{\longleftrightarrow} H \overset{+}{\longleftrightarrow} X$. The ease with which such structures can be formed will depend on the polar properties of the organic compound, hindered by electron withdrawing groups, and aided by electron-donating groups. It is possible therefore to make the following predictions about the course of attack by a radical $X\cdot$ on an aliphatic compound. If HX has little polar character, that hydrogen atom which on abstraction yields the most stable alkyl radical will be removed preferentially. If HX is very polar the hydrogen abstraction will be favoured at the site which can most easily accommodate a positive charge. In both cases the selectivity of $X\cdot$ will depend mainly on the strength of the $H-X$ bond being formed. The two effects can be in opposition, in which case the course of the reaction will be determined by the polarity of HX . The common radicals can be arranged in the order $Br > CH_3 > Cl > OH > F$ for selectivity, but the extent to

which they will be affected by polar substituents will be in the order $F > OH > Cl > Br > Me$. The picture built up from the results has been developed into a general picture of hydrogen abstraction by free radicals⁴⁴.

(d) The "Vicinal Effect" and the Mechanism of Allylic Halogenation

It will be noticed that in Table I no data is given about the rate of chlorination at the 2-position in butyl bromide. It will be seen in the experimental section that some 1-bromo-2-chlorobutane was formed but comparatively very little. At the same time 1,2-dichlorobutane was formed. This is undoubtedly due to decomposition of the intermediate bromobutyl radical.



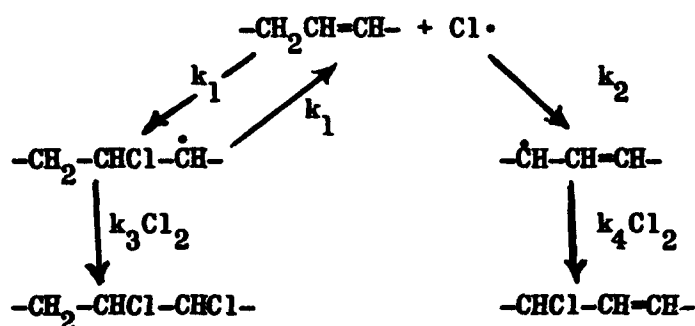
This type of phenomenon has been reported several times previously. Rust and Vaughan⁸ found that at high temperatures the rate of substitution at the β -carbon atom in butyl chloride dropped until at 320° and all temperatures above no 1,2-dichlorobutane was formed in their reaction. Ash and Brown appear to be the first workers to give the correct explanation

for this "vicinal effect"¹³.

In the present results it will be noticed that the vicinal effect is present in the halogenation of alkyl bromides at room temperature and to a lesser extent with alkyl chlorides at room temperature. The present chlorination results suggest that decomposition of the chlorobutyl radicals only became significant above 120°. But the fluorination of n-butyl chloride or more particularly sec-butyl chloride shows quite definitely that these radicals are decomposing at room temperature. There are two possible explanations, either this effect is masked in chlorination reactions by the subsequent addition of chlorine to the butene so formed, or alternatively the chlorobutyl radicals are relatively "hot" when formed in fluorination. The latter explanation seems less likely, for although the hydrogen abstraction step is very exothermic, most of this heat will be found in the HF molecule rather than in the chlorobutyl radical⁴⁵.

These results have some considerable bearing on the mechanism of allylic halogenation. The normal reaction of a free radical with an olefinic double bond is one of addition. However, under certain circumstances the addition reaction may be superseded by a substitution reaction in which the free radical abstracts an allylic hydrogen atom. The best known example of this phenomenon is atomic halogenation of olefins which can result in addition (common at low temperatures and with high concentrations of molecular halogen) or substitution, usually allylic

(occurring at higher temperatures or in the presence of very low concentrations of molecular halogen)²². The preparation of allyl chloride by high temperature chlorination of propene has been in the text books for nearly fifteen years and yet the explanation of this reaction was not given until 1956. The essential key to this mechanism is the reversibility of the addition of a chlorine atom to an olefin. The addition reaction (k_1) is always faster than the abstraction of the allylic hydrogen atom (k_2), but

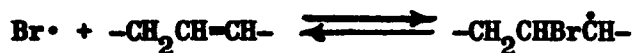


dissociation of the initial addend (k_{-1}) is of comparable rate. It is easy to see how lowering the concentration of molecular halogen will favour substitution. Similarly, an increase of temperature will increase both k_{-1} and k_2 more rapidly than k_1 , which is already very fast.

Allylic bromination by N-bromosuccinimide has long been regarded as a free radical process and it is usually assumed to involve succinimido-radicals⁴⁸. Goldfinger suggested an alternative mechanism in which the function of the N-bromosuccinimide is to provide molecular bromine at



very low concentrations⁴⁷. Allylic bromination rather than addition is to be expected provided the concentration of molecular bromine is low, and this low concentration is maintained by the reaction of hydrogen bromide with N-bromosuccinimide. Goldfinger provided evidence of the rapid reaction



of hydrogen bromide with N-bromosuccinimide. But until the present work evidence for the extremely labile nature of the $-\text{CHBr}-\dot{\text{C}}\text{H}-$ radicals was lacking.

(e) Stereospecific Free Radicals

The halogenation of the 2,3-dibromobutanes must yield two 2,3-dihalo-butanes. It is a matter of considerable interest that the two 2,3-isomers are not formed in equal amounts.

TABLE VIII. PROPORTION OF ERYTHRO AND THREO 2,3-ISOMERS FORMED DURING THE HALOGENATION OF 2-HALOBUTANES

<u>Temp.</u>	<u>Erythro</u>	<u>Threo</u>
(a) Chlorination of 2-Chlorobutane		
35°	71.4	28.6
78°	70.3	29.7
(b) Fluorination of 2-Chlorobutane		
21°	66.6	33.4
(c) Bromination of 2-Fluorobutane		
146°	64.3	35.7
(d) Chlorination of 2-Fluorobutane		
35°	59.4	40.6
78°	59.6	40.4
(e) Fluorination of 2-Fluorebutane		
21°	60.2	39.8

These results clearly imply that the reaction between the intermediate 2-halo-1-methylpropyl radicals ($\text{CH}_2\text{CHCl}\dot{\text{C}}\text{HCH}_3$) and the halogen molecule is stereospecific. A possible explanation may be that the two such radicals have preferred conformations both of which favour substitution from one direction. If it is assumed that the three bonds about the carbon atom carrying the odd electron approximate to sp^2 and are nearly planar, then the other three bonds on the tetrahedral carbon can rotate relative to this plane. However, they will have preferred conformations in which the methyl group of the tervalent carbon atom will be close above the hydrogen

atom of the tetrahedral carbon slightly to either side (see Fig. I). The incoming halogen molecule must approach approximately perpendicularly to the free radical plane and this approach will be easier on the side away from the substituent halogen atom so that in both cases it will yield the erythro compound. Table III shows that the size of the substituent halogen has a greater effect on the proportions of the two stereo-isomers formed, than the reactivity of the attacking atom. This would be in accord with the suggested mechanism.

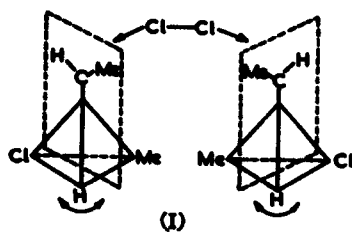


Fig. I

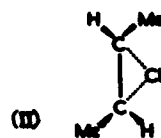


Fig. II

An alternative explanation would be the formation of a bridged structure (II) which would occur most readily with the methyl groups in a "trans"- position and would therefore favour the formation of an erythro-compound. This seems a less probable explanation, particularly as there has been no evidence for the migration of the substituent halogen.

This work was announced two months after Kooyman had also reported a stereospecific radical reaction occurring in the gas phase⁴⁹.

(f) Solvent Effects in Halogenation Reactions

In their pioneering work Hass and McBee found that chlorination in the liquid phase was less selective than in the gas phase^{6,7}. Since the present work has been carried out exclusively in the gas phase, while the majority of previous work was carried out in the solvent phase, a reinvestigation of this problem was necessary. The results are summarised in Table IX.

TABLE IX. CHLORINATION OF N-HEXANE IN THE GAS AND LIQUID PHASES
(Relative Selectivity R_p^s)

<u>Temperature</u>	<u>Liquid Phase</u>	<u>Gas Phase</u>
-78°	3.2	-
-30°	2.8	-
0°	2.3	-
14°	-	3.0
20°	2.2	-
40°	-	2.7
80°	2.0	-
120°	-	-
160°	-	2.4

The figures in Table IX give $k_s/k_p = 1.9 \exp. (250 \pm 50 \text{ cal./RT})$ for the gas phase reaction and $k_s/k_p = 1.1 \exp (430 \pm 50 \text{ cal./RT})$ for the liquid phase reaction. The explanation of this difference is not obvious. Russell has shown that in the liquid phase a large number of solvents all give almost exactly identical isomer distribution in chlorination reactions, but another group of solvents, particularly aromatic hydrocarbons, gives isomer ratios that vary from solvent to solvent⁵⁰. Russell was able to

show that the selectivity of a reaction in a "complexing" solvent was related to the basicity of the solvent. Thus it seemed that the latter solvents formed a charge transfer complex with the chlorine atoms, while the former solvents were inert. The present results were carried out in carbon tetrachloride, which is regarded as an inert solvent. However, the fact that there is a detectable difference between the reaction in carbon tetrachloride and in the gas phase, suggests that even here some weak complex is formed. Walling found that carbon disulphide was an even more powerful complexing solvent than any aromatic compound³¹. It seemed to be of interest to see if complexing could be detected in the gas phase, so hexane was chlorinated at 40° and 120° using carbon dioxide as the diluent instead of nitrogen. The results were identical within experimental error.

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