(a) an investigation of chloro-fluorocyclohexanes (b) the action of chlorine trifluoride on trichloroacetic acid

Cuthberson, F.

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(a) AN INVESTIGATION OF CHLOROFUOROCYCLOHEXANES

(b) THE ACTION OF CHLORINE TRIFLUORIDE ON TRICHLOROACETIC ACID

A thesis submitted by P. Cuthbertson in candidature for the degree of Doctor of Philosophy

Durham Colleges in the University of Durham 1957
Acknowledgements

I should like to acknowledge my indebtedness to Dr. W. K. R. Musgrave who supervised the work described in this thesis and whose help and encouragement have been invaluable, to the Department of Scientific and Industrial Research and the Durham County Education Committee for maintenance grants, and to the Imperial Smelting Corp. for supplying samples of halogenated methanes and other chemicals used in the work.
SUMMARY

An investigation of Chlorofluorocyclohexanes

Two new compounds of this class, containing small numbers of halogen atoms, have been isolated. Both the 1,1-difluoro- and the 1-chloro-1-fluorocyclohexane were prepared from hydrogen fluoride and 1-chloro-cyclohexene and were isolated by gas chromatography. For this purpose an apparatus was developed to separate liquids boiling up to 180°C. in 10 g. portions. The physical and chemical properties of the new compounds were investigated and the results found to agree with the structures given.

Other syntheses, both by standard and previously unpublished methods have been attempted but no desirable products were isolated.

The reaction between chlorine trifluoride and trichloroacetic acid

The reaction was investigated at 80°C. and 100°C. and the products found to be mostly carbon dioxide and halogenated methanes (containing up to three fluorine atoms). Smaller amounts of carbonyl halides (containing chlorine and fluorine), oxygen, carbon monoxide, hexachloroethane and acid halides were also isolated. Quantitative results were obtained which agreed with the amounts of starting materials used in the reaction.
The reaction between chlorine trifluoride and trichloroacetyl chloride was also investigated at the higher temperature as the acid chloride was thought to be a possible intermediate. Free radical mechanisms have been suggested to account for the products in both cases.
AN INVESTIGATION OF CHLOROFLUOROCYCLOHEXANES
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>References 1-17</td>
<td>6</td>
</tr>
<tr>
<td><strong>Attempted syntheses of chlorofluoro-cyclohexanes, -cyclohexenes and -cyclohexadienes</strong></td>
<td></td>
</tr>
<tr>
<td>Preparation of 1-chlorocyclohex-1-ene</td>
<td>8</td>
</tr>
<tr>
<td>Action of hydrogen fluoride on 1-chlorocyclohex-1-ene</td>
<td></td>
</tr>
<tr>
<td>without catalysts</td>
<td>9</td>
</tr>
<tr>
<td>with catalysts</td>
<td>13</td>
</tr>
<tr>
<td>Structure of products</td>
<td>16</td>
</tr>
<tr>
<td>Mechanism of reaction</td>
<td>20</td>
</tr>
<tr>
<td>Properties of 1,1-dihalocyclohexanes</td>
<td>22</td>
</tr>
<tr>
<td><strong>Fluorination of 1,1,2-trichlorocyclohexane</strong></td>
<td></td>
</tr>
<tr>
<td>with hydrogen fluoride</td>
<td>23</td>
</tr>
<tr>
<td>with antimony trifluoride</td>
<td>24</td>
</tr>
<tr>
<td>with potassium fluoride</td>
<td>25</td>
</tr>
<tr>
<td>with mercuric fluoride</td>
<td>26</td>
</tr>
<tr>
<td><strong>Fluorination of 1,2-dibromocyclohexane</strong></td>
<td></td>
</tr>
<tr>
<td>with hydrogen fluoride</td>
<td>26</td>
</tr>
<tr>
<td>with mercuric fluoride</td>
<td>27</td>
</tr>
<tr>
<td>with argentic fluoride</td>
<td>27</td>
</tr>
</tbody>
</table>
Fluorination of 1,2-dichlorocyclo-hex-1-ene

with lead tetrafluoride 28

Action of potassium fluoride on sulphonlic acid esters of cyclohexanols 28

Action of phosphorus pentafluoride on ketones 29

References 18-54 31

Chromatographic separation of chlorofluorocyclohexanes 33

Practical Details

Preparation of 1-chlorocyclohexene 43

Action of hydrogen fluoride of 1-chlorocyclohexene

without catalysts 45

with catalysts 48

Comparative hydrolyses of the 1,1-dihalocyclohexanes 51

Attempted reduction of the 1,1-dihalocyclohexanes 54

The addition of hydrogen chloride to 1-chlorocyclohex-1-ene 55

Preparation of 1,1,2-trichloro-cyclohexane 56

Fluorination of 1,1,2-trichlorocyclo-cyclohexane

With hydrogen fluoride 58

with antimony fluoride 60

with potassium fluoride 61

with mercuric fluoride 62
<table>
<thead>
<tr>
<th>Topic</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorination of 1,2-dibromocyclohexane</td>
<td></td>
</tr>
<tr>
<td>with hydrogen fluoride</td>
<td>64</td>
</tr>
<tr>
<td>with mercuric fluoride</td>
<td>64</td>
</tr>
<tr>
<td>with argentie fluoride</td>
<td>66</td>
</tr>
<tr>
<td>Fluorination of 1,2-dichlorocyclohex-1-ene</td>
<td></td>
</tr>
<tr>
<td>with lead tetrafluoride</td>
<td>67</td>
</tr>
<tr>
<td>Action of potassium fluoride solutions on sulphonic acid esters of</td>
<td></td>
</tr>
<tr>
<td>cyclohexanols</td>
<td>69</td>
</tr>
<tr>
<td>Action of phosphorus pentafluoride on ketones</td>
<td></td>
</tr>
<tr>
<td>References 55–63</td>
<td>72</td>
</tr>
</tbody>
</table>
INTRODUCTION

Workers in these laboratories have studied the action of chlorine trifluoride on benzene under varying conditions. Ellis and Musgrave found that when chlorine trifluoride was passed into solutions of benzene in carbon tetrachloride at 0°C there were formed mainly simple substitution products. When the reaction between benzene and chlorine trifluoride occurred in the vapour phase however a complex mixture resulted. This mixture consisted of chlorofluoro-cyclohexanes, -cyclohexenes and possibly -cyclohexadienes. As little was known about these types of compounds it was considered interesting to attempt their preparation by unambiguous routes and to investigate their properties.

The introduction of fluorine into cyclohexane or its derivatives in such a way that the structure of the product can be easily determined might be accomplished in several ways:

(a) The addition of anhydrous hydrofluoric acid to an olefin, either simple or substituted, can give good yields
of fluorinated materials. In this way cyclohexyl fluoride has been made from cyclohexene\textsuperscript{3} and 2,2-difluoro-pentane from 2-chloro-pent-1-ene.\textsuperscript{4} Whereas the former reaction was accomplished at -78\textdegree{}C, the latter requires the use of elevated temperature and pressure. It is thus seen that reaction conditions have to be matched with the organic starting material.

(b) The action of anhydrous hydrofluoric acid can be accelerated or even modified by the use of suitable inorganic reagents. Boron trifluoride has been used\textsuperscript{5} among other substances to facilitate the less ready addition of hydrogen fluoride to a double bond while lead dioxide has been used to cause the effective addition of fluorine to the double bond\textsuperscript{6} in the presence of hydrogen fluoride.

(c) Suitable metallic fluorides can replace the halogen (other than fluorine) in alkyl halides and can in some cases replace hydrogen.

Antimony trifluoride with bromine as catalyst and 2,2-dichloro-propane give a good yield of 2,2-difluoro-propane.\textsuperscript{7}

Mercuric fluoride can be used as such and in this way 2-fluoro-1,2,3-trichloro-propane was prepared from 1,2,2,3-tetrachloro-propane,\textsuperscript{8} or the mercuric fluoride
can be generated in situ by the action of hydrogen fluoride on mercuric oxide as in the preparation of 1,1-difluoro-heptane from the dichloride.⁹

Argentic fluoride is rather more vigorous in reaction than mercuric fluoride and tends to replace hydrogen at higher temperatures.

(d) Anhydrous potassium fluoride, when heated in a suitable solvent with alkyl halides can give good yields of the corresponding fluoro compound. This method has been used by Hoffman¹⁰ to prepare ω,ω-difluoro alkanes containing three to six carbon atoms in good yield using ethylene glycol as solvent.

Anhydrous potassium fluoride without solvent has been used under varying conditions to replace by fluorine the chlorine in monochloro-acetic acid¹¹ and its esters.

(e) A recently discovered method of indirectly replacing a hydroxyl group by fluorine consists of heating the benzene sulphonyl esters of the alcohols with a saturated solution of potassium fluoride. In this way¹² 1-chloro-2-fluoroethane has been prepared from 2-chloroethyl benzene-sulphonate. If the yields obtained with the simpler types of compound can be obtained with alcohols derived from cyclohexane then this will be a useful reaction.
(f) The attractive idea of reducing aromatic fluoro compounds has been investigated by Swarts\textsuperscript{13} who found that when noble metal catalysts were used the first step in the reduction was the removal of the fluorine from the ring as hydrofluoric acid. As other methods for the reduction of benzene rings using other catalysts require even more vigorous conditions of temperature and pressure this line of approach was not attempted.

The use of phosphorus pentafluoride to replace the alcoholic hydroxyl group by fluorine has been shown to yield esters of phosphoric acid.\textsuperscript{14} The action of phosphorus pentafluoride on ketones has not been reported and will be investigated.

Suitable organic starting materials for the methods (a) - (d) will be halogenated cyclohexanes, cyclohexenes or cyclohexadienes. The most readily available chloro olefin in this case is 1-chlorocyclohexene, which has been prepared by several authors,\textsuperscript{15} by the action of phosphorus pentachloride on cyclohexanone under varying conditions. Chlorine can be added onto\textsuperscript{16} the double bond and from the resulting 1,1,2-trichloro-cyclohexane, hydrochloric acid can be removed to give a mono or diolefin. 1,2-dibromo cyclohexane is readily
made by the addition of bromine to cyclohexene.\textsuperscript{17}

The esters for the method (e) could be made by standard methods from the alcohols.
1. J.F. Ellis Ph.D. Thesis
   J.F. Ellis et al. J.C.S. 1950 3608
2. R.E. Banks Ph.D. Thesis
4. M.W. Renoll J.A.C.S. 64 1115 (1942)
5. R.C. Arnold C.A. 46 1022h
   C.A. 48 1406e
8. A.L. Henne Organic Reactions Vol II page 85
   John Wiley and Sons, Inc. New York.
9. A.L. Henne J.A.C.S. 60 1569 (1938)
11. B.C. Saunders et al. J.C.S. 1948 1773
12. C.A. 43 6154e
13. F. Swarts Bull. sci. acad. roy. Belg. 22 122-4
    (1936)
   C.A. 30 4154^4
15. a E.A. Braude et al. J.C.S. 1950 2014
   d B. Carroll et al. J.A.C.S. 73 5382 (1951)
15  H.C. Stevens et al.  J.A.C.S. 74 4878 (1952)
16  D.V. Tischenko  C.A. 33 4190 (1939)
    Vol II page 171 John Wiley and Sons, Inc. New York
ATTEMPTED SYNTHESIS OF CHLOROFUORO-CYCLOHEXANES, -Cyclohexenes and -Cyclohexadienes.

It was decided that the following were desirable starting materials.
1-chlorocyclohex-1-ene, 1,1,2-trichloro-cyclohexane, 1,2-dichlorocyclohex-1-ene, 1,2-dibromocyclohexane and the p-toluene-sulphonyl esters of cyclohexanol and 2-chlorocyclohexanol.

PREPARATION OF 1-CHLOROCYCLOHEX-1-ENE.
1-chlorocyclohex-1-ene has been known for more than fifty years but its preparation on a large scale has only recently been described. Although it occurs in the products of the reduction of 1,2-dichlorocyclohex-2-ene with zinc and ethyl alcohol and in the dehydrochlorination of cis-1,2-dichlorocyclohexane with quinoline the only suitable starting materials for litre scale preparation are phosphorus pentachloride and cyclohexanone. In the present work the different methods were tried, as described later in the experimental section and the results are tabulated below. From this it was decided to employ the method of Braude and Coles. As well as the higher yields, this method has the merit of requiring simple apparatus (A 1 litre flask with air condenser) and hence saves time in both preparing and cleaning apparatus.
Author of Method\textsuperscript{15} & Yield of Olefin
Quoted & Found \\
Mousseron et al. & 80\% & 40\% \\
Carroll et al. & 46\% & 31\% \\
Braude and Coles & 60\% & 60\% \\
Stevens et al. & 20\% & – \\

ACTION OF HYDROGEN FLUORIDE ON 1-CHLOROCYCLOHEX-1-ENE

(a) WITHOUT CATALYSTS

Estimation of reaction conditions

Although a great many reactions have been carried out with simple and halogenated olefins the reaction conditions required depend very much upon the structure of the olefin. Olefins with chlorine on one doubly bonded carbon atom require more vigorous conditions than unsubstituted olefins but reaction still occurs readily. When both doubly bonded carbon atoms have chlorine attached then addition of hydrogen fluoride requires still more vigorous conditions or does not take place at all. When the double bond is at the end of the carbon chain and chlorine is attached to the terminal carbon atom then reaction is not very easily accomplished, but if the terminal carbon atom has two chlorine atoms attached reaction occurs at reasonable temperatures. In both cases several reaction products are formed. The
<table>
<thead>
<tr>
<th>Starting Substance</th>
<th>Max. Reaction Temp. °C.</th>
<th>Product of Reaction</th>
<th>Yield %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄H₈</td>
<td>-25</td>
<td>C₄H₉F</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>CH₂=CCl-C₂H₅</td>
<td>35</td>
<td>CH₃CF₂C₂H₅</td>
<td>67</td>
<td>4</td>
</tr>
<tr>
<td>cis CH₃CCl=CHCl</td>
<td>95</td>
<td>CH₃CF₂CH₂Cl</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃CFCl-CH₂Cl</td>
<td>8</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>olefin</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>trans CH₃CCl=CHCl</td>
<td>95</td>
<td>CH₃CF₂CH₂Cl</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃CFCl-CH₂Cl</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>olefin</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>CHCl=CHCl</td>
<td>No reaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHCl=CH-CH₂H₅</td>
<td>65</td>
<td>CHF₂C₃H₇</td>
<td>traces</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CHFCl-C₃H₇</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>olefin</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₁H₈Cl₂</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂CH=CCl₂</td>
<td>65</td>
<td>C₃H₇CF₂Cl</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₃H₇CFCl₂</td>
<td>28</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>olefin</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>CH₂Cl-CCl=CH₂</td>
<td>50 to 60</td>
<td>CH₂Cl-CF₂CH₃</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₂Cl-CFCl-CH₃</td>
<td>74</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>olefin</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>CCl₂=CCl-CCl₃</td>
<td>No addition but substitution of the CCl₃ group at higher temperatures.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH₃)₂C=CHCl</td>
<td>0 to -23</td>
<td>(CH₃)₂C=CHClF</td>
<td>65</td>
<td>20</td>
</tr>
<tr>
<td>CH=CH-(CH₂)₃CH₂</td>
<td>20</td>
<td>CHF-(CH₂)₄CH₂</td>
<td>70</td>
<td>3</td>
</tr>
</tbody>
</table>
presence of chlorine in other parts of the molecule seems to retard the reaction while the presence of a methyl group on a doubly bonded carbon atom accelerates the reaction. In only one case, that of cyclohexene, has the addition of hydrogen fluoride to a cyclic olefin been reported. (For examples see Table I).

In order to obtain an estimate of suitable reaction conditions for a preliminary reaction between 1-chlorocyclohex-1-ene and hydrogen fluoride conditions for reactions between hydrogen fluoride and olefins of comparable structure to 1-monochloro-cyclohex-1-ene are given. (Table II).

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Max. React. Temp. °C.</th>
<th>Products of Reaction</th>
<th>Yield %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂=CCl-C₂H₅</td>
<td>35 to 46</td>
<td>CH₃CF₂C₂H₅</td>
<td>67</td>
<td>4</td>
</tr>
<tr>
<td>CH₃CH=CCl-CH₃</td>
<td>35 to 46</td>
<td>CH₃CF₂C₂H₅</td>
<td>67</td>
<td>4</td>
</tr>
<tr>
<td>CH₂=CCl-CH₂C₂H₅</td>
<td>35 to 46</td>
<td>CH₃CF₂CH₂C₂H₅</td>
<td>64</td>
<td>4</td>
</tr>
<tr>
<td>CH₃CH=CCl-C₂H₅</td>
<td>35 to 46</td>
<td>CH₃CH₂CF₂C₂H₅</td>
<td>60</td>
<td>4</td>
</tr>
<tr>
<td>CH₂=CCl-CH₂CH(CH₃)₂</td>
<td>35 to 46</td>
<td>CH₃CF₂CH₂CH(CH₃)₂</td>
<td>70</td>
<td>4</td>
</tr>
<tr>
<td>CH₃CCl-CH-(CH₂)₄CH₃</td>
<td>35 to 46</td>
<td>CH₃CF₂-(CH₂)₅CH₃</td>
<td>59</td>
<td>4</td>
</tr>
<tr>
<td>C₈H₁₅Cl</td>
<td>35 to 50</td>
<td>CH₃CF₂-C₆H₁₃</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>CH₂CH₂CH-CH-CH₂CH₂</td>
<td>20</td>
<td>CH₂CH₂CHF-CH₂CH₂CH₂</td>
<td>70</td>
<td>3</td>
</tr>
</tbody>
</table>
Although in these the maximum temperature was 50° it was thought advisable to allow a generous margin and to increase the final reaction temperature to 100° for the preliminary reaction so that the main product would be the lower boiling difluoride. The separation and purification of this might be relatively easy and when its properties were known the investigation of the lower temperature reactions would perhaps be more easily accomplished.

**Products of reactions.**

In exploratory experiments the olefin and hydrogen fluoride in a 3:1 ratio at a maximum temperature of 100° yielded mixtures inseparable by simple distillation. The use of a 15 plate distillation column gave two pure compounds analysing to \( \text{C}_6\text{H}_{10}\text{F}_2 \) and \( \text{C}_6\text{H}_{10}\text{Cl}_2 \). When the reagents were used in a 1:1 mole ratio at a maximum temperature of 20° and a similar technique applied severe decomposition of less stable products which were now formed in greater quantity resulted during the distillation.

The application of Gas Chromatography to the above reaction mixtures showed the presence of four compounds, 1,1-difluoro-, 1,1-dichloro- and 1-chloro-1-fluoro-cyclohexane and unchanged olefin. At the lower
temperature less tar and higher yields of both the chlorofluoro and dichloro compound were produced.

(b) WITH CATALYSTS

Estimation of reaction conditions

The addition of hydrogen fluoride to a double bond has been catalysed by a variety of metal and non-metal halides. For the present work boron trifluoride, stannic chloride and aluminium trichloride were selected since they appeared to be the most suitable and the most readily available.

Anhydrous boron trifluoride has been used to catalyse the less ready addition of hydrogen fluoride to chlorinated olefins. Both addition and substitution of the chlorine occur with polymer formation at higher temperatures. The same reagent also facilitates the addition of hydrogen chloride to simple olefins, sometimes yielding dimers in addition to the expected chlorohydrocarbons.

Stannic chloride and hydrogen fluoride replace chlorine by fluorine in halohydrocarbons while stannic chloride catalyses the addition of hydrogen chloride to simple and halogenated olefins.

Aluminium trichloride has been used to aid fluorinations but few details are given. It catalyses
TABLE III

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Catalyst</th>
<th>Other Reagents</th>
<th>Max. Temp.</th>
<th>Products</th>
<th>Yield</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCCl=CHCl</td>
<td>BF$_3$</td>
<td>HF</td>
<td>160</td>
<td>MeCF$_2$CH$_2$Cl</td>
<td>4.4</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHCl=CHCl</td>
<td>BF$_3$</td>
<td>HF</td>
<td>95</td>
<td>CH$_2$ClCHClF</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>polymer</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>CHCl=CHCl</td>
<td>BF$_3$</td>
<td>HF</td>
<td>25</td>
<td>CH$_2$ClCHClF</td>
<td>3</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>polymer</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=CHPr</td>
<td>BF$_3$/H$_3$PO$_4$</td>
<td>HCl</td>
<td>55</td>
<td>MeCIClPr</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>MeCH=CHMe</td>
<td>BF$_3$/H$_2$O</td>
<td>HCl</td>
<td>55</td>
<td>C$_4$H$_9$Cl</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C$_8$H$_7$Cl</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>MeCHCl$_2$</td>
<td>SnCl$_4$</td>
<td>HF</td>
<td>100</td>
<td>CH$_3$CHClF</td>
<td>40</td>
<td>27</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH$_3$CF$_2$</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>CH=CCl-(CH$_2$)$_3$CH$_2$SnCl$_4$</td>
<td>HCl</td>
<td>10</td>
<td>C$<em>6$H$</em>{10}$Cl$_2$</td>
<td></td>
<td>15b</td>
<td></td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>SnCl$_4$</td>
<td>HCl</td>
<td></td>
<td>C$_3$H$_7$Cl</td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>C$_6$H$_5$CH=CH$_2$</td>
<td>SnCl$_4$</td>
<td>HCl</td>
<td>25</td>
<td>C$_6$H$_5$CHClMe</td>
<td></td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>polymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me$_2$CH=CH=CH$_2$</td>
<td>AlCl$_3$</td>
<td>HCl</td>
<td>-80</td>
<td>MeCHCHClMe</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>polymer</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_5$CF$_3$</td>
<td>AlCl$_3$</td>
<td>MeCOCl</td>
<td>70</td>
<td>C$_6$H$_5$CCl$_3$</td>
<td>86</td>
<td>31</td>
</tr>
<tr>
<td>CCl$_2$=CHCl</td>
<td>AlCl$_3$</td>
<td>HCl</td>
<td>50</td>
<td>C$_6$Cl$_6$C$_4$HCl$_5$</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CCl$_3$CH$_2$Cl</td>
<td>(CHCl$_2$)$_2$</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C$_4$H$_3$Cl$_5$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the addition of hydrogen chloride to simple olefins and causes much polymerisation. This reagent can also replace organically held fluorine by its own chlorine and cause the rearrangement of the halogens in organic molecules. (For examples to illustrate the above see Table III)

**Products of reaction**

Preliminary experiments using excess hydrogen fluoride and boron trifluoride as catalyst indicated that $C_6H_{10}F_2$ was formed as the major product while the use of stochiometric amounts of hydrogen fluoride produced greater amounts of high boiling products. When the former reaction products were separated by gas chromatography the main component was found to be $C_6H_{10}F_2$. This method of analysis was not applied to the second reaction but distillation showed that the products were probably similar to those obtained by using stannic chloride and aluminium chloride.

The initial experiments with both stannic and aluminium chlorides yielded mixtures containing fair amounts of high boiling products that were inseparable by simple distillation and unstable to fractionation at atmospheric pressure. Gas chromatography showed that the major products were $C_6H_{10}ClF$ and $C_6H_{10}Cl_2$ with
smaller amounts of $C_6H_{10}F_2$ and unchanged olefin.

**STRUCTURES OF THE PRODUCTS**

From the reactions between hydrogen fluoride and 1-chloro-cyclohexene, both with and without catalyst, there have been isolated four compounds, two of which have not previously been described in the literature. From the positions of the peaks on the chromatograms (Fig. 1) it seems reasonable to assume that the four compounds produced are in each case the same four compounds. This is confirmed by the constancy of the refractive indices of the samples of the compounds isolated and might be expected from the similar nature of the reactions.

The first peak on the chromatograms is due to diethyl ether as was shown by direct comparison of the peak position with that due to authentic diethyl ether and the isolation of a sample

\[ n_D^{20} = 1.3538 \quad \text{For pure diethyl ether } n_D^{20} = 1.3526 \]

The majority of this was introduced into the sample from that retained by the syringe after washing out the previous sample. This was not objectionable as it was used as a marker in order to eliminate uncertainty in the time of introduction of the sample.
DIAGRAM 1

HF and 1-chloro-cyclohexene at 100°.

HF and 1-chloro-cyclohexene at 20°.

HF, BF₃ and 1-chloro-cyclohexene at 20°.

HF, SnCl₂ and 1-chloro-cyclohexene at 20°.

HF, AlCl₃ and 1-chloro-cyclohexene at 20°.

Diethyl ether 1-chlorocyclohexene 1,1-dichloro-cyclohexane

Time in min.: 10 20 30

Galvanometer Reading
Compound 1

1,1-difluoro-cyclohexane

\[ n_D^{20} = 1.3906 \quad \text{b.p.} \quad 101.5^\circ \text{ at 75.5 cm.s.} \]

The identity of this substance with the similar compound obtained by distillation was shown by direct comparison of the peak positions. The molecular formula is \( \text{C}_6\text{H}_{10}\text{F}_2 \). The compound was very resistant to hydrolysis in either acid or alkaline medium. Aqueous solutions of sodium hydroxide up to 10N had no detectable effect while solutions of sodium ethoxide in absolute ethanol and of hydrochloric acid in 80% ethanol produced reaction amounting to a few per cent, it being greater in the case of the acid. Cold aqueous permanganate solutions had no effect but refluxing for long periods produced decomposition with no identifiable organic products. Concentrated nitric acid destroyed the compound to give hydrogen fluoride while palladium carbon in 85% ethanol did not catalyse the reduction with hydrogen.

If we ignore the directing influence of the chlorine atom we might expect three possible products. The two 1,2-difluorocyclohexanes would be expected to have similar properties to cyclohexyl fluoride. The
latter hydrolyses more readily in acid solution\(^{33}\) (5% reaction in 1 hr.) and in alkaline solution\(^{34}\) (5% reaction in 7 hr.) and dehydrohalogenates and polymerises in the presence of hydrogen fluoride at 100\(^{0}\),\(^{3}\) the very conditions under which the new compound can be prepared. These differences between the properties of compound 1 and cyclohexyl fluoride show that we have no \(>\text{CHF}\) groupings present and hence it must be 1,1-difluoro-cyclohexane.

**Compound 2**

1-chloro-1-fluoro-cyclohexane

\[ n_D^{20} 1.4382 \text{ b.p. } 138.2 \text{ at } 755 \text{ mms.} \]

The molecular formula is \(\text{C}_6\text{H}_{10}\text{ClF}_2\). N. Hydrochloric acid in 80% ethanol and N. sodium ethoxide in absolute ethanol produced 50% reaction. The compound was inert to cold aqueous permanganate solutions and resisted reduction with a palladium carbon catalyst. By analogy to compounds 1 and 4, compound 2 is designated 1-chloro-1-fluorocyclohexane.

**Compound 3**

1-chloro-cyclohexene

The sample obtained contained a small amount of compound 2. Both analysis by gas chromatography and analysis for halogens indicated the presence of 11.3% \(\text{C}_6\text{H}_{10}\text{ClF}\).
The unsaturation detected with acid permanganate solution and a comparison of the chromatograms of this and authentic 1-chloro-cyclohexene showed that compound 3 was unchanged olefin.

**Compound 4**

1,1-dichloro-cyclohexane

The molecular formula is $\text{C}_6\text{H}_{10}\text{Cl}_2$. Sodium ethoxide in absolute ethanol caused 50% reaction and N. hydrochloric acid in 80% ethanol caused 10% reaction. Palladium carbon did not catalyse reduction.

The three possible isomers that could be compound 4 have been prepared$^{15d}$ and a comparison of physical constants indicates that we have 1,1-dichloro-cyclohexane

<table>
<thead>
<tr>
<th>Compound 4</th>
<th>$n_D^{20}$</th>
<th>b.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1dichloro-cyclohexane</td>
<td>1.4801</td>
<td>164-8</td>
</tr>
<tr>
<td>cis 1,2-dichloro-cyclohexane</td>
<td>1.4967</td>
<td>206.9</td>
</tr>
<tr>
<td>trans 1,2-dichloro-cyclohexane</td>
<td>1.4902</td>
<td>189</td>
</tr>
</tbody>
</table>

This was confirmed by hydrolysis to cyclohexanone$^{15d}$ which was identified as its semicarbazone.

**MECHANISM OF REACTION**

The products of the reactions were all the 1,1 isomers. It seems that we have normal ionic, as
opposed to radical, addition of the acid HX to the double bond, whose ionisation is governed by the mesomeric effect of the vinylic chlorine atom. This is in complete agreement with the results of many other workers, (Table I & ref. 35) but not with those of Mousseron et al.\textsuperscript{36} who claim to have isolated from the stannic chloride catalysed addition of hydrogen chloride to 1-chlorocyclohexene a product whose identity was found from a density at unspecified temperature to be the trans 1,2 isomer. Mousseron postulates an ionic addition in which the polarisation of the double bond is governed by the inductive effect of the chlorine atom and also states that the 1,1 isomer is unstable at room temperature.

This work of Mousseron et al was repeated and the product found to be 1,1-dichlorocyclohexane. As the addition of HX, must proceed by either an ionic mechanism, to give the 1,1 isomer or by radical mechanism to give the cis 1,2 isomer\textsuperscript{35} the isolation of trans 1,2-dichlorocyclohexane is very strange and we must consider Mousseron's identification of the isomer as in error.

The formation of the dichloro and chloro-fluoro compound is explained by the above when HX is either
HCl or HF. The formation of the difluoro compound can be by substitution of the chlorine of the dichloro, or more probably the chloro fluoro compound. An alternative mechanism, similar to that of Henne et al\textsuperscript{25}, involving the formation of 1-fluorocyclohexene seems improbable as none of the latter was detected.

**PROPERTIES OF THE 1,1-DIHALOCYCLOHEXANES**

The properties given for these compounds call for little comment except in the case of reduction and solvolysis or dehydrohalogenation. It appears strange that even the dichloro and chloro fluoro compounds do not lose halogen when attempts are made to reduce them while fluoro benzene\textsuperscript{13} is reduced to cyclohexane and hydrofluoric acid under similar conditions. It appears that cyclohexyl halides are resistant to reduction however as the fluoride does not lose hydrofluoric acid on attempted reduction.\textsuperscript{13}

The unexpected results in the hydrolysis are associated with the chloro fluoro and dichloro compounds. Here reaction stops when half of the halogen is removed. This is in agreement with work by Goering et al.\textsuperscript{37} on the dichloro and chlorobromocyclohexanes. Both the 1,1 and cis 1,2 isomers lose half their halogen
to give 1-halocyclohexene which is not further attacked while only the trans 1,2 isomer loses one molecule of halogen hydrazide to give the 2-halocyclohexene which rapidly loses its second molecule of acid and thus loses all its halogen.

**FLUORINATION OF 1,1,2-TRICHLOROCYCLOHEXANE**

a) **WITH ANHYDROUS HYDROGEN FLUORIDE**

As in the previous work, with hydrogen fluoride and 1-chlorocyclohexene and in the examples in Tables I and II, it seems that hydrogen fluoride, with and without catalyst, substitutes chlorine by fluorine an attempt was made to fluorinate the above trichloro compound with hydrogen fluoride at 100°. All that resulted was a solid polymer. Under less rigorous conditions, for example with stannic chloride as catalyst, no reaction occurred at 20° while boron trifluoride produced much polymerisation and negligible yields of volatile liquids at temperatures as low as -78°. Since it seems that the trichloro compound polymerises almost completely in the presence of free hydrogen fluoride under conditions which might produce substitution it was decided to try other fluorinating agents.
b) WITH ANTIMONY TRIFLUORIDE

Many fluorinations have been carried out with fluorides of antimony in the presence of at least some pentavalent antimony. Much of the work has been carried out with highly halogenated aliphatic and aromatic hydrocarbons but this reagent has been used to fluorinate heterocyclic compounds and lightly halogenated ethanes, propanes and butanes. Table IV gives relevant examples.

TABLE IV.

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Temp. oC</th>
<th>Product</th>
<th>Yield</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>70</td>
<td>CH$_3$CClF$_2$</td>
<td>85%</td>
<td>41</td>
</tr>
<tr>
<td>CH$_3$CCl$_3$</td>
<td>70</td>
<td>CH$_3$CCl$_2$F</td>
<td>85%</td>
<td>41</td>
</tr>
<tr>
<td>Me$_2$CCl$_2$</td>
<td>70</td>
<td>Me$_2$CF$_2$</td>
<td>85%</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MeCClF</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>MeCCl$_2$Et</td>
<td>Spontaneous</td>
<td>MeCF$_2$Et</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>MeCCl$_2$Pr</td>
<td>Reaction</td>
<td>MeCF$_2$Pr</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>MeCH$_2$CHCl$_2$</td>
<td>much decomposition</td>
<td></td>
<td>42</td>
<td></td>
</tr>
</tbody>
</table>

From this it seems that in some cases even large hydrogen-rich molecules can be fluorinated by antimony trifluoride while other similar compounds decompose. As 1,1,2-trichloro cyclohexane possesses one of the groups that facilitate fluorination, a CCl$_2$ group remote from the ends of a carbon chain, this method seemed promising.
However there were isolated from the reactions only very small amounts of unsaturated liquids containing little fluorine and probably containing large amounts of a chloro-cyclohexadiene.

c) WITH POTASSIUM FLUORIDE

Early work was carried out with anhydrous potassium fluoride and anhydrous organic compounds at elevated temperatures and pressures. In this way undecyl and hexyl fluorides were made as well as a variety of ethers and esters, from the corresponding chloro compound although the yields were generally low. The use of xylene as reaction medium in the fluorination of chloroacetamide was the first attempt to remove the need for pressure resistant apparatus. Most of the work involving solvents has been carried out with aliphatic di and poly-hydroxy compounds and in this way a series of \( \omega,\omega \)-difluoroalkanes have been prepared. In more recent publications the reaction between the organic compound and the potassium fluoride is brought about at ambient temperature and pressure by ultraviolet irradiation.

When glycerol was used as solvent for trichlorocyclohexane and reaction conditions were as for the preparation of 1,5-difluoropentane the product was a
liquid composed mostly of a dichloro cyclohexane.

Without solvent even higher temperatures were required to promote reaction and a similar product was obtained.

The lack of fluorine in the products indicates that the high temperature required for the reaction causes elimination of hydrogen chloride to give olefins. Olefins are formed as by products in similar reaction.  

d) WITH MERCURIC FLUORIDE

Although it is more convenient to use nascent mercuric fluoride generated from hydrogen fluoride and mercuric oxide, in view of the instability of the trichloro cyclohexane to hydrogen fluoride the dry mercuric fluoride was prepared by the action of chlorine trifluoride on mercuric oxide, or chloride. The reaction of this fluorinating agent was extremely vigorous and difficult to control, yielding products that decomposed when attempts were made to distil them.

FLUORINATION OF TRANS 1,2-DIBROMOCYCLOHEXANE

a) WITH HYDROGEN FLUORIDE

Although it is more common to use hydrogen fluoride to replace chlorine in halohydrocarbons there are isolated examples in which bromine has been replaced. An attempt to use this method with the above dibromo compound produced only
a solid polymer.

b) **WITH MERCURIC FLUORIDE**

Considering the success with which bromo compounds can exchange their bromine for fluorine by means of nascent mercuric fluoride it seemed probable that 1,2-difluorocyclohexane might be formed by the action of this reagent on 1,2-dibromo-cyclohexane. Attempts to do this merely confirmed the lack of success reported by Henne et al. 47

A further attempt was made using dry mercuric fluoride but the product were unsaturated liquids containing bromine and a little fluorine.

c) **WITH ARGENTIC FLUORIDE**

**Preparation of Argentic Fluoride**

As the action of fluorine on silver chloride gives rise to low melting intermediates argentous fluoride was oxidised to argentic fluoride with chlorine trifluoride to give a solid containing 27% of the desired argentic fluoride

**Products of reaction**

At 0° a small amount of unsaturated liquid was produced which analysis showed contained more fluorine than required for the simple replacement of bromine by fluorine. We must therefore have, in addition,
replaced some hydrogen by fluorine.

**FLUORINATION OF 1,2 DICHLOOROCYCOHEX-1-ENE**

**Preparation of starting material**

The dehydrochlorination of 1,1,2-trichlorocyclohexane was carried out with quinoline as described by Tischenko.\(^{16}\)

**WITH LEAD TETRAFLUORIDE**

This reagent can under suitable conditions add on fluorine to a double bond and replace by fluorine halogens other than fluorine and hydrogen.

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Temp.</th>
<th>Product</th>
<th>Yield</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl=CHCl</td>
<td>100°C</td>
<td>(CHClF)(_2)</td>
<td>17.1%</td>
<td>51</td>
</tr>
<tr>
<td>CHCl=CCl(_2)</td>
<td></td>
<td>CHClFCCl(_2)F</td>
<td>18%</td>
<td>52</td>
</tr>
</tbody>
</table>

As it was thought advisable to attempt to prepare the more fully fluorinated compound 1,1,2,2-tetrafluoro=cyclohexane, the reaction was conducted at 100°C but only polymers resulted.

**ACTION OF POTASSIUM FLUORIDE ON SULPHONIC ACID ESTERS OF CYCOHEXANOLS**

As the action of saturated solutions of potassium fluoride on β-halo ethyl esters of benzene sulphonylic acid produced good yields of chloro fluoro ethanes\(^{12}\) while anhydrous reaction conditions produced:
poorer yields the action of potassium fluoride solutions on esters of cyclohexanol and 2 chlorocyclohexanol was investigated

\[ R'\text{C}_6\text{H}_4\text{SO}_3\text{R} + \text{KF} \rightarrow R'\text{C}_6\text{H}_4\text{SO}_3\text{Na} + \text{RF} \]

As tosyl esters were easily prepared by standard methods these were used.

From the reaction product of these esters with potassium fluoride solutions no pure products were isolated but the evidence points to the formation of olefins which can then polymerise in the presence of hydrofluoric acid, formed either by elimination from any organic fluoride formed or from hydrochloric acid eliminated and the potassium fluoride present.

Subsequent work has been carried out in which the tosyl esters of highly halogenated alcohols have been converted into chlorides, bromide and iodides\(^{53,54}\) in hydroxylic solvents without undue loss due to olefin formation or solvolysis of the ester but when this technique was applied to cyclohexyl p-toluene sulphonate and potassium fluoride only cyclohexene was isolated.\(^{54}\)

**Action of phosphorus pentafluoride in ketones**

As phosphorus pentachloride reacts with ketones to give two possible products, as shown overleaf
it seems possible that phosphorus pentafluoride might react in a similar manner. Lucas et al.\textsuperscript{14} state that when phosphorus pentafluoride reacts with amyl alcohol it does not yield amyl fluoride but no reaction between phosphorus pentafluoride and ketones has been reported.

When PF$_5$ was passed into cyclohexanone, both pure and diluted with ether there were isolated no fluorine containing compounds but only tars and a high boiling unsaturated phosphorus containing compound. When methyl ethyl ketone was similarly treated only tars were isolated. The high boiling compound is probably a phosphoric acid ester of the enol form of cyclohexanone.
     C.A. 40 4682
19 C.A. 35 Pl413
20 A.L. Henne and E.D. Pludeman  J.A.C.S. 65
     1271 (1943)
21 A.L. Henne and F.W. Haeckl  J.A.C.S. 63 2692
     (1941)
22 M.W. Renoll  C.A. 40 P973 (1946)
23 C.A. 48 Pl406e
24 R.C. Arnold  C.A. 46 Pl022g
25 A.L. Henne and R.C. Arnold  J.A.C.S. 70 758
     (1948)
26 W.N. Axe  C.A. 42 2265 b.d.
27 W.B. Whalley  C.A. 43 2217i
28 E.B. Hjerpe and W.A. Gruse  C.A. 32 1956
29 G. Williams and H. Thomas  J.C.S. 1948 1867
30 J.J. Leendertse, A.J. Tulleners and H.J. Waterman
     Rec.trav.chim. 52 515 (1933)
31 A.L. Henne and M.S. Newman  J.A.C.S. 60 1697
     (1938)
32 E. Muller and C. Honn  J.prakt.Chem. 133 289
     (1932) C.A. 26 34801
33 N.B. Chapman and J.L. Levy  J.C.S. 1952 1577
34 N.B. Chapman and J.L. Levy  J.C.S. 1952 1673
35 H.L. Goering et al. J.A.C.S. 77 3465 (1955)
37 H.L. Goering et al. J.A.C.S. 78 1454 (1956)
39 Ind. and Eng. Chem. 39 Pages 378 onwards (1947)
41 A.L. Henne et al. J.A.C.S. 58 889 (1936)
42 A.L. Henne et al. J.A.C.S. 61 938 (1938)
44 B.C. Saunders et al. J.C.S. 1948 1773
45 C.W. Bradley C.A. 40 P. 6498
46 G. Olah et al. C.A. 48 7533b
47 A.L. Henne et al. J.A.C.S. 58 884 (1936)
49 W.S. Struve et al. Chem. and Ind. 39 353 (1947)
50 E.T. McBeek et al. C.A. 45 29751
51 T.P. Walkes C.A. 43 P. 5031f
52 A.L. Henne et al. J.A.C.S. 67 1639 (1945)
53 G.V.D. Tiers et al. J.A.C.S. 75 5978 (1953)
54 W.F. Edgell et al. J.A.C.S. 77 4899 (1955)
CHROMATOGRAPHIC SEPARATION OF CHLOROFUORO CYCLOHEXANES

By the action of hydrogen fluoride on 1-chloro-
cyclohexene a mixture of the above substances and
unchanged starting material had been obtained. In
view of the thermal instability of some of them it was
necessary to develop a means of separation in which
the time of heating was of the order of hours and in
which the hydrogen fluoride formed by their decomposi-
tion was not allowed to collect and autocatalyse
further decomposition. Vapour phase chromatography
seemed promising and to determine the conditions
necessary to produce a good separation in a reasonable
time investigations were carried out with the
homologous series of hydrocarbons from benzene to
p-cymene (these substances covering the range of
boiling points similar to those of the possible
products) on a column packed with 'dinonyl' phthalate
on Celite at 113°C.

When the gas stream left the column at atmospheric
pressure benzene was detected but p-cymene condensed in
the tubes immediately after the column. When the
exit pressure was reduced to 36 mms. p-cymene gave
a reasonable deflection and the separation produced by
a new column was acceptable but deteriorated with use.
When this filling was employed in macro scale work it was found that the ester decomposed into nonene, phthalic anhydride and water and so a search was conducted to find a more stable stationary phase. Of the packings tried (see diag. 2.) Edwards 8a high vacuum oil gave the best separation and the addition of stearic acid merely increased the retention volume under the condition of the test (126°C, 65 mms. \( N_2 \) flowrate 33 mls./min.).

**Apparatus and Method of operation**

In the apparatus finally adopted for semi-micro work (Fig. 3) the nitrogen was dried (\( P_2O_5 \)) and passed into the first arm of the detector (Two catharometers and two resistances or four catharometers connected in a Wheatstone bridge network) via a flow-meter, manometer and surge tank. From the detector the nitrogen went to the chromatographic column and the exit gases and vapours were passed through the second arm of the detector and through a cooled trap to a vacuum pump. Valves were inserted between the vacuum pump and the cold trap (\( V_3 \)), between the manometer and the detector (\( V_2 \)) and before the drying tube (\( V_1 \)) to control the rate of flow of nitrogen and the pressure of the gas in the system. The pressure was atmospheric.
DIAGRAM 2

Examination of possible substances for stationary phase

a) with mixture of equal parts of toluene, ethyl benzene and p-cymene.

Silicone fluid M.S. 550 containing 10% stearic acid (3 parts) on Celite 545 (7 parts)

Edwards 8a high vacuum oil (4 parts) on Celite 545 (10 parts)

Edwards 8a high vacuum oil containing 10% stearic acid (4 parts) on Celite 545 (10 parts)

10 Time in min. 20 30

b) Reaction products from HF, SnCl₄ and 1-chlorocyclohexene at 200°

Silicone fluid M.S. 550 containing 10% stearic acid (3 parts) on Celite 545 (7 parts)

Edwards 8a high vacuum oil (4 parts) on Celite 545 (10 parts)

Edwards 8a high vacuum oil containing 10% stearic acid (4 parts) on Celite 545 (10 parts)

10 Time in min. 20 30
**Diagram 3**

Block diagram of vapour phase chromatography apparatus

**Semi-micro**

\[ N_2 \rightarrow V_1 \quad \text{Drier} \quad \text{Flow Meter} \quad \text{Manometer} \quad \text{Column} \quad V_2 \quad \text{Detector} \]

\[ \text{Surge Tank} \quad \text{Pump} \quad V_3 \quad \text{Cold trap} \]

**Macro**

\[ N_2 \rightarrow V_1 \quad \text{Drier} \quad \text{Flow Meter} \quad V_2 \quad \text{Preheater} \quad \text{Column} \quad \text{Detector} \]

\[ \text{Surge Tank} \quad \text{Manometer} \quad \text{Pump} \quad V_3 \quad \text{Trapping System} \]

**Electrical Circuits**

2 Catharometers and 2 resistances

4 Catharometers

\[ N_2 \rightarrow \text{Arms} \]

\[ \text{Arms} \rightarrow \text{Collector} \]
**Diagram 4**

Copper detector

Elevation and part section (actual size)

- Insulation and support for 0.02 mm. diam. nickel wire (60Ω)
- Gas inlet with copper coils to bring gas stream to the temperature of central copper block
- Copper block housing four catharometers
- Gas outlets

**Details of A and B**

- The tungsten wires (a) sealed into the glass and to the ends hard soldered nickel cylinders (d). To these nickel cylinders soft soldered the nickel filament (b) and the connecting wires (c).
- Insulating glass tube.
Plan of copper detector (actual size)

Gas outlet  Gas inlet

Gas inlet  Gas outlet

DIAGRAM 5
Diametric and vertical sections of heater
large V.P.C. column (1/4 actual size)

Iron pipe
Asbestos insulation containing heating element
Asbestos pipe
Glass wool

Chromatogram of macro scale separation
Idealised graph for 10 ml. of reaction product from action of HF on 1-chlorocyclohexene at 1000

Calv. defln.

0 1 2 3 4 5 6
Time

Et2O C6H10O2
C6H10ClF
C6H9Cl
C6H10Cl2
DIAGRAM 6

Trapping system 1/4 full size

This unit repeated six times

From detector

To Manometer

To pump

Section at C

One all glass catharometer

The tungsten wires (a) sealed into the glass and to the ends hard soldered the nickel filament (b) [0.02 mm. diam. 60 Ω] and the copper connections (c).

18 cms.
**Diagram 7**

**Small vapour phase chromatography column**
- **Dimensions in cms.**
  - 16
- Glass wool plugs to retain packing
- Preheater to vapourise sample quickly
- Packing
- Serum caps
- Asbestos insulation containing heating element
- Iron tube
- Rubber bung

**Large vapour phase chromatography column**
- **Half of column** 1/2 size
- **Dimensions in cms.**
  - 130
  - 120
  - 28
- Burette
  - Pressure (6cm.) N₂ applied to force sample into column
- Isotape on preheater
- Glass wool
- To second half
- B7 on second half only
- Fits into preheater
- Packing
up to $V_2$, falling to the value given in the condition of chromatography up to $V_3$ (The pressure drop being mostly over the column) while beyond $V_3$ the pressure was of the order of a few mms. Details of the construction of the detectors (Both types of which were satisfactory), the columns and electrical circuit are given in Diagrams 3-7.

For macro work the apparatus was modified as follows. The larger column was preceded by a pre-heater (Fig. 3 & 7 to ensure rapid vapourisation of the large sample and a system of traps (Fig. 3 & 6) was incorporated to collect separately the various samples.

Analytical separations were carried out on small amounts (0.01 ml.) of substance which were introduced with an Agla micrometer syringe and galvanometer readings taken for 30 mins. Larger amounts of liquid (up to 10 ml.) were added with a burette (Fig. 7) and as the pure compounds emerged, as indicated by the galvanometer, they were lead through the appropriate trap cooled in liquid $N_2$. Complete elution of a sample took 6-8 hours, depending on the age of the packing and although chromatograms of such separations were not constructed an idealised example is given
(Diag. 5).

The Celite 545 was prepared for this work by extracting with concentrated hydrochloric acid, 2N sodium hydroxide solution and grading and the fillings prepared from the stated amounts of material. The semimicro columns contained about 15 g. and the macro columns about 1,000 g. of filling.
PRACTICAL DETAILS

PREPARATION OF 1 CHLORO CYCLOHEXENE

The methods of preparation consist of dropping cyclohexanone onto phosphorus pentachloride. The differences in the methods lie in the use of solvents, the method of working up and the inclusion or omission of a dehydrochlorination stage.\textsuperscript{15} The alternative method of mixing reagents, namely the addition of the solid phosphorus pentachloride to the cyclohexanone, although more easily accomplished, yielded upon hydrolysis of the reaction mixture only tar (see below). In view of the favourable yield and the simplicity of the method that of Braude and Coles was adopted. Gas chromatographic analysis of the olefin so prepared showed the presence of 16\% of 1,1-dichlorocyclohexane.

The preparations were carried out as described by the authors but the following observations were made.

a) Carrol et alia\textsuperscript{15d}

The steam distillation of the reaction product yielded an initially cold distillate that rapidly warmed. This was thought to be due to hydrolysis
of the 1,1-dichlorocyclohexane present. To overcome this loss of product the steam distillate was separated and the organic layer dried as quickly as possible.

b) Mousseron et alia

The ethereal solution of the reaction products rapidly warmed and eventually boiled in the presence of water and it was found advisable to have ice present until the ethereal solution was dried.

c) Braude et alia

An additional wash of the crude product with sodium bisulphite solution, to remove any cyclohexanone, did not lower the yield. It was also found that the dry neutral product could be distilled at atmospheric pressure if the distillation was completed in under four hours.

d) Addition of phosphorus pentachloride to cyclohexanone

Cyclohexanone (653 g. 0.68 mole) was stirred in a three necked flask equipped with reflux condenser and phosphorus pentachloride (1,800 g. 0.68 mole) was added from a conical flask via a wide rubber tube with the exclusion of the air while the temperature was kept below 30° by an ice bath. Working up by steam distillation or ice hydrolysis yielded negligible
quantities of olefin.

**ACTION OF HYDROGEN FLUORIDE ON**

**1 CHLORO CYCLOHEXENE**

WITHOUT CATALYSTS

a) **With excess hydrogen fluoride**

1-Chloro cyclohexene (50 g. 0.43 mole) was put into a cold autoclave (0°C.) and hydrogen fluoride (26 ml. 1.4 mole) added. The autoclave was rotated, allowed to come to room temperature (30 mins.) and the temperature raised to 100° over one hour when the pressure was 15 atmospheres. After rotating at this temperature for one hour it was allowed to cool overnight and then cooled in ice. The autoclave was vented and the contents sucked out onto crushed ice (200 g.). The resulting heavy dark brown oil was diluted with ether until the relative density of the solution was less than one, washed with sodium bicarbonate solution and then water until neutral and dried (MgSO₄). After distillation to remove most of the ether and leave the tar (10 g.) the remainder, which distilled between 60° and 200° was fractionated through a 15 plate concentric tube column to give intermediate fraction (1 ml.) b.p. 60-100°; 1,1-difluoro cyclohexane
After a similar experiment the reaction mixture was distilled to remove ether, tar (10.0 g) and high boiling residues (6 g., b.p. > 200°) and the product (19 g. b.p. 60-200°) analysed chromatographically and found to contain 1,1-difluorocyclohexane (5.9 g.) 1-chloro-1-fluorocyclohexane (2.7 g.), 1-chlorocyclohexene (1.5 g.) and 1,1-dichlorocyclohexane (8.9 g.)

b) With equivalent amount of hydrogen fluoride

The previous experiment was repeated using 1-chlorocyclohexene (50 g. 0.43 mole) and hydrogen fluoride (8.6 ml. 0.43 mole) but after coming to room temperature the mixture was allowed to stand overnight without heating. No pressure developed and the product was worked up as before. After removal of the ether the crude product (46 g.) was put into the 15 plate concentric-tube still but in bringing it to equilibrium considerable decomposition took place with elimination of halogen acids and formation of tar.

A similar experiment gave on rapid distillation of the ethereal solution of reaction products a
Diagram 8

Reactor used in preparation of AgF₂ and HgF₂

1/3 actual size

Heater consisting of glass tube around which electrical heating element wound and covered with asbestos

Stirrer consisting of brass rod with steel paddles attached to brass discs

Gopper tube with brass stirrer bearings

BF₃ Generator

P.V.C. tubing

CaCl₂ tube

B₂O₃ in

H₂SO₄

NaBF₄ and

H₂SO₄, B₂O₃

Safety trap

Safety valve

Water condenser

BF₃ in anisole
crude material (40 g. b.p. 60-180°), still residue (4 g. b.p. > 180°) and tar (2.5 g.). When analysed by gas chromatography the first fraction was shown to contain 1,1-difluorocyclohexane (6.6 g.), 1-chloro-1-fluorocyclohexane (13.3 g.), 1-chlorocyclohexene (2.1 g.) and 1,1-dichlorocyclohexene (18 g.).

**WITH CATALYSTS**

Boron trifluoride

This gas was prepared by the action of concentrated sulphuric acid on a mixture of sodium borofluoride and boric anhydride as described by H.S. Booth et al.\textsuperscript{63} in a glass and polyvinyl chloride apparatus (Diag. 8) and stored in anisole solution, from which it was recovered by heating.

Aluminium trichloride was used without further purification but the stannic chloride was redistilled.

a) **With boron trifluoride and excess hydrogen fluoride**

1-Chlorocyclohexene (60.5 g. 0.54 mole) and hydrogen fluoride (17.2 g. 0.86 mole) were placed in a brass reaction vessel equipped with a condenser cooled with a solid CO\textsubscript{2}/ethanol mixture, and a stream of boron trifluoride passed for two hours. The viscous reaction product was dissolved in ether and
and the ethereal solution washed with sodium bicarbonate solution and water until neutral and dried (MgSO₄). Repeated distillations gave intermediate fraction (b.p. <100°, 2.5 g.), impure 1,1-difluorocyclohexane (b.p. 100-110° nD²₀ = 1.3981, 9.5 g.) intermediate fraction (b.p. 107°- 158° 4 g.) and a mixture of 1,1-dichlorocyclohexane and 1-chlorocyclohexene formed by decomposition of former during distillation (5 g. b.p. 158-84°/36 mm. 42% Cl 0.35% F).

A similar experiment was conducted using 1-chlorocyclohexene (50 g. 0.43 mole) and hydrogen fluoride (26 ml. 1.3 mole) and the crude product (9 g. b.p. 60-180°) separated from tarry residues (6.5 g.) and liquid residues (3 g. b.p. 80-100/24 mm). When the crude product was analysed by gas chromatography it was found to contain 1,1-difluorocyclohexane (8.9 g.) and negligible amounts of 1-chlorocyclohexene and chlorofluorocyclohexane.

With boron trifluoride and equivalent amount of hydrogen fluoride

The experiment was repeated using 1-chlorocyclohexene (50 g. 0.43 mole) and hydrogen fluoride (8.6 ml. 0.43 mole). Less tar and undistillable residues (4 g.) were obtained and larger amounts of a mixture (35 g. b.p. 80° at At.press. to 96° at 14 cms.)
whose composition was probably similar to that produced when aluminium trichloride and stannic chloride were used. The mixture was not analysed by gas chromatography.

b) With stannic chloride

1-chlorocyclohexene (50 g. 0.43 mole) was cooled to -78°C in a brass reaction vessel of about 150 ml. capacity, anhydrous stannic chloride (1 g.) and hydrogen fluoride (8.6 ml. 0.43 mole) were added and the vessel fitted with a screw on lid carrying a delivery tube attached to a calcium chloride tube. The mixture was allowed to warm up to room temperature overnight as the solid CO₂ evaporated, poured onto ether and washed with water, sodium bicarbonate solution, water until neutral and dried (MgSO₄). Distillation of this solution yielded a mixture (40.3 g. b.p. 60°-190°) liquid residues (3 g., b.p. 190°-200°) and tar (1.5 g.). The mixture was analysed by gas chromatography and shown to contain 1,1-difluorocyclohexane (5.5 g.), 1-chloro-1-fluorocyclohexane (11.3 g.), 1-chlorocyclohexene (4.0 g.) and 1,1-dichlorocyclohexane (19.4 g.).

c) With aluminium trichloride

The previous experiment was repeated using
aluminium trichloride (1 g.) as catalyst instead of stannic chloride. The ethereal solution of reaction products yielded a mixture (42 g. b.p. 60°-180°), liquid residues (3 g. b.p. 180°) and tar (1.5 g.). Gas chromatographic analysis of the mixture showed that it contained 1,1-difluorocyclohexane (1.9 g.), 1-chloro-1-fluorocyclohexane (18.7 g.), 1-chlorocyclohexene (3.7 g.) and 1,1-dichlorocyclohexane (17.8 g.).

The addition of aluminium trichloride to 1-chlorocyclohexene at room temperature produced a vigorous reaction in the absence of hydrogen fluoride and most of the reaction mixture was lost.

**COMPARATIVE HYDROLYSES OF THE DIHALO-CYCLOHEXANES**

As the difluoro compound was expected to be the least reactive of these three compounds experiments were carried out to find conditions that would just produce hydrolysis of this compound and apply these conditions to the chloro-fluoro and dichlorocyclohexanes.

**Hydrolyses with aqueous solutions:**

1,1-difluorocyclohexane (0.8925 g.) was refluxed on a water bath with 25 ml. N. sodium hydroxide.
solution samples (0.5 ml.) were removed after 5 hours and 8½ hours and the alkali present titrated with N. acid. Comparison with a blank experiment run in parallel showed that no hydrolysis had occurred.

The sodium hydroxide was brought up to 4N. After a further 5 hours heating qualitative tests: (zirconium nitrate and sodium alizarin sulphonate in acid solution) showed the absence of fluoride ion.

After adding more sodium hydroxide to bring the solution to 10 N, the mixture was heated for a further 9 hours. A sample (0.1 ml.) when passed through a cation exchange column (Amberlite IR 120: H) showed, when compared with the blank experiment, that no hydrolysis had occurred.

**Hydrolyses in ethanolic solutions**

Dry reduced ethanol was used throughout and simply by dissolving metallic sodium in this solvent the sodium ethylate solutions were prepared. The hydrochloric acid solutions were made up from ethanol, water and A.R. hydrochloric acid. The hydrolysis mixtures were sealed into hard glass tubes and heated in an oil bath at 130°. At the end of the required time the tubes were cooled to -78°, opened and the contents made up to 100 ml. after
### TABLE V

<table>
<thead>
<tr>
<th>Cpd (g)</th>
<th>Reagent</th>
<th>Reaction time (hours)</th>
<th>Alk. required for 10ml. aliquot - Blank (ml.)</th>
<th>Strength of Alkali</th>
<th>% Hydrol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}<em>6\text{H}</em>{10}\text{F}_2) (0.7080)</td>
<td>1.042 N.HCl</td>
<td>16</td>
<td>0.42</td>
<td>0.1016 N</td>
<td>3.6</td>
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<tr>
<td>(\text{C}<em>6\text{H}</em>{10}\text{ClF}) (0.2520)</td>
<td>in 80% EtOH</td>
<td></td>
<td>1.64</td>
<td>NaOH</td>
<td>45.1</td>
</tr>
<tr>
<td>(\text{C}<em>6\text{H}</em>{10}\text{Cl}_2) (0.6067)</td>
<td>and 20% H(_2)O</td>
<td></td>
<td>0.76</td>
<td></td>
<td>9.7</td>
</tr>
<tr>
<td>(\text{C}<em>6\text{H}</em>{10}\text{F}_2) (0.4848)</td>
<td>1.482 N.NaOEt</td>
<td>16</td>
<td>0.87</td>
<td>0.02238</td>
<td>2.4</td>
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<tr>
<td>(\text{C}<em>6\text{H}</em>{10}\text{ClF}) (0.3412)</td>
<td>in EtOH</td>
<td>16</td>
<td>10.82</td>
<td>NaOH</td>
<td>48.5</td>
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<tr>
<td>(\text{C}<em>6\text{H}</em>{10}\text{Cl}_2) (0.6116)</td>
<td></td>
<td></td>
<td>17.21</td>
<td></td>
<td>48.2</td>
</tr>
</tbody>
</table>

### TABLE VI

<table>
<thead>
<tr>
<th>Cpd (g)</th>
<th>Reagent</th>
<th>Reaction time (hours)</th>
<th>Alk. required for 10ml. aliquot - Blank (ml.)</th>
<th>Strength of Alkali</th>
<th>% Hydrol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}<em>6\text{H}</em>{10}\text{F}_2) (0.6374)</td>
<td>0.375 N NaOEt in abs. EtOH</td>
<td>(17\frac{3}{4})</td>
<td>0.53</td>
<td>0.02224</td>
<td>1.1</td>
</tr>
<tr>
<td>(\text{C}<em>6\text{H}</em>{10}\text{F}_2) (0.5466)</td>
<td>1.483 N NaOEt in abs. EtOH</td>
<td>(17\frac{1}{2})</td>
<td>1.06</td>
<td>0.02224</td>
<td>2.6</td>
</tr>
<tr>
<td>(\text{C}<em>6\text{H}</em>{10}\text{F}_2) (0.4886)</td>
<td>1.042 N.HCl in 80% EtOH</td>
<td>(17\frac{1}{2})</td>
<td>0.42</td>
<td>0.1016</td>
<td>5.2</td>
</tr>
</tbody>
</table>
removal of the organic layer in the case of acid hydrolysis.

The amount of reaction in alkaline hydrolyses was determined by passing an aliquot (10 ml.) through a cation exchange column (Amberlite I.R. 120 H) and estimating the halide ion as the halogen hydracid. Blank reaction were run in parallel to allow for the attack of glass.

In acid hydrolyses there was much loss of hydrochloric acid as ethyl chloride. The amount of reaction was estimated from the difference in the acid present in the sample and in a blank experiment. It was found necessary to heat the aliquot to boiling to sharpen the end point. (Tables give details of the reagents etc.)

**Attempted reduction of 1,1-dihalocyclohexanes**

Samples of the organic halide (0.2-0.5 g.) were shaken with 85% ethanol in the reaction flask of a Towers Atmospheric Pressure Hydrogenation apparatus in the presence of palladised carbon (0.2 g.) at a pressure 1 cm. greater than atmospheric pressure for 1-2 hours. In no case was any hydrogen absorbed or any free halogen acid detected in excess of that liberated in a blank experiment carried out with
catalyst and solvent only.

Preparation of cyclohexanone from 1,1-dichlorocyclohexane

A mixture of 1,1-dichlorocyclohexane (11.0 g.) and concentrated sulphuric acid (110 ml.) was stirred and warmed on a water bath at 45°. There was a vigorous evolution of hydrogen chloride and after 1 hour the mixture was poured onto ice. After neutralising with sodium carbonate and allowing the crystals of sodium sulphate to settle the mixture was ether extracted (4 x 25 ml.), the extract dried (MgSO₄) and the ether distilled to leave cyclohexanone (4 g. 57%, b.p. 157° $n^\text{D}_{20} 1.4512$ semicarbazone m.p. 165.5° mixed m.p. with authentic specimen 166°).

The Addition of Hydrogen Chloride to 1-Chlorocyclohexene

1-Chlorocyclohexene (50 g.) and stannic chloride (2.5 ml.) were cooled to 0° in a flask fitted with a stirrer and calcium chloride tube while anhydrous hydrogen chloride was passed in at the rate of three bubbles per second. After two hours the weight had increased by 6 g. and did not increase on further passage of hydrogen chloride. After dissolving in ether the reaction mixture was washed with dilute hydrochloric acid, water, sodium bicarbonate solution
and then water until neutral and dried (MgSO₄).

Distillation failed to give pure samples of either starting material or dichlorocyclohexane and so the product, after removal of the ether, was separated roughly into a mixture of monochlorocyclohexene and dichlorocyclohexane (44.5 g. b.p. 100-180°), liquid residues (3 g. b.p. >180°) and tar (1 g.). The mixture was analysed chromatographically and shown to contain 1-chlorocyclohexene (16.4 g.) and 1,1-dichlorocyclohexane (28.0 g.). Allowing for the dichlorocyclohexane already present and for the recovered olefin this represents a yield of 55%.

**PREPARATION OF 1,1,2-TRICHLOROCYCLOHEXANE**

As 1,1,2-trichlorocyclohexane produced by the action of phosphorus pentachloride on 2-chlorocyclohexanone¹⁵ contains in addition chloro olefins, the trichloro compound was prepared by the direct addition of chlorine to 1-chlorocyclohexene as described by Tischenko¹⁶.

1-chlorocyclohexene (160 g. 1.4 mole) had chlorine bubbled through until the theoretical increase in weight occurred. (11 hours). The mixture was diluted with ether, washed with water and dried. After several distillations 1,1,2-trichlorocyclohexane
(28 g., 0.15 mole, 10.8% yield) was obtained.

(b.p. 104/19.5 mms - 107/15 mms: Cl found 56.7% required for C₆H₅Cl₂ 54.5% nD 1.5360 - 1.5300).

By analogy to the additive chlorination of cyclohexene⁲¹ an attempt was made to increase the yield and decrease the reaction time by addition of 1/4 of the theoretical amount of chlorine.

1-Chlorocyclohexene (1,074 g. 9.06 mole), sodium carbonate (10 g.) and anhydrous magnesium sulphate (10 g.) were kept below 20° in a cylindrical reaction vessel while chlorine (170 g. 2.4 mole) was absorbed. In spite of the sodium carbonate, some of which remained, there was a copious evolution of hydrogen chloride. The reaction mixture was poured onto dilute sodium carbonate solution, the organic material ether extracted, washed, dried (MgSO₄) and distilled. After several distillations 1,1,2-trichlorocyclohexene (379 g., 2 mole, 83% yield with respect to chlorine absorbed) was obtained and 1-chlorocyclohexene (304 g. 2.6 mole 29%) recovered. In view of the labour involved in recovering unchanged olefin and the losses this involves this method was not adopted.

In the third attempt chlorine was passed down
the stirrer into the olefin (170 g. 1.4 mole) in a cylindrical ice cooled reaction vessel in the dark until the solution was green (dissolved chlorine). After stirring for 5 mins. to allow hydrogen chloride to escape the mixture was poured onto ice, and the organic layer washed dried and distilled. Over a series of reactions the product \( \left( \nu_D^{20} 1.4499 - 1.5290 \right) \) was isolated in yields of 36-49%.

**FLUORINATION OF 1,1,2-TRICHLOROCYCLOHEXANE**

**WITH HYDROGEN FLUORIDE**

1,1,2-Trichlorocyclohexane (37 g. 0.20 mole) and hydrogen fluoride (60 mls. 3.0 mole) were placed in an autoclave and heated to 100° and 18 atmospheres and then allowed to cool overnight. The contents of the autoclave, a viscous oil, contained much hydrogen fluoride and when poured onto ice yielded only a solid, soluble in benzene.

**WITH BORON TRIFLUORIDE AND HYDROGEN FLUORIDE**

The trichloride (50 g. 0.27 mole) and hydrogen fluoride (10.6 ml. 0.53 mole) mixed in a brass reaction vessel and boron trifluoride (11 g.) passed for 45 mins. The thick tarry product in ether solution was washed with sodium bicarbonate solution, water until neutral and dried (\( \text{MgSO}_4 \)). Distillation of this solution
yielded a negligible amount of unsaturated liquid (b.p. 58-99/29 mm., n<br>20^0 1.4924), acid fumes and solid polymer.

**WITH BORON TRIFLUORIDE AND HYDROGEN FLUORIDE AT -78°**

1,1,2-Trichlorocyclohexane (50 g. 0.27 mole) and hydrogen fluoride (10.6 ml., 0.53 mole) were mixed in a brass reaction vessel at -78° and boron trifluoride passed for 1 hour. When allowed to warm up the contents were found to be only tars. As the tarring might occur during the warming up the above experiment was repeated but immediately the reaction was completed the contents were poured onto ether and the ethereal solution washed with sodium bicarbonate solution, with water until neutral and dried (MgSO₄). Distillation of this solution yielded an unsaturated liquid (3.5 g. b.p. 78-88/17 mm. n<br>20^0 1.4938) and much polymer.

**WITH STANNIC CHLORIDE AND HYDROGEN FLUORIDE**

The trichloride (50 g. 0.27 mole) and hydrogen fluoride (10.6 ml. 0.53 mole) and stannic chloride (1 g.) were mixed in a brass reaction vessel at -78° and allowed to come to room temperature. The contents were poured onto ether and the ethereal solution washed, dried and distilled to give mainly
starting material (8.5 g. b.p. 38°/75 cms. 88°/23 mms. \( n_D^{20} 1.4946 \)) containing a little low boiling substance and unreacted starting material (19.5 g. b.p. 88/23 mm. - 96°/20 mms. \( n_D^{20} 1.5056 \)).

**WITH ANTIMONY TRIFLUORIDE**

The antimony trifluoride was purified by recrystallisation from dry methanol\(^59\) and the antimony pentachloride was redistilled.

**a.** 1,1,2-trichlorocyclohexane (20 g. 0.11 mole) and antimony trifluoride (20 g. 0.11 mole) and antimony fluoride chloride (3 g. prepared by passing chlorine into molten antimony trifluoride) were mixed in a distillation flask and heated until reaction took place (280°). The distillate was dissolved in ether, washed with sodium bicarbonate solution and water until neutral and dried (CaCl\(_2\)). Distillation of the ether solution gave an unsaturated liquid (1 g. b.p. 140-150° \( n_D^{15} = 1.4786 \)).

Slight alterations of the experimental technique were tried

**b.** Antimony trifluoride (18 g. 0.10 mole) and antimony pentachloride (1 g.) were mixed and heated to 180° in a flask equipped with dropping funnel and condenser in distillation position. The trichloride
(18 g. 0.10 mole) was added slowly and the distillate worked up as before to give an unsaturated liquid (1 g. b.p. 146-156 \( n_D^{20} \) 1.4734 34.7% Cl 8.3% F) c. 1,1,2-Trichlorocyclohexane (20 g. 0.11 mole) and antimony pentachloride (1 g.) were heated together to 180\(^\circ\) in a flask equipped for distillation and antimony trifluoride (20 g. 0.11 mole) added with the exclusion of air. The distillate was worked up as before and yielded an unsaturated liquid (3 g. b.p. 146-170 \( n_D^{19} \) = 1.4790).

**WITH POTASSIUM FLUORIDE**

The potassium fluoride was dried under reduced pressure (about 2.0 cms.) at 170\(^\circ\). The glycerol was distilled under reduced pressure rejecting the initial distillate. The samples used had the following properties b.p. 173\(^\circ\)/16 mms. \( n_D^{20} \) 1.4741.

a) **With solvent**

Potassium fluoride (12 g. 0.21 mole) and glycerol (30 g.) were stirred at 180\(^\circ\) in a creased flask equipped with dropping funnel and delivery tube to cooled receiver. 1,1,2-Trichlorocyclohexane (20 g. 0.18 mole) was added slowly over 3 minutes. A vigorous reaction then took place and after 10 minutes 8 mls. of liquid had distilled over. The apparatus
was flushed with CO₂ (30 mins.) and the distillate (10 g.) washed with water, sodium bicarbonate solution, water until neutral and dried (MgSO₄). Distillation gave an unsaturated liquid (b.p. 79°/24 mm. \( n_\text{D}^{19} \) 1.4994 43.4% Cl, negligible F) which appeared to be mostly dichlorocyclohexenes.

b. Without solvent

Potassium fluoride (20 g. 0.35 mole) was heated to 150° and the trichloro compound (20 g., 0.18 mole) added slowly as above. No reaction occurred until the temperature was raised to 210° when a rapid distillation took place which subsided after 10 minutes. The distillate was worked up as before to give an unsaturated liquid (8.5 g. b.p. 80-92/18 mm. \( n_\text{D}^{19} \) 1.5083 44.2% Cl negligible F) as well as small amounts of a more volatile unsaturated fraction (3.5 g. 54°/26 mm-80/19 mms. \( n_\text{D}^{19} \) 1.4940.) It thus seems we again have the formation of dichlorocyclohexenes with the possibility of some chlorocyclohexadienes.

WITH MERCURIC FLUORIDE

Préparation de mercuric fluoride

The reactor (Diag. 8 ) was charged with mercuric chloride (100 g. 0.36 mole) and the temperature raised to 150° while chlorine trifluoride initially
diluted with nitrogen was passed for 5 hours (27 g. 0.29 mole). The pale yellow product contained negligible chlorine.

The use of mercuric oxide (100 g. 0.47 mole) and chlorine trifluoride (36 g. 0.39 mole) in a similar but unstirred reactor at 150° produced a solid containing 75% of mercuric fluoride.

**Attempted fluorination**

1,1,2-trichlorocyclohexane (34.5 g. 0.18 mole) was placed in a brass reaction vessel and mercuric fluoride (71 g. of 75% pure, 0.22 mole) was added portionwise. As a vigorous reaction took place immediately the reaction vessel was cooled and a condenser attached. After standing 30 minutes at room temperature the products were dissolved in ether and the organic layer washed with water only and dried. When distillation of this solution was attempted decomposition occurred at 40°.
ATTEMPTED FLUORINATION OF 1,2-DIBROMOCYCLOHEXANE

a. WITH HYDROGEN FLUORIDE

1,2-Dibromocyclohexane (64 g. 0.25 mole) and hydrogen fluoride (21 mls. 1 mole) were sealed in an ice cold autoclave and heated to 100° and then allowed to cool. The product (solid and a little liquid) was poured onto ice and ether and the ethereal solution washed with sodium bicarbonate solution and water until neutral and dried (MgSO₄). When distilled this yielded only ether while there was recovered from the washings a solid polymer (10 g.).

b. WITH MERCURIC FLUORIDE

i) Nascent mercuric fluoride. 1,2-Dibromocyclohexane (121 g. 0.5 mole) and mercuric oxide (100 g. 0.5 mole) were stirred together in a brass reaction pot and hydrogen fluoride added until the red colour of the mercuric oxide disappeared (8 hours). Ether (300 ml.) was added, the solid mercuric bromide washed with ether and the ethereal solutions washed with water only and dried (MgSO₄).

Distillation produced complete decomposition of the distilland at 160°C, up to which point only ether had distilled. This reaction was repeated.
and the distillation carried out under reduced pressure
to give a liquid (20.5 g. b.p. 22°/29 mms. - 55°/18 mms)
that decomposed completely when attempts were made
to redistil at atmospheric pressure.

b.ii) **Solid mercuric fluoride.** 1,2-Dibromocyclohexane
(36 g. 0.15 mole) was placed in a cooled brass vessel
and mercuric fluoride (24 g. of 75% 0.07 mole) added
portionwise. After standing 30 minutes the products
were dissolved in ether and ice added. The ethereal
solution was washed with water only and dried (MgSO₄).
Distillation yielded a liquid containing negligible
fluorine (5 g. b.p. 40°/At. Press. -45/25 mm.
\(n D^{19.5}=1.3690\), 5.2% Br 2% F) and starting material
(14 g. b.p. 45°/25 mms - 96°/11 mms) and 7 g.
residue. More vigorous conditions were tried.

Mercuric fluoride (36 g. 0.15 mole) was placed
in a flask equipped with dropping funnel, stirrer
and lead to condenser in distillation position
and receivers at -78°C. 1,2-Dibromocyclohexane
(36 g. 0.15 mole) was added, the temperature being
raised after the first few drops were added until
reaction occurred and then the addition being
completed slowly. There were recovered from the cold
traps two very small samples of liquid. The first
was unsaturated (9.1% F, 18.7% Br) while the second was saturated and probably contained starting material (0.6% F and 40.1% Br).

c. **WITH ARGENTIC FLUORIDE**

**Preparation of argentic fluoride** Argentous fluoride (102 g, 0.8 mole) was placed in a reactor and heated while nitrogen was passed to dry the substance. Chlorine trifluoride was then passed for 9 hours (21 g, 0.23 mole) and the dark powder so produced analysed by titrating the iodine it liberates from aqueous potassium iodide solution, showed it to be 27% AgF₂.

**Attempted fluorination** Argentic fluoride (73 g, of 27% 0.14 mole) was placed in an ice cooled flask equipped with stirrer, dropping funnel and lead to traps at -78°. 1,2-Dibromo-cyclohexane (15.5 g, 0.06 mole) was added when a vigorous reaction took place. When this subsided the pressure was reduced to ensure removal of volatile products to the cooled traps. The reaction products when distilled from solid potassium fluoride yielded two unsaturated liquids (½ ml. b.p. < 20⁰/10 mms. 27.8% F) and (½ ml. b.p. > 20⁰/10 mm. 30.3% F, 10.4% Br) in both of which
hydrogen as well as bromine had been replaced by fluorine.

**FLUORINATION OF 1,2-DICHLOROCYCLOHEX-1-ENE**

**Preparation of 1,2-dichlorocyclohex-1-ene**  
1,1,2-trichlorocyclohexane (50 g. 0.27 mole) and quinoline (34.5 g. 0.27 mole) were mixed and heated under reflux to 210° during 25 minutes and kept there for 20 minutes by which time the vigorous reaction had subsided. The reaction product was poured onto water, ether extracted, washed with water only and dried. Distillation gave a mixture of the desired olefin with the lower boiling chlorocyclohexadiene as a liquid with a wide boiling range (24 g. 60% b.p. 76°/200 mms - 84/12 mms.).

As the diolefin was formed by the elimination of two molecules of hydrogen chloride from one molecule of starting material the trichlorocyclohexane (234 g. 1.19 mole) was heated to 210° and quinoline (153 g. 1.19 mole) was added slowly and the temperature raised when a violent reaction set in at 235°. The reaction mixture was cooled, poured onto water, and ether extracted. The ethereal solution was washed with 2N hydrochloric acid, 2N sodium bicarbonate.
solution, with water until neutral and dried (MgSO₄). Distillation gave 1,2-dichlorocyclohex-1-ene containing less of the chlorocyclohexadiene (130 g.
0.86 mole 72° b.p. 62/35 mms - 96°/10 mms).

As potassium fluoride at 190° caused the dehydrochlorination of 1,1,2-trichlorocyclohexane an attempt was made to use this on a preparative scale with potassium fluoride that had only been oven dried at 100°. The product was mainly starting material. The second method of preparation was adopted.

**Attempted fluorinations.** Dry lead dioxide, (79 g. 0.33 mole) hydrogen fluoride (68 ml. 3.4 mole) precooled to -78° and 1,2-dichlorocyclohex-1-ene (50 g. 0.33 mole) also precooled to -78° were sealed in an autoclave at 0° and heated to 100°. After cooling overnight the contents in ether were washed with hydrochloric acid and water until neutral and dried (MgSO₄). Distillation of this solution gave only tar and an unsaturated liquid (a few drops, b.p. 54°/25 mms) probably the decomposition product of the tar. There remained in the autoclave a resin like solid.
ACTION OF POTASSIUM FLUORIDE SOLUTIONS ON SULPHONIC ACID ESTERS OF CYCLOHEXANOLS

Preparation of esters A modification of one of the methods given by Wild\textsuperscript{61} for the esterification of phenols was used. Tosyl chloride (20 g, 0.1 mole) & cyclohexanol (10 g, 0.1 mole) were dissolved in pyridine (15 ml, 0.19 mole) and left overnight.

The excess pyridine was then removed with 2N hydrochloric acid to give the crude ester (24.0 g, 0.094 mole, 94%).

Recrystallisation from petroleum ether gave the pure ester, m.p. 44-44.5\textdegree (reported 43.3-43.8\textsuperscript{54}, 44-44.5\textsuperscript{62}). The tosyl ester of trans-2-chlorocyclohexanol was prepared in a similar way from the alcohol in 83% yield and after recrystallisation from methylated spirit the pure ester (m.p. 52-52.5\textdegree) was obtained.

Attempted fluorination Cyclohexyl tosylate (15 g, 0.06 mole) and aqueous potassium fluoride solution (7.8 ml. of 50% solution, 0.13 mole) were sealed in a glass tube and heated to 150\textdegree for 8\frac{3}{4} hours. The tube was then cooled, opened and the contents washed out onto more water. The oily product was ether extracted and the ether solution washed, dried
(MgSO₄) and distilled to give 1 ml. of an ether solution of product (1.4% F, smells of cyclohexene) and tar while the reaction tube was etched.

The second ester (0.03 mole) and aqueous potassium fluoride solution (4 mls. of 50% solution, 0.03 mole) were similarly treated to yield an unknown solid and an etched reaction tube.

**ACTION OF PHOSPHORUS PENTAFLUORIDE ON KETONES**

**Preparation of phosphorus pentafluoride** Calcium fluoride (500 g. 6.4 mole) was ignited in an iron vessel for 1 hour and then sealed and allowed to cool. Phosphorus pentoxide (220 g. 1.6 mole) was stirred in and the iron vessel resealed and heated, the phosphorus pentafluoride being allowed to escape for 5 mins. to flush the apparatus out and then lead through the ketone in a brass reaction pot equipped with water condenser and calcium chloride tube.

**Attempted fluorinations** When cyclohexanone (25 ml. 0.24 mole) was used the reaction products were dissolved in ether, washed with water only and dried (MgSO₄). Distillation gave only ether and a tar that decomposed at 190°. When the cyclohexanone (47 ml. 0.46 mole) was diluted with ether (200 ml.) and the reaction mixture similarly worked up there was produced an ethereal
solution from which the ether was removed at 20° under reduced pressure to leave a tar which distilled up to 260°/15 mms. The distillate was redistilled to give a liquid (b.p. 107/25.5 cms. to 120°/4.2 cms.) containing cyclohexanone. The latter was removed as the bisulphite compound and the insoluble liquid ether extracted, washed with water and dried (MgSO₄). On distillation this yielded a liquid (b.p. 140-44/21 mms. 5 g.) containing phosphorus but no fluorine, possibly a phosphoric acid ester of the enol form of the ketone.

Similar experiments with methyl ethyl ketone yielded only unchanged starting material and tar.
57 H. Lund et al. Chem. Ber. 1931 64 210
58 Handbook of Chemistry and Physics 1948 Chem. Rubber Publishing Co. Page 2536
59 F.A. Andersen C.A. 47 8569a
62 S. Winstein et al. J.A.C.S. 70 816 (1948)
THE REACTION BETWEEN CHLORINE TRIFLUORIDE
AND TRICHLOROACETIC ACID
CONTENTS

Introduction 75
References 1-18 79
Development of method 80
Table of results 90
Mechanism of reaction 91
References 19-25 102
Gas chromatography 103
Analysis 110

Experimental details

Action of chlorine on some hydrocarbons 115
Action of chlorine trifluoride on some hydrocarbons 115

Action of chlorine trifluoride on trichloroacetic acid and trichloroacetethyl chloride

Apparatus 116
Preparation of reagents 121
Method of operation 123

Results

Action of ClF$_3$ on CCl$_3$COOH at 100° 127
Action of ClF$_3$ on CCl$_3$COOH at 70-80° 130
Action of ClF$_3$ on CCl$_3$COCl at 100° 136

Experiment to determine the degree of substitution of the CCl$_3$- group 146

Experiment to determine the effect of the number of reaction vessels 143

References 26-28 145
INTRODUCTION

In the pursuit of an ionising solvent for liquid phase reactions with chlorine trifluoride, Tanner \(^1\) found that chlorine trifluoride decomposed trifluoro- and trichloro-acetic acids and trichloroacetyl chloride and fluoride. Although few quantitative results were obtained, the presence of inert halocarbons (carbon tetrachloride and hexachloro-ethane), carbonyl chloride, carbon monoxide, carbon dioxide, oxygen and chlorine was shown while, in the case of trichloroacetic acid, trichloroacetyl chloride was also detected.

Little work has been published on the decomposition of pure trichloroacetic acid. Various catalysts and reagents have been used to promote the thermal decomposition of this acid into products similar to those above. (Table I). The decomposition of solutions of acetic acid and its salts has been more extensively studied and the products are again similar to those above. (Table II).

The decomposition of the acid chloride can only be compared to the pyrolysis of trifluoroacetyl bromide to yield trifluoromethyl bromide \(^2\) and of trichloroacetyl chloride and bromide to give carbon tetrachloride and
bromotrichloromethane respectively. 3

There are several reactions that although not directly connected with the reaction being studied have from the similarity of the products some possible connection with the reaction and for this reason are included in the example given (Table III).

Table I

Thermal decomposition of CCl₃COOH

catalyst or reagent | Temp. °C. | Product | Ref.
--- | --- | --- | ---
C | 250-300 | CHCl₃, CO₂ (little CO, C₂Cl₄, C₂Cl₆, HCl) | 4
ThO₂ | 260-320 | CO₂, CO, CHCl₃, C₂Cl₄ (little C₂Cl₆, COCl₂) | 4
Kaolin | 230 | | 4
C | 135 | CHCl₃, CO₂ | 5
ThO₂ | 165 | CO₂, NaCl, COCl₂ (also CO₂) from COCl₂ + H₂O in apparatus | 5
Pumice stone | 180 | | 5
Aniline | 100 | CHCl₃ + CO₂ | 6
Table II

Decomposition of $\text{CCl}_3\text{COOH}$ in solution

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp.</th>
<th>Products</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>70-90</td>
<td>$\text{CHCl}_3 &amp; \text{CO}_2$</td>
<td>7</td>
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<tr>
<td>$\text{PhNMe}_2$</td>
<td>70</td>
<td>$\text{CHCl}_3 &amp; \text{CO}_2$</td>
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<tr>
<td>$\text{PhNET}_2$</td>
<td>45</td>
<td>$\text{CHCl}_3$ and $\text{CO}_2$</td>
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</table>

Decomposition of salts of $\text{CCl}_3\text{COOH}$ in solution

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Salt</th>
<th>Activation</th>
<th>Products</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>Trace of $\text{Fe}^{3+}$ in acid</td>
<td>$\text{hv}$</td>
<td>$\text{CO}_2 &amp; \text{C}_2\text{Cl}_6$</td>
<td>10</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>all $\text{Fe}^{3+}$</td>
<td>$\text{hv}$</td>
<td>$\text{CO}_2 &amp; \text{CHCl}_3$</td>
<td>10</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$\text{K}^+$</td>
<td>$\text{hv}$</td>
<td>$\text{CCl}_3\text{CHO}, \text{HCl}$</td>
<td>10</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$\text{Na}^+$</td>
<td>40 - 100</td>
<td>$\text{CHCl}_3$</td>
<td>11</td>
</tr>
<tr>
<td>Starting Material</td>
<td>Temp.</td>
<td>Activation</td>
<td>Products</td>
<td>Ref.</td>
</tr>
<tr>
<td>-------------------</td>
<td>-------</td>
<td>------------</td>
<td>---------------------------</td>
<td>------</td>
</tr>
<tr>
<td>CCl₃CHO + O₂</td>
<td>90</td>
<td>hv+Cl₂</td>
<td>COCl₂, HCl, CO</td>
<td>12</td>
</tr>
<tr>
<td>CCl₃CHO + O₂</td>
<td>90</td>
<td>hv+Br₂</td>
<td>COCl₂, CO, HCl</td>
<td>13</td>
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<td></td>
<td></td>
<td></td>
<td>BrCl, H₂O</td>
<td></td>
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<tr>
<td>CCl₃CHO + Br₂</td>
<td>90</td>
<td>hv</td>
<td>CO, HBr, CCl₃Br</td>
<td>14</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>COBr₂ &amp; CHCl₃</td>
<td></td>
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<tr>
<td>CCl₃CHO + Cl₂</td>
<td>90</td>
<td>hv</td>
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<tr>
<td>CF₃COONa</td>
<td>170</td>
<td>-</td>
<td>CF₃H &amp; CO₂</td>
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<tr>
<td>CF₃COOH + Br₂</td>
<td>540</td>
<td>active</td>
<td>CF₃Br</td>
<td>3</td>
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<tr>
<td></td>
<td></td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCl₃COOH and KF in PhNO₂ soln.</td>
<td>130</td>
<td>-</td>
<td>CHCl₃, CO₂</td>
<td>17</td>
</tr>
<tr>
<td>CHCl₃ and O₂</td>
<td></td>
<td>rays</td>
<td>COCl₂, HCl, Cl₂</td>
<td>18</td>
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</tbody>
</table>
References

1. M.C. Tanner M.Sc. thesis
3. J.D. LaZerte et al. C.A. 48 P 7622h (1954)
4. J.B. Senderens C.r. 172 155 (1921)
5. J.B. Senderens C.r. 204 209 (1937)
6. A.S. Sultanov C.A. 41 6223e (1947)
7. A.N. Kappanna C.A. 26 2640 (1932)
8. H. Sildberstein Ber. 17 2660 (1884)
10. F.M. Jaeger J.C.S. 1921 2070
11. R.A. Fairclough J.C.S. 1938 1186
12. W.A. Alexander et al. C.A. 34 6766 (1946)
13. J. Stauff et al. C.A. 35 39052 (1941)
14. H. Clug et al. C.A. 35 9798 (1941)
15. W.A. Alexander et al. C.A. 33 91451 (1939)
17. A.N. Nesmeyanov et al. C.A. 42 4924h (1948)
DEVELOPMENT OF METHOD

The experiments carried out were required to furnish quantitative information about the reaction products. These products can be classified as active or inert according to their behaviour towards alkaline sodium sulphite solutions. Into the former class fall halogens, acid halides (including carbonyl halides); halogen hydracids and carbon dioxide while the inert materials appear from Tanner's work to be mostly fully halogenated methanes and ethanes with small amounts of oxygen and carbon monoxide.

From Tanner's thesis it appeared difficult to design an apparatus such that all the desired information could be derived from one experiment. Accordingly it was decided to derive the information by comparison of the results of several experiments.

As gas chromatography was considered to be the most promising means of identifying and estimating the halogenated methanes the first necessity was to obtain them as gases or liquids in the absence of halogens and acids, or substances capable of generating acids. As chlorine trifluoride is probably present among the products of the reaction an alkaline solution of sulphite seemed a reasonable scrubbing liquid. Preliminary
experiments in which the reaction products were scrubbed with such a solution and then passed through a series of cooled traps showed that the halogenated methanes were satisfactorily retained by the use of ethanol/Drikold and liquid oxygen cooled traps while the halogenated ethanes were retained by the water cooled condenser in the metal apparatus. Gas chromatographic analysis could be satisfactorily carried out on the samples of halogenated methanes so obtained.

The estimation of the active constituents required rather more development. The first necessity was a means of removing the excess chlorine trifluoride from the reaction products and leaving other halogens. It was found that when chlorine trifluoride was passed over both liquid and solid hydrocarbons the chlorine trifluoride was either inefficiently absorbed or chlorine was generated. When pure chlorine was passed into or over the hydrocarbons it was found to dissolve or react, in some cases quite appreciably.

These facts were utilised to develop a method of phosgene analysis. The chlorine trifluoride was removed with benzene and the chlorine was removed by antimony metal leaving only the phosgene together with carbon dioxide and inert materials which did not interfere with the iodometric determination of the phosgenes.
DIAGRAM 1

Block diagram of apparatus used to investigate the action of ClF₃ on CCl₃COOH & CCl₃COCl

Metal apparatus common to all experiments.

Glass apparatus

Experiment type A

Experiment type B

Experiment type C
It was also found that the whole of the reaction products could be safely passed into a solution of sodium iodide in dry acetone, thus giving the total amount of halogens and phosgenes including the excess chlorine trifluoride.

Estimates of the carbon dioxide, oxygen and carbon monoxide were easily obtainable by use of a standard Orsat apparatus to analyse the gas stream emerging from the solution of sodium iodide in acetone used to estimate the phosgene. Attempts to remove the entrained acetone failed but it was found not to interfere with the gas analysis. No direct figures were obtained for the halogen hydracids and trichloroacetyl halides but estimates were made by comparison of the results of all three experiments.

In order that the reliability and mode of expression of the results given may be more easily understood a short description of the three types of experiment finally adopted will be given.

In all experiments the reaction occurred in metal apparatus from which the products passed through a water cooled condenser. (See diag. 1).

**Type A.** The active components were removed by an alkaline sulphite scrubber from which the resultant gas
stream was dried and passed through traps cooled in ethanol/Drikold and liquid oxygen.

**Type B.** The reaction products were passed through benzene, over potassium fluoride, antimony metal and then into sodium iodide dissolved in dry acetone. The iodine liberated according to the equation

\[ \text{COX}_2 + 2\text{NaI} \rightarrow \text{CO} + \text{I}_2 + 2\text{NaX} \]

being estimated by titration with sodium thiosulphate solution. The gas stream was analysed by means of an Orsat apparatus for carbon dioxide, oxygen and carbon monoxide.

**Type C.** The reaction products were passed into a solution of sodium iodide in dry acetone and the iodine estimated as before. In experiments of types B and C some of the iodine containing solutions had their fluoride content estimated.

The previous results have been calculated on the assumption that

a. No substitution of the \( \text{CCl}_3 \) group occurs in the \( \text{CCl}_3\text{COOH} \) prior to its decomposition.

b. There was a negligible amount of carbonyl halides in the acid residues in the reaction vessels.

c. The halogenated ethanes were confined to the metal apparator before the reflux condenser and that none of the more fluorinated ethanes
were present in the liquid in the cooled traps.

d. No carbon containing compounds were carried out on the N₂ stream.

Attempts were made to justify these conclusions by performing the following experiments.

a and b An experiment of type A was carried out for three hours at 100°. A sample of the residual acid was converted to the methyl ester by a method designed not to lose low boiling compounds. Chromatographic analysis of these esters showed only the presence of dimethyl carbonate and methyl trichloroacetate. This experiment also yielded information about the rate of formation of the halogenated methanes.

c Samples of halogenated methanes from the cooled traps were chromatographed for periods much in excess of those required to elute carbon tetrachloride but no further peaks occurred in the chromatogram showing the absence of other compounds. This was also apparent from the fact that during analysis the weights of detected components gave a reasonable value for the density of the sample, which would not be the case if a component was omitted.

d Samples of the exit gases were analysed by gas chromatography and found not to give peaks. Hence low
boiling halogenated methanes, in particular carbon tetrafluoride, were not being lost.

The results given in table I are the results of types B and C give the variation of the rate of production of some of the products with time (diags. 2, 3 and 4). The rate of production of carbon dioxide was found to pass through two maxima. When the reaction was carried out in a larger single reaction vessel the rate of production of carbon dioxide rose initially and then slowly decreased.
DIAGRAM 2

Variation of rate of production of CO$_2$ with time

ClF$_3$ and CCl$_3$COOH at 100$^\circ$C

ClF$_3$ and CCl$_3$COOH at 80$^\circ$C

ClF$_3$ and CCl$_3$COCl at 100$^\circ$C

in single reaction vessel
DIAGRAM 3

Variation of rate of production of phosgenes with time

\[ \text{ClF}_3 \text{ and } \text{CCl}_3\text{COOH at } 100^\circ \]

\[ \text{ClF}_3 \text{ and } \text{CCl}_3\text{COOH at } 80^\circ \]

\[ \text{ClF}_3 \text{ and } \text{CCl}_3\text{COCl} \text{ at } 100^\circ \]

\[ \text{ClF}_3 \text{ and } \text{CCl}_3\text{COOH at } 100^\circ \text{ in a single reaction vessel} \]

Decimoles per hour

Time 0

0

1

2

3

4

5

6

7

8

9

in 10 hours
DIAGRAM 44

Variation of rate of production of halogens and phosgenes with time

$\text{ClF}_3$ and $\text{CCl}_3\text{COOH}$ at 100°

Variation of rate of production of halogens with time

$\text{ClF}_3$ and $\text{CCl}_3\text{COOH}$ at 100°

Decimoles per hour

Time in hours

1 2 3 4 5 6

1 2 3 4 5 6
Products of reaction from 0.62 mole acid (or acid chloride) and 0.31 mole of ClF₃.

<table>
<thead>
<tr>
<th>Product</th>
<th>Acids at 100°C</th>
<th>Acids at 80°C</th>
<th>Acid halides at 100°C</th>
<th>Acids at 100°C (50% reaction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g. mole</td>
<td>g. mole</td>
<td>g. mole</td>
<td>g. mole</td>
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<tr>
<td>O₂Cl₂</td>
<td>6.5  0.028</td>
<td>16.8  0.070</td>
<td>2.5  0.011</td>
<td>14.8  0.062</td>
</tr>
<tr>
<td>CO₁₄</td>
<td>19.2  0.13</td>
<td>11.2  0.075</td>
<td>1.5  0.0098</td>
<td>4.9  0.032</td>
</tr>
<tr>
<td>CO₁₉F₆</td>
<td>6.1  0.045</td>
<td>7.7  0.056</td>
<td>6.9  0.050</td>
<td>1.6  0.011</td>
</tr>
<tr>
<td>CO₁₂F₂</td>
<td>1.8  0.015</td>
<td>0.2  0.0015</td>
<td>0.1  0.00083</td>
<td>0.3  0.0025</td>
</tr>
<tr>
<td>CO₁₅F₃</td>
<td>4.9  0.046</td>
<td>0.1  0.0096</td>
<td>0.1  0.00096</td>
<td>0.2  0.0019</td>
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<tr>
<td>CO₂</td>
<td>14.5  0.33</td>
<td>22.3  0.54</td>
<td>5.1  0.12</td>
<td>6.7  0.15</td>
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<tr>
<td>O₂</td>
<td>0.2  0.0047</td>
<td>0.1  0.0032</td>
<td>0.1  0.0031</td>
<td>0.1  0.0031</td>
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<tr>
<td>00</td>
<td>0.3  0.0011</td>
<td>2.3  0.0083</td>
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<td>0.2  0.0071</td>
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<tr>
<td>O₂Cl₂O₂Cl₂</td>
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<td>0.5  0.0027</td>
<td>76.5</td>
<td>-</td>
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<tr>
<td>O₂Cl₂O₂F₂</td>
<td>-</td>
<td>2.0  0.012</td>
<td>-</td>
<td>1.5  0.0091</td>
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<tr>
<td>O₂Cl₂O₂H</td>
<td>11.0 0.067</td>
<td>1.0  0.0062</td>
<td>-</td>
<td>40.3  0.25</td>
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CO₂ containing:

<table>
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<tr>
<th></th>
<th>g. mole</th>
<th>g. mole</th>
<th>g. mole</th>
<th>g. mole</th>
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<tbody>
<tr>
<td>O₂</td>
<td>2.3  0.084</td>
<td>3.7  0.13</td>
<td>0.5  0.019</td>
<td>0.7  0.026</td>
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<tr>
<td>Cl</td>
<td>2.6  0.073</td>
<td>6.5  0.18</td>
<td>0.8  0.023</td>
<td>0.8  0.023</td>
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<tr>
<td>F</td>
<td>1.8  0.095</td>
<td>1.6  0.084</td>
<td>0.3  0.015</td>
<td>0.6  0.029</td>
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</table>

Halogen containing:

<table>
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<th>g. mole</th>
<th>g. mole</th>
<th>g. mole</th>
<th>g. mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>14.7  0.41</td>
<td>5.9  0.17</td>
<td>26.0  0.73</td>
<td>3.7  0.105</td>
</tr>
<tr>
<td>F</td>
<td>3.3  0.17</td>
<td>3.0  0.16</td>
<td>2.9  0.15</td>
<td>0.7  0.037</td>
</tr>
</tbody>
</table>

OCl₂OX & HX containing:

<table>
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<th></th>
<th>g. mole</th>
<th>g. mole</th>
<th>g. mole</th>
<th>g. mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>8.2  0.23</td>
<td>9.1  0.25</td>
<td>6.2  0.18</td>
<td>4.5  0.13</td>
</tr>
<tr>
<td>F</td>
<td>7.2  0.39</td>
<td>9.8  0.52</td>
<td>4.6  0.24</td>
<td>6.4  0.34</td>
</tr>
</tbody>
</table>
MECHANISM OF REACTION

Trichloracetic acid

The action of chlorine trifluoride on trichloroacetic acid has been shown to produce a variety of products. Carbon dioxide occurred in the greatest amount with smaller quantities of halogenated methanes (mostly carbon tetrachloride) and carbonyl halides while traces of hexachloroethane, carbon monoxide, oxygen and acid halides were detected. The hydrogen of the carboxyl group was assumed to be evolved as halogen hydracid.

Taking into account the similarity between the products obtained in this reaction and those products obtained in other reactions proceeding by free radical mechanisms (Table III), a free radical mechanism is proposed for this reaction. This is supported by the isolation of hexachloroethane, whose presence can be most readily accounted for by such a mechanism.

Although only traces of acid halides were detected at the end of the reaction it is possible that quite large amounts were present during the process but that during the period in which all traces of chlorine trifluoride were blown out with N₂ gas
they, especially the more volatile fluoride, were carried out of the reaction vessels. The more reactive acid fluoride\textsuperscript{1} would also be speedily removed by reaction. It is thus possible that the acid halide might be an intermediate in the reaction. Cady and Kellog\textsuperscript{19}, by the action of fluorine on trifluoroacetic acid, have prepared trifluoroacetyl hypofluorite. It is possible that analogous hypohalites might take part in the present reaction. Bearing in mind the unstable nature of trifluoroacetyl hypofluorite it is not expected that, at the temperature of the experiment, the suggested trichloroacetyl hypohalite would exist for long periods or would be isolated.

The free radicals necessary to initiate the process probably came from the chlorine trifluoride. Tanner\textsuperscript{1} suggests that chlorine trifluoride splits as below

\[
\text{ClF}_3 \rightarrow 2F^* + \text{ClF}.
\]

but since the present work throws no further light on the subject we will merely assume that chlorine trifluoride furnishes fluorine and chlorine atoms. An alternative source of free radicals is from the suggested trichloroacetyl hypohalite
1. $\text{CCl}_3\text{COOH} + X_2 \rightarrow \text{CCl}_3\text{COOX} + \text{HX}$

2. $\text{CCl}_3\text{COOX} \rightarrow \text{CCl}_3\text{CO}^* + X^*$

However, the attack of halogen atoms on the acid would probably be as follows:

3. $\text{CCl}_3\text{COOH} + X^* \rightarrow \text{CCl}_3\text{COO}^* + \text{HX}$

so if either, or a combination, of the above mechanisms operates, the result is the formation of $\text{CCl}_3\text{COO}^*$ and $X^*$ radicals and HX.

The rapid production of large amounts of carbon dioxide is almost certainly due to reaction or decomposition of the $\text{CCl}_3\text{COO}^*$ radical. Several possible mechanisms are given below.

4. $\text{CCl}_3\text{COO}^* \rightarrow \text{CCl}_3^* + \text{CO}_2$

5. $\text{CCl}_3\text{COO}^* + X_2 \rightarrow \text{CCl}_3X + \text{CO}_2 + X^*$

6. $\text{CCl}_3\text{COO}^* + X^* \rightarrow \text{CCl}_3X + \text{CO}_2$

The decomposition of $\text{CH}_3\text{COO}^*$ in analogous manner to reaction 4 is not observed in the gas phase but methyl radicals have been detected in the liquid phase decomposition of acetic acid. In the liquid phase the reunion of two radicals has a low probability so that reaction 6 should occur only to a limited extent.

Thus the initial formation of carbon dioxide is probably due to reactions 4 and/or 5. The action of chlorine
trifluoride on trichloroacetyl chloride also produces carbon dioxide and therefore this source must be considered. The mechanism of the production of carbon dioxide from the acid chloride will be dealt with later.

The carbonyl halides can be formed by one of two sets of reactions

a) From carbon monoxide and halogen atoms and molecules according to the Bodenstein mechanism. \[ CO + X^* \rightarrow \cdot COX \]

\[ \cdot COX + X_2 \rightarrow COX_2 + X^* \]

but the reaction 9 is doubtful in the liquid phase reaction.

b) By oxidation of the \( CCl_3^- \) radical by the oxygen known to be present in very small amounts.

\[ CCl_3^- + O_2 \rightarrow COCl_2 + \cdot OCl \]

To furnish the required carbon monoxide and trichloromethyl radicals a trichloroacetyl radical is the most probable precursor. This radical can originate in several ways

10. a) From the acid halide

10. b) \( CCl_3COO^- \rightarrow CCl_3CO^- + O^* \)

The dichlorodifluoromethane and chlorotrifluoro-
methane are easily explained as being derived from the other halogenated methanes.

21. a) \( \text{CCl}_4 + F^- \rightarrow \text{CCl}_2F + \text{Cl}^- \)
   
   b) \( \text{CCl}_2F + F^- \rightarrow \text{CCl}_2F_2 + \text{Cl}^- \)
   
   c) \( \text{CCl}_2F_2 + F^- \rightarrow \text{CClF}_3 + \text{Cl}^- \)

or even from the hexachloroethane.

22a. \( \text{CCl}_3\text{CCl}_3 + F^- \rightarrow \text{CCl}_3F + \text{CCl}_3^- \)

The required \( \text{CCl}_4 \) and \( \text{CCl}_3F \) can be formed as below

22b. \( \text{CCl}_3^- + X_2 \rightarrow \text{CCl}_3X + X^- \)

Thus, by a series of reactions, many of which have been accepted as parts of the mechanism of other reactions most of the reaction products have been accounted for.

**Trichloroacetyl chloride**

The same reaction products were obtained but in slightly different proportions and because of this and the different oxygen content of the trichloroacetyl chloride alternative reaction mechanisms must be postulated. The initial evolution of large quantities of chlorine and little else indicate we have the formation of the acid fluoride

\[ 2\text{CCl}_3\text{COCl} + \text{ClF}_3 \rightarrow 2\text{CCl}_3\text{COF} + 2\text{Cl}_2 \]

The radical mechanism

\[ \text{CCl}_3\text{COCl} + F^- \rightarrow \text{CCl}_3\text{CO}^- + \text{FCl} \]

is ruled as it would yield the active trichloroacetyl
radical and there would be much more fluorine in the exit gases in the early stages. When the concentration of the acid fluoride is sufficiently large in the acid chloride (which acts as diluent, to moderate the vigorous reaction between chlorine trifluoride and the acid fluoride\(^1\)) reaction sets in. The initial reaction below is postulated

12. \[ \text{CCl}_3\text{COF} + X^* \rightarrow \text{CCl}_3\text{CO}^* + FX \]

The trichloroacetyl radical can then react as below

13. \[ \text{CCl}_3\text{CO}^* + X_2 \rightarrow \text{CCl}_3\text{X} + \text{CO} + X^* \]

14. \[ 2\text{CCl}_3\text{CO}^* \rightarrow \text{C}_2\text{Cl}_6 + 2\text{CO} \]

(Reaction 14 only to a very small extent since little hexachloroethane was isolated in the reaction between chlorine trifluoride and trichloroacetyl chloride). The lack of even traces of carbon monoxide in the exit gases must be attributed to the presence there of much halogen and the formation of one halogen atom per molecule of carbon monoxide formed.

Tanner\(^1\) suggested a different mechanism

15. \[ \text{CCl}_3\text{COF} + X^* \rightarrow \text{CCl}_3^* + \text{COFX} \]

This followed by

\[ 2\text{CCl}_3^* + \text{M} \rightarrow \text{C}_2\text{Cl}_6^* + \text{M}^* \]

(to a very small extent)
\[
\text{CCL}_3^* + X_2 \rightarrow \text{CCL}_3X + X^*
\]
would equally well explain the observed facts.

There remain to be explained, in the case of the acid chloride, the presence of oxygen and carbon dioxide and in the case of the acid, the presence of the acid halides and of oxygen. The more obvious route for the formation of the acid halide from the acid

1. & 2. or 3. \[\text{CCL}_3\text{COOH} \rightarrow \text{CCL}_3\text{COO}^*\]

10b. \[\text{CCL}_3\text{COO}^* \rightarrow \text{CCL}_3\text{CO}^* + O^*\]

16a. \[\text{CCL}_3\text{CO}^* + X_2 \rightarrow \text{CCL}_3\text{COX} + X^*\]

\[\text{b. CCL}_3\text{CO}^* + X \rightarrow \text{CCL}_3\text{COX}\]

is not possible as the alternative reaction

\[\text{CCL}_3\text{CO}^* + X_2 \rightarrow \text{CCL}_3X + \text{CO}_2 + X^*\]
occurs\(^{24}\) while 16b is very unlikely to take place to any appreciable extent in view of the improbability of two radicals meeting.\(^{21}\) Hence the acid halide must come directly from the acid

\[\text{e.g. 17. CCL}_3\text{COOH} + X^* \rightarrow \text{CCL}_3\text{COX} + \cdot \text{OH}\]
or as suggested by Tanner\(^{1}\)

\[\text{18. CCL}_3\text{COOH} + X_2 \rightarrow \text{CCL}_3\text{COCl} + \text{HX} + 0^*\]
The hydroxyl and oxygen radical can then produce molecular
oxygen as below

19. \( \cdot O + \cdot O + M \rightarrow O_2 + M \)
20. \( \cdot OH + X_2 \rightarrow \cdot O + HX + X \cdot \)

The oxygen atoms can also be removed by the reaction:

25. \( CX_4 + \cdot O \rightarrow COX_2 + X_2 \)

This is also an alternative route to the phosgene.

The production of carbon dioxide from the acid chloride (via the acid fluoride) is very difficult to account for and the following reactions are highly speculative. They are not considered to be the only reaction mechanisms if they are even possible.

26. \( CC\ell_3CO \cdot + CCl_3COCl \rightarrow CCl_3CO-CO-CC\ell_3 + Cl \cdot \)

The \((CC\ell_3CO)_2\) being immediately attacked by halogen atoms or radicals.

27a. \( CCl_3CO-CO-CC\ell_3 + X_2 \rightarrow CCl_3X + C_2Cl_2X + CO_2 \)
27b. \( CCl_3CO-CO-CC\ell_3 + X \cdot \rightarrow CCl_3 \cdot + C_2Cl_2X + CO_2 \)

and the \( C_2Cl_2X \) then being completely halogenated.

28. \( C_2Cl_3X + X_2 \rightarrow C_2Cl_3X_3 \)

An alternative route can involve the oxygen atom or hypofluorite radical.

29. \( CCl_3COF + X \cdot \rightarrow C_2Cl_3X +OF \)
30. \( OF + CCl_3COF \rightarrow CCl_3F + CO_2 + F \cdot \)

or the hypofluorite radical can give atomic oxygen

31. \( OF + X_2 \rightarrow XF + X \cdot + O \cdot \)
which could easily react as below

32. \[ \text{CCl}_3\text{COF} + O\cdot \rightarrow \text{CCl}_3\text{F} + \text{CO}_2 \]

Thus the above mechanisms can explain all the products obtained. The two maxima in the rate of production of carbon dioxide when the experiment was carried out in the two reaction vessels can be explained as follows. The initial reaction occurs in the first vessel where acid halides are formed which distil over into the second vessel, carrying some acid with them, where they are retained by the reflux condenser. As the reaction proceeds the amount of organic material in the first vessel decreases, both by reaction and distillation and the radicals have a smaller chance of meeting molecules with which they can react but there is a larger chance now of recombination and a less efficient use of radicals formed, leading to a drop in the rate of production of carbon dioxide. When the centre of reaction is transferred to the second reaction vessel the same cycle of events takes place.

There was always found (in the reaction involving the acid) a quantity of hexachloroethane in the first reaction vessel. This would react with chlorine
trifluoride to give some chlorofluorinated ethanes and, by fission of the carbon bond halogenated methanes. The accounts for the isolation of less halogenated ethanes after 6 hours reaction than after 3 hours reaction.
POSSIBLE REACTION ROUTES

\[
\begin{align*}
&\text{CO}_2 \\
&\text{CCl}_3 \\
&\text{CCl}_3X \\
&\text{CCl}_2F_2 \\
&\text{CCl}_3F_3 \\
&\text{CCl}_3CO\text{Cl} \\
&\text{CCl}_3\text{COOH} \\
&\text{CCl}_3\text{COO} \cdot \\
&\text{CCl}_3\text{CO} \cdot \\
&\text{COX}_2 \\
\end{align*}
\]
References

19 G.H. Cady et al. J.A.C.S. 75 2501 1953
20 E.W.R. Steacie Atomic and Free Radical
Reactions page 384 reaction VII 69
21 D.H. Hey et al. Chemical Reviews 21 175 (1937)
22 E.W.R. Steacie Atomic and Free Radical
Reactions page 246
3 189 1931
24 E.W.R. Steacie Atomic and Free Radical
Reaction page 415 reaction IX 67
Reinhold Publishing Corp. New York (1946)
25 E.W. Steacie Atomic and Free Radical Reactions
page 406 reaction IX 9
Reinhold Publishing Corp. New York (1946)
The application of this technique to the present problem can be divided into two parts.

(a) The estimation of carbon tetrachloride in the mixtures of halogenated methanes and the separation of methyl esters of trihaloacetic acids were carried out using the semi-micro apparatus as described in the first part of this thesis. (pages 33-42). The conditions and packing were suitably modified to obtain a reasonable separation.

(Esters - 'dinonyl' phthalate (4 parts) on Celite 545 (10 parts) 126°, pressure 18 cms., N₂ flowrate 34 ml./min.

CCl₄ 'dinonyl' phthalate (as above) 60°, pressure 37 cm., N₂ flowrate 30 ml./min.)

(b) The chromatography of the gaseous halogenated methanes required a modified apparatus (Diag. 7). The nitrogen was passed through a drier, surge tank and manometer as before and then through the first arm of the detector. From here the nitrogen passed through the gas pipette and into the column, packed with di-n-butyl phthalate (4 parts) on Celite 545 (10 parts). The emergent mixture of nitrogen and vapours passed through the second arm of the detector and out to the atmosphere via a cold trap, flowmeter and drying tube.
DIAGRAM 5

Chromatograms for the separation of halogenated methanes at 20°

- Calibration
  - CClF₃
  - CCl₂F₂
  - CCl₃F

Gaseous sample of inerts

- Time in min.: 10 20

Liquid sample of inerts

- Time in min.: 10 20

Chromatograms for the separation of halogenated methanes at 60°

- Authentic CCl₄

- Unknown mixture

- Time in min.: 5 10 15
Chromatograms for the separation of the methyl esters of trihaloacetic acids and connected compounds

Mixture of methyl esters prepared from reaction residue

- Dimethyl carbonate
- Methyl trichloroacetate

10 Time in min.  20

Authentic methyl trichloroacetate

10 Time in min.  20

Authentic dimethyl carbonate

10 Time in min.  20

Authentic methanol

10 Time in min.  20

Authentic methyl trifluoroacetate
Block diagram of apparatus for gas chromatography of gaseous halogenated methanes
DIAGRAM 8

Gas pipette

Calibrated portion (8.09 ml.)

To vacuum apparatus

Vacuum apparatus

McLeod gauge fits in here

Bulb b.

Bulb a.

To cold trap and pump.

To 2nd 1 l. bulb

CCl₃F, CCl₂F₂, CCl₃F

To gas pipette

To manometer
The gas pipette was connected to a vacuum system in which pure samples of halogenated methanes and the unknown mixtures could be handled.

**Method of operation**

The condensed sample of halogenated methanes produced in the reaction was allowed to warm up to room temperature and pressure and the gas produced allowed to leave the trapping system (Diag 10) by tap 8 and was collected in a reservoir of similar construction to those in Diag, III, rejecting the initial portion used to remove air from the connecting tubes. The removable bulb of the vacuum apparatus (bulb a, Diag 8) was filled with the gas and then attached to the vacuum apparatus. The apparatus (including the calibrated portion of the gas pipette, which had taps 2, 3 & 4 open and taps 1 & 5 closed) was evacuated and then the pump and its protecting cold trap sealed off from the vacuum system. Tap 6 was closed and tap 7 opened and the sample condensed onto Anhydrone in bulb b to remove any water present. The sample was then allowed to warm up and expand into the gas pipette to a known pressure through tap 6 which was now opened. Tap 2 was closed, the gas pumped out of the space between taps 2, 3 & 5 and then tap 3 closed.

The chromatography apparatus having previously been allowed to come into equilibrium (Column temperature 20°, N₂ flowrate 33 ml/min. entry press. atmospheric ± 10 cm.)
with the nitrogen flowing through tap 4 all that remained was to introduce the sample without disturbing the equilibrium. To accomplish this the tap 5 was opened (causing a deflection of the galvanometer) and after a few minutes tap 2 was opened momentarily to bring the pressure of the calibrated portion of the pipette to that of the $N_2$ stream. When all was again in equilibrium the sample was blown into the column by opening tap 2 and then in one movement opening tap 1 and shutting tap 4. The gas stream now passed through taps 5, 2 & 1.

The calibration of the apparatus was carried out in a similar fashion, using pure samples of $CCl_3F$, $CCl_2F_2$ and $CClF_3$. The estimation of these gases when dissolved in the $CCl_4$ produced in the reaction was carried out by injecting a known volume of solution containing them through the serum cap onto the column in the normal way.
Estimation of chloride

During these experiments it frequently became necessary to determine the amount of chloride ion present in solutions of varying origin (from the alkaline sulphite scrubber, solutions of the trichloroacetic acid in the reaction vessels, solutions of sodium halides precipitated in the determination of COX₂ and X₂), usually containing a large excess of other solutes. On this account adsorption indicators did not seem an attractive proposition and in view of the errors possible in other measurements (e.g. the ClF₃ could only be measured to ± 1 g., i.e. ± 3%) it was not considered necessary or desirable to produce an elaborate method of analysis. The estimation of chloride by titration with silver nitrate solution in neutral solution with potassium chromate as indicator proved entirely satisfactory.

Reagents

- AgNO₃ 0.01 N
- K₂CrO₄ 2 g./100 ml. aq. solution
- NaOH and HNO₃ 2N, 0.1N and 0.02N
- CaCO₃ Analar.

Solutions containing sulphite were heated to boiling with excess concentrated nitric acid to remove
the sulphite as \( \text{SO}_2 \) or by oxidation to sulphate. The solution was cooled and then treated in the same manner as those of other origin. The solution was neutralised, using phenol phthalein as indicator with progressively more dilute acids and alkalis. (An alternative procedure is to add acid, if necessary, and excess calcium carbonate). The estimation was then carried out by titrating the chloride with silver nitrate using potassium chromate solution as indicator. (1 ml.) The size of the aliquot was so chosen that a titre of 5 to 50 ml. in a final volume of 50-150 ml. was obtained.

Estimation of fluoride

As in the estimation of chloride various solutions had to be analysed for fluoride. The titration with thorium nitrate in a buffered solution, using sodium alizarin sulphonate as indicator was suitable for the simpler solutions but the solution from the alkaline sulphite scrubber produced poor end points. The spread of the end point was caused by the presence of sulphate as was demonstrated by performing the titrations in the presence of sulphate. As sulphate is formed in the process of absorbing halogen

\[ X_2 + Na_2S_3O_3 + 2NaOH \rightarrow Na_2SO_4 + 2NaX + H_2O \]

little could be done to better this defect and it was considered sufficient to acknowledge that an
error of \( \pm 10\% \) might be present in the figures for fluoride determinations.

Reagents

\[
\text{Th(NO}_3\text{)}_4 \quad 0.05\text{N}
\]

Buffer solution \( 2\text{ g. NaOH } 9.448\text{ g.} \)

\[
\text{CH}_2\text{ClCOOH in 100 ml.}
\]

Sodium alizarin \( 0.05\% \text{ aq. solution} \)

\[
\text{NaOH}_4\text{HNO}_3 \quad 2\text{N, 0.1N & 0.02N solutions}
\]

The sample (if containing sulphite) was heated to boiling with excess conc. nitric acid. After cooling sodium alizarin sulphonate was added and the solution made neutral. The buffer solution (\(2\text{ ml./100 ml. of solution}\)) was added and the titration carried out with thorium nitrate solution. Further neutral samples were prepared and buffer added. Enough thorium nitrate solution was added to precipitate most of the fluoride, the precipitate was filtered off and the titration completed on the filtrate.

**Estimation of carbon dioxide**

In order to check the amounts of carbon dioxide calculated from the gas analyses conducted in the Orsat apparatus the sodium carbonate present in the solution from the alkaline sulphite scrubber was decomposed by acid to give carbon dioxide which was measured as
a gas.

A sample of the solution containing the sodium carbonate (5 ml.) was placed in a flask with sodium chloride (to reduce the solubility of the carbon dioxide), sodium hydroxide (½ g.) and iodine (2 g.), to oxidise the sulphite according to the equation

$$SO_3^2^- + 2OH^- + I_2 \rightarrow SO_4^{2-} + H_2O + 2I^-$$

Concentrated hydrochloric acid was added in a separate container and the flask attached to a gas burette. When steady conditions were obtained the concentrated acid was tipped into the alkaline solution and the liberated carbon dioxide measured after conditions were again steady. A blank experiment was carried out to allow for the carbon dioxide in the original alkaline sulphite solution.

**Estimation of trichloroacetic acid**

The alkaline sulphite solutions could easily contain sodium trichloroacetate carried over as the acid halide and several attempts were made to obtain the free acid. Samples of the scrubbing solution were made acid with hydrochloric acid (nitric and sulphuric acids would be extracted at a later stage and are difficult to remove) the $SO_2$ boiled off and the solution, saturated with sodium chloride, continuously ether extracted. Negligible amounts of acid were obtained from the ether extract.
Attempts to isolate the S-benzyl thiuronium salt were more successful and the presence of trichloroacetic acid was clearly demonstrated (m.p. of S-benzyl thiuronium salt 149°C. mixed melting point with authentic specimen 149°C.) but attempts to make the method quantitative were not successful. In spite of attempts to reduce the solubility of the partly saturated with sodium chloride the results were not reproducible. Consequently attempts to estimate trichloroacetic acid were abandoned.
EXPERIMENT DETAILS

ACTION OF CHLORINE ON SOME HYDROCARBONS

Chlorine, diluted with nitrogen was passed through bubblers of the liquid (2 x 12.5 ml.) or over the solid hydrocarbon packed in a glass tube (50 cm. x 1.5 cm. I.D.). The emergent chlorine was passed into N. aqueous potassium iodide solution and the liberated iodine titrated with sodium thiosulphates solution.

Paraffin wax (cubes of $\frac{1}{2}$ cm. edge) absorbed the least (25%) followed by isopropyle benzene (41%), naphthalene (cubes of $\frac{1}{2}$ cm. edge 84%) and benzene (86%). The amount absorbed was calculated after steady values were obtained and takes no account of the amounts used to produce saturation of the solution which took longer in the case of benzene and isopropyl benzene (6 mins.) than for naphthalene and paraffin wax (1 min.). The amount of chlorine in solution was also estimated iodometrically and found to be very small in comparison with that retained by any of the absorbents.

ACTION OF CHLORINE TRIFLUORIDE ON SOME HYDROCARBONS

The chlorine trifluoride was diluted with nitrogen and passed through bubblers of the liquid (2 x 12.5 ml.) or through tubes (50 cm. x 1.5 cm. I.D.) packed with
the solid. Paraffin wax (cubes of 1/2 cm. edge) would not remove chlorine trifluoride at a rate of 1/2 g./hour when diluted with nitrogen (75 ml./min.). Cyclohexane would not remove chlorine trifluoride at a rate of 1 g./hour when diluted with nitrogen (60 ml./min.). Doubling the amount of cyclohexane did not improve the results. Benzene did not remove chlorine trifluoride passed under the same conditions as for cyclohexane. As the liquid hydrocarbon became green during these experiments and in view of the reactive nature of chlorine trifluoride it was thought that the emergent halogen (detected by starch/potassium iodide paper) was in fact chlorine but no attempts were made at accurate analysis.

**ACTION OF CHLORINE TRIFLUORIDE ON TRICHLOROACETIC ACID AND TRICHLOROACETYL CHLORIDE**

**APPARATUS**

The apparatus can most easily be described if it is divided up into sections, some of which are common to several types of experiment.

*All metal section in which reaction occurs*

The chlorine trifluoride was passed through a flowmeter and mixed with nitrogen that had been passed
All metal apparatus (brass and copper where in contact with reaction mixture) [Half size] (dimensions in cm.)

Bottom of reaction vessels and safety traps

Knife edge

Holes for 6 x 2BA bolts to hold on lid

Lead seal

Lid of 1st. reaction vessel

Water condenser and top of 2nd reaction vessel lid

Top of safety trap

1/2" Instantor compression union (not to scale)
through a copper furnace and over sodium hydroxide pellets to remove oxygen, carbon dioxide and water. The mixed gases then passed through a safety trap into the two reaction vessels in series, the second of which was surmounted by a watercooled condenser. The reaction products then passed into the second safety trap and leave this section of the apparatus.

Experiment type A

The reaction products left the second safety trap and passed through a stainless steel tube into a solution of sodium hydroxide (140 g. 3.5 mole) and sodium sulphite (442 g. of the heptahydrate 1.73 mole) in water (to make 1,750 ml. of solution) contained in a 2L. three necked flask equipped with a mercury seal stirrer and lead for the unreacted gases. These were then lead over anhydrous calcium chloride (tube 50 cm. x 1.5 cm. I.D.) and into the trapping system (diag. 19). The incondensable gases were passed through a flowmeter and collected in an aspirator.

Experiment type B

In this case the second safety trap was filled with soft glass tubes to prevent attack of the glass immediately after the glass-to-metal connection by prior removal of all substances liable to attack glass. The reaction
Trapping system for halogenated methanes

This unit repeated three times

Benzene bubblers

The glass to metal seal consisted of a Neoprene washer around a glass tube so that it came between the nipple and seating of a petrol union.
products were passed through benzene (2 x 12.5 ml.) in bubblers (diag.10), designed to facilitate speedy replacement of the glass-to-metal joint and then over dry potassium fluoride (in tube 50 cm. x 1.5 cm. I.D.). After passing over antimony metal (2-6 mm. diam.) in a tube designed to prevent blockage (diag. 11) and over antimony metal powder on glass wool (to ensure complete removal of halogen) the gas stream was lead into one of the bubblers containing the solution of sodium iodide in acetone (diag.11 ) and from there to one of the two gas storage bulbs (diag. 11).

**Experiment type C**

The safety trap was prepared as for B. The reaction products were led into the solution of sodium iodide in acetone in the bubbler and the exit gases passed out of the apparatus via a flowmeter and calcium chloride tube.

**PREPARATION OF REAGENTS:**

**Trichloroacetic acid**

This was distilled under reduced pressure, rejecting the initial water containing distillate.

**Trichloroacetyl chloride**

This was prepared according to the method of 28.

Rabczewicz et al. Trichloroacetic acid (420 g. 2.6 mole)
and anhydrous zinc chloride (25 g.) as catalyst were heated to \(150^\circ\) in a 1L. flask equipped with dropping funnel and reflux condenser. Redistilled benzotrichloride (580 g. 2.96 mole) was added dropwise (40 min.) and heating continued for a further 60 min. when little hydrogen chloride was being given off. The crude product was then distilled off up to \(155^\circ\) (480 g.). This was redistilled to give pure trichloroacetyl chloride (b.p. 117-120\(^\circ\) 326 g. 1.8 mole 70% yield. eq. wt. by hydrolysis 90.2 theory requires 90.9).

**Sodium iodide**

Heating at \(184^\circ\) for 6 hours at 2.0 cm. pressure produced a sufficiently dry sample.

**Potassium fluoride**

As for sodium iodide.

**Acetone**

This was distilled after standing over potassium permanganate and anhydrous magnesium sulphate.

**Benzene**

Redistilled from sodium wire.

**Antimony metal**

Oven dried at \(110^\circ\).

The displacing liquid in the gas storage bulbs and in the Orsat apparatus was a mixture of glycerol (500 ml.),
water (430 ml.) and conc. sulphuric acid (70 ml.).

**METHOD OF OPERATION**

**Experiment type A**

The clean dry apparatus was purged with $N_2$. The trichloroacetic acid (or acid chloride) was weighed into the reaction vessels (80% in the first reaction vessel), the alkaline sulphite solution was placed in the flask and the apparatus again purged with $N_2$. The cold traps were immersed in refrigerant and when equilibrium was established chlorine trifluoride was admitted, diluted with $N_2$. The initial chlorine trifluoride rate of 1 g./hour was increased after 5 min. to 5 g./hour at which rate it was maintained for 6 hours. The rate of flow of $N_2$ was kept as low as was necessary to prevent blocking of the stainless steel tube (8 m I.D.) leading into the alkaline sulphite scrubber (30 ml./min.). At the end of the 6 hours the chlorine trifluoride cylinder was shut and $N_2$ passed for 1/2-hour to ensure complete removal of the volatile products from the reaction vessels. The apparatus was then sealed off into various sections. The trapping system containing the halogenated methanes was dealt with as described in the chromatography section. The alkaline sulphite scrubbing solution was made up to 2L. and aliquots used
to determine the chloride, fluoride, carbon dioxide and trichloroacetic acid as described in the analytical section.

The contents of the reaction vessels were usually solid. This solid was melted out and dissolved in water. The halogenated ethanes were filtered off and the aqueous filtrate made up to a known volume in order that the chloride and fluoride present might be determined.

In experiments using the acid chloride an aliquot of the liquid remaining in the reaction vessel was placed in a flask equipped with dropping funnel and ethanol/Drikold reflux condenser. Excess conc. sodium hydroxide solution was added and the halogenated ethanes filtered off as before and the filtrate made up to a known volume.

The connecting tubes, lids of reaction vessels and condenser were washed with methanol and the halogenated ethanes so removed precipitated by adding excess water to the methanol solution. The gas in the aspirators was analysed for oxygen and carbon monoxide.

**Experiment type B**

The clean dry apparatus was purged with $\text{N}_2$. 
The trichloroacetic acid (or acid chloride) was weighed into the reaction vessels and the apparatus again purged with $N_2$. The solution of sodium iodide in dry acetone (saturated - about $N$.) was placed in the bubblers and when equilibrium was established chlorine trifluoride was passed as in the previous type of experiment.

The gas stream, after removal of halogens and hydrogen fluoride, was passed for 30 min. through the iodide solution. For the first 10 min. period of this time the gases leaving the iodide solution were allowed to leave the apparatus via a flowmeter. At the end of this 10 min. period it was assumed that the acetone was saturated with carbon dioxide etc. and for the next 20 mins. the gases passing from the solution of sodium iodide in acetone were collected to be analysed later for carbon dioxide, oxygen and carbon monoxide in an Orsat apparatus, using as adsorbents 30% KOH solution, alkaline pyrogallol and ammoniacal cuprous chloride. At the end of the 30 minutes the phosgene containing gas stream was diverted into the second sodium iodide in acetone bubbler and the collection of the gas sample stopped. The previous cycle of operations was then repeated during the next and subsequent 30 min. intervals and in this way 12 gas samples and 12 solutions
containing iodine (equivalent to the phosgene absorbed) were obtained. The solution of sodium iodide in acetone containing iodine was washed into a beaker with dry acetone and the iodine titrated in acid solution with 2N sodium thiosulphate solution. The bubbler was immediately refilled with a fresh solution of sodium iodide in acetone. The reaction vessels were treated as for experiment type A.

Experiment type C

The apparatus was prepared and charged with trichloroacetic acid (or acid chloride) and solutions of sodium iodide in acetone as for experiment type B. The iodide solution was changed and the iodine titrated every 30 minutes as above but no gas samples were collected. The reaction vessels were treated as for experiment type A. The samples of iodide solution retained for fluoride determination were filtered and the sodium chloride and fluoride (insoluble in dry acetone) washed free of iodine and most of the sodium iodide with dry acetone. The sodium halides were then dissolved in water and fluoride determined as described in the analytical section.
Action of ClF₃ on CCl₃COOH at 100°

Experiment type A

Starting Materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (g)</th>
<th>Mole (mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₃COOH</td>
<td>105.5</td>
<td>(0.64 mole)</td>
</tr>
<tr>
<td>ClF₃</td>
<td>35.0</td>
<td>(0.38 mole)</td>
</tr>
</tbody>
</table>

Products

The alkaline sulphite scrubbing solution contained

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mass (g)</th>
<th>Mole (mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>25.5</td>
<td>(0.72 mole)</td>
</tr>
<tr>
<td>F⁻</td>
<td>11.9</td>
<td>(0.63 mole)</td>
</tr>
<tr>
<td>CO₂</td>
<td>18.2</td>
<td>(0.41 mole)</td>
</tr>
</tbody>
</table>

Halogenated methanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (g)</th>
<th>Mole (mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>19.2</td>
<td>(0.13 mole)</td>
</tr>
<tr>
<td>CCl₃F</td>
<td>6.1</td>
<td>(0.045 mole)</td>
</tr>
<tr>
<td>CCl₂F₂</td>
<td>1.8</td>
<td>(0.015 mole)</td>
</tr>
<tr>
<td>CClF₃</td>
<td>4.9</td>
<td>(0.046 mole)</td>
</tr>
</tbody>
</table>

Halogenated ethanes

6.5 g. (C₂Cl₆ containing a little fluorinated material - 0.028 mole.)

Recovered CCl₃COOH 11 g. (0.067 mole.)

Experiment type B

Starting Materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (g)</th>
<th>Mole (mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₃COOH</td>
<td>106.5</td>
<td>(0.65 mole)</td>
</tr>
<tr>
<td>ClF₃</td>
<td>26.5</td>
<td>(0.29 mole)</td>
</tr>
</tbody>
</table>
**Products**

CO\textsubscript{2} \textsubscript{2} \textsubscript{2} 0.167 eq. as estimated according to the equation.

\[
\text{COX}_2 + 2\text{NaI} \rightarrow \text{CO} + \text{NaX} + \text{I}_2
\]

The approximate composition is

\[
\begin{align*}
\text{CO} & \quad 2.3 \text{ g.} \\
\text{Cl} & \quad 2.6 \text{ g.} \\
\text{F} & \quad 1.8 \text{ g.}
\end{align*}
\]

There were recovered 1 g. of C\textsubscript{2}Cl\textsubscript{6}, 34 g. of unreacted CCl\textsubscript{3}CCOH, containing 0.3 g. Cl and 0.2 g. F.

Analysis of the exit gases showed that they contained

\[
\begin{align*}
\text{CO}_2 & \quad 12.8 \text{ g.} \\
\text{O}_2 & \quad 0.15 \text{ g.} \\
\text{CO} & \quad 2.9 \text{ g.} \text{ (including that from COX}}_2) \\
\end{align*}
\]

There were formed 0.167 eq. COX\textsubscript{2} which is equivalent to 2.4 g. CO i.e. actual CO produced is 0.3 g.

**Experiment type C**

**Starting Material**

\[
\begin{align*}
\text{CCl}_3\text{COOH} & \quad 101 \text{ g.} \text{ (0.38 mole.)} \\
\text{ClF}_3 & \quad 35 \text{ g.} \text{ (0.62 mole.)}
\end{align*}
\]

**Products of reaction**

COX\textsubscript{2} + X\textsubscript{2} 0.736 equivalents containing approximately
CI 17.3 g. (0.49 mole.)  
F 4.7 g. (0.25 mole.)

There were also recovered

C₂Cl₆  3.5 g. (0.015 mole.)
and unreacted CCl₃COOH 16.5 g. (0.10 mole.)

Combining these results it is seen we have from
105.5 g. of CCl₃COOH and 35.0 g. of ClF₃ the
following:

<table>
<thead>
<tr>
<th>Products</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂Cl₆</td>
<td>6.5 g.</td>
<td>(0.028 mole.)</td>
</tr>
<tr>
<td>CCl₄</td>
<td>19.2 g.</td>
<td>(0.13 mole.)</td>
</tr>
<tr>
<td>CCl₃F</td>
<td>6.1 g.</td>
<td>(0.045 mole.)</td>
</tr>
<tr>
<td>CCl₂F₂</td>
<td>1.8 g.</td>
<td>(0.015 mole.)</td>
</tr>
<tr>
<td>CClF₃</td>
<td>4.9 g.</td>
<td>(0.046 mole.)</td>
</tr>
</tbody>
</table>

Carbonyl halides containing CO

| Cl  | 2.3 g.| (0.084 mole.) |
| F   | 1.8 g.| (0.095 mole.) |

Halogens containing

| Cl  | 14.7 g.| (0.41 mole.) |
| F   | 3.3 g.| (0.17 mole.) |

Halogens as CCl₃COX and HX

| Cl  | 8.2 g.| (0.23 mole.) |
| F   | 7.2 g.| (0.39 mole.) |

CO₂ (from alkaline sulphite scrubber after correction for that from COX₂)  
14.5 g. (0.33 mole.)
CO₂ (By gas analysis 17.2 g. (0.39 mole.))
O₂ 0.2 g. (0.0047 mole.)
CO 0.3 g. (0.0011 mole.)

**Action of ClF₃ or CCl₃COOH at 70-80°**

**Experiment type A.**

**Starting Material.**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Amount</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₃COOH</td>
<td>100 g.</td>
<td>(0.61 mole.)</td>
</tr>
<tr>
<td>ClF₃</td>
<td>29 g.</td>
<td>(0.31 mole.)</td>
</tr>
</tbody>
</table>

**Products**

The alkaline sulphite scrubbing solution contained

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Amount</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>21.5 g.</td>
<td>(0.61 mole.)</td>
</tr>
<tr>
<td>F⁻</td>
<td>14.4 g.</td>
<td>(0.76 mole.)</td>
</tr>
<tr>
<td>CO₂</td>
<td>28.0 g.</td>
<td>(0.64 mole.)</td>
</tr>
</tbody>
</table>

**Halogenated methanes**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Amount</th>
<th>Mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>9.1 g.</td>
<td>(0.059 mole.)</td>
</tr>
<tr>
<td>CCl₃F</td>
<td>7.7 g.</td>
<td>(0.056 mole.)</td>
</tr>
<tr>
<td>CCl₂F₂</td>
<td>0.2 g.</td>
<td>(0.0015 mole.)</td>
</tr>
<tr>
<td>CClF₃</td>
<td>0.1 g.</td>
<td>(0.0009 mole.)</td>
</tr>
</tbody>
</table>

**Halogenated ethanes**

13.5 g. (C₂Cl₆ containing a little fluorinated material) (0.057 mole.)
The 1st. reaction vessel contained the C₂Cl₆ above but the second reaction vessel and 2nd safety trap contained a liquid (about 18 g.) consisting of CCl₃COOH, CCl₃COX and halogenated methanes and ethanes. This was analysed as follows. A known weight (3.3556 g.) was shaken with water and the acid titrated with alkali using phenol phthalein as indicator (31.76 ml. of 0.2110 N. NaOH 0.0670 eq.). The neutral organic layer was washed and the aqueous solution and washing made up to 100 ml. and halogens estimated (Cl⁻ 0.00053 eq. F⁻ 0.00226 eq.). The organic layer was dried (MgSO₄) and distilled under a static vacuum to give a liquid (1.2940 g.). By sublimation and by ethanol extraction of the MgSO₄, a solid (C₂Cl₆ 0.3836 g.) was obtained. These facts are interpreted as follows.
The 3.3556 g. of mixture contain

CCl₃COF  0.376 g.  (0.00452 eq.)
CCl₃COCl  0.096 g.  (0.00106 eq.)
CCl₃COOH  0.184 g.  (0.00112 eq.)

(Total acid  0.6670 eq.)

CX₄  1.294 g.
C₂X₆  0.384 g.

Total  2.334 g.

The deficit of 1.022 is attributed to loss of CX₄ and C₂X₆ in the washing procedure. Accordingly this amount is added in proportion to each of the values obtained for the amounts of CX₄ and C₂X₆ present. i.e.

CCl₃COF  0.376 g.
CCl₃COCl  0.096 g.
CCl₃COOH  0.184 g.
CX₄  1.294 + 0.788 = 2.082 g.
C₂X₆  0.384 + 0.234 = 2.618 g.

A sample of the CX₄ when analysed by gas
chromatography was shown to be mostly $\text{CCl}_4$ with negligible amounts of $\text{CCl}_3\text{F}$ and $\text{CCl}_2\text{F}_2$. The presence of carbonyl halides has been ignored but other experiments (see later) showed that the amount of halogen present as carbonyl halides was negligible.

Thus in the 18 g. of liquid we have

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CCl}_4$</td>
<td>11.2 g</td>
</tr>
<tr>
<td>$\text{CCl}_3\text{COF}$</td>
<td>2.0 g</td>
</tr>
<tr>
<td>$\text{CCl}_3\text{COCl}$</td>
<td>0.52 g</td>
</tr>
<tr>
<td>$\text{CCl}_3\text{COOH}$</td>
<td>0.99 g</td>
</tr>
<tr>
<td>$\text{C}_2\text{Cl}_6$</td>
<td>3.3 g</td>
</tr>
</tbody>
</table>

Exit gases: Oxygen 2 g.

Hence in this reaction we have accounted for

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CCl}_4$</td>
<td>20.3 g</td>
</tr>
<tr>
<td>$\text{CCl}_3\text{F}$</td>
<td>7.7 g</td>
</tr>
<tr>
<td>$\text{CCl}_2\text{F}_2$</td>
<td>0.2 g</td>
</tr>
<tr>
<td>$\text{CClF}_3$</td>
<td>0.1 g</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>30.0 g</td>
</tr>
<tr>
<td>$\text{Cl}^-$</td>
<td>21.5 g</td>
</tr>
<tr>
<td>$\text{F}^-$</td>
<td>14.4 g</td>
</tr>
<tr>
<td>$\text{CCl}_3\text{COF}$</td>
<td>2.0 g</td>
</tr>
<tr>
<td>$\text{CCl}_3\text{COCl}$</td>
<td>0.5 g</td>
</tr>
<tr>
<td>$\text{CCl}_3\text{COOH}$</td>
<td>1.0 g</td>
</tr>
<tr>
<td>$\text{C}_2\text{Cl}_6$</td>
<td>16.8 g</td>
</tr>
</tbody>
</table>
Experiment type B.

Starting Materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (g)</th>
<th>Mole (eq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₃COOH</td>
<td>99.5</td>
<td>0.61</td>
</tr>
<tr>
<td>ClF₃</td>
<td>30.5</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Products

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (g)</th>
<th>Mole (eq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>3.7</td>
<td>0.13</td>
</tr>
<tr>
<td>Cl</td>
<td>6.5</td>
<td>0.18</td>
</tr>
<tr>
<td>F</td>
<td>1.6</td>
<td>0.084</td>
</tr>
</tbody>
</table>

Analysis of the exit gases showed that they contained

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>17.2</td>
</tr>
<tr>
<td>O₂</td>
<td>0.1</td>
</tr>
<tr>
<td>CO</td>
<td>6.0</td>
</tr>
</tbody>
</table>

The 0.266 eq. of CO₂ generated 3.7 g. CO

Therefore the actual CO produced is 2.3 g.

The 1st. reaction vessel contained a solid (C₂Cl₆) while the second contained a liquid (15 g.) containing CCl₃COX (.011 eq. Cl⁻, 0.013 eq. F⁻) similar to that of the previous experiment.

From this liquid and other parts of the apparatus 9.5 g. C₂Cl₆ were recovered. A more complete analysis was not attempted.

Experiment type C.

Starting Materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (g)</th>
<th>Mole (eq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₃COOH</td>
<td>102</td>
<td>(0.62 mole)</td>
</tr>
</tbody>
</table>
ClF$_3$  34.5 g.  (0.37 mole.)

**Products**

0.592 eq. of halogen as COX$_2$ and X$_2$ was detected. The approximate composition was

- Cl  12.4 g.  (0.35 mole.)
- F    4.6 g.  (0.24 mole.)

From the 1st reaction vessel only C$_2$Cl$_6$ was recovered while the second yielded a liquid (11 g.) as before. No attempts were made at a complete analysis. In all 13.5 g. (0.057 mole.) of C$_2$Cl$_6$ were recovered. Combining these results it is seen that we have from 100 g. of CCl$_3$COOH and 29 g. of ClF$_3$ the following products:

- C$_2$Cl$_6$  16.8 g.  (0.070 mole.)
- CCl$_4$   11.2 g.  (0.075 mole.)
- CCl$_3$F  7.7 g.  (0.056 mole.)
- CCl$_2$F$_2$  0.2 g.  (0.0015 mole.)
- CClF$_3$  0.1 g.  (0.0009 mole.)

Carbonyl (CO)  3.7 g.  (0.13 mole.)
halides containing

- Cl  6.5 g.  (0.18 mole.)
- F    1.6 g.  (0.084 mole.)

Halogen containing

- Cl  5.9 g.  (0.017 mole.)
- F    3.0 g.  (0.016 mole.)

CO$_2$ (from alkaline sulphite scrubber after correction for that generated from COX$_2$)  22.3 g.  (0.51 mole.)
\[
\begin{align*}
\text{CO}_2 \text{ (by gas analysis) } &\quad 17.2 \text{ g.} \quad (0.39 \text{ mole.}) \\
\text{CO} &\quad 2.3 \text{ g.} \quad (0.083 \text{ mole.}) \\
\text{Actually isolated (CCl}_3\text{COF)} &\quad 2.0 \text{ g.} \quad (0.012 \text{ mole.}) \\
\text{(CCl}_3\text{COCl)} &\quad 0.5 \text{ g.} \quad (0.0027 \text{ mole.}) \\
\text{(CCl}_3\text{COOH)} &\quad 1.0 \text{ g.} \quad (0.0062 \text{ mole.}) \\
\text{halogens as HX and CCl}_3\text{COX } &\quad \{ \text{Cl} \quad 9.1 \text{ g.} \quad (0.25 \text{ mole.}) \\
&\quad \{ \text{F} \quad 9.8 \text{ g.} \quad (0.52 \text{ mole.}) \\
\text{O}_2 &\quad 0.1 \text{ g.} \quad (0.0032 \text{ mole.})
\end{align*}
\]

**Action of ClF\textsubscript{3} on CCl\textsubscript{3}COCl at 100°**

**Experiment type A.**

**Starting Materials**

\[
\begin{align*}
\text{CCl}_3\text{COCl} &\quad 111.5 \text{ g.} \quad (0.61 \text{ mole.}) \\
\text{ClF}_3 &\quad 3.2 \text{ g.} \quad (0.35 \text{ mole.}) \\
\end{align*}
\]

**Products** The alkaline sulphite solution contained

\[
\begin{align*}
\text{Cl}^- &\quad 33.0 \text{ g.} \quad (0.93 \text{ mole.}) \\
\text{F}^- &\quad 7.8 \text{ g.} \quad (0.41 \text{ mole.}) \\
\text{CO}_2 &\quad 5.9 \text{ g.} \quad (0.13 \text{ mole.}) \\
\end{align*}
\]

The halogenated methanes were composed of

\[
\begin{align*}
\text{CCl}_4 &\quad 1.5 \text{ g.} \quad (0.0098 \text{ mole.}) \\
\text{CCl}_3\text{F} &\quad 6.9 \text{ g.} \quad (0.050 \text{ mole.}) \\
\text{CCl}_2\text{F}_2 &\quad 0.1 \text{ g.} \quad (0.00083 \text{ mole.}) \\
\text{CClF}_3 &\quad 0.1 \text{ g.} \quad (0.00096 \text{ mole.}) \\
\end{align*}
\]

The first reaction vessel was empty and the liquid remaining in the second reaction vessel (79.0 g.) was analysed as follows:
A sample (9.5 g.) was dissolved in excess NaOH solution and the \( \text{C}_2\text{Cl}_6 \) filtered off (0.2 g.). The filtrate was made up to 250 ml. and the halide estimated (0.0013 eq. Cl\(^-\) and 0.037 eq. F\(^-\)). This indicates the presence of

\[
\begin{align*}
\text{CCl}_3\text{COCl} & \quad 0.2 \text{ g.} \\
\text{CCl}_3\text{COF} & \quad 6.1 \text{ g.} \\
\text{C}_2\text{Cl}_6 & \quad 0.2 \text{ g.}
\end{align*}
\]

This rather large deficit is accounted for in the loss of the volatile liquid during the vigorous neutralisation in spite of the CO\(_2\)/Ethanol condenser. The relative proportions of these products was therefore used and the liquid from the reaction vessels is considered to be

\[
\begin{align*}
\text{CCl}_3\text{COCl} & \quad 2.5 \text{ g.} \quad (0.014 \text{ mole.}) \\
\text{CCl}_3\text{COF} & \quad 74.0 \text{ g.} \quad (0.50 \text{ mole.}) \\
\text{C}_2\text{Cl}_6 & \quad 2.5 \text{ g.} \quad (0.011 \text{ mole.})
\end{align*}
\]

Exit gases contained \( \text{O}_2 \) 0.1 g. (0.0031 mole.)

Hence in the experiment we have accounted for 134.4 g. of products.

**Experiment type B.**

**Starting Materials**

\[
\begin{align*}
\text{CCl}_3\text{COCl} & \quad 115.0 \text{ g.} \quad (0.63 \text{ mole.}) \\
\text{ClF}_3 & \quad 35.0 \text{ g.} \quad (0.38 \text{ mole.})
\end{align*}
\]

**Products**

0.0384 eq. of phosgenenes were detected, of
approximate composition

CO 0.53 g.  
Cl 0.83 g. (0.023 mole.)  
F 0.29 g. (0.015 mole.)

Analysis of the exit gases showed that they contained

CO₂ 3.4 g. (0.077 mole.)  
O₂ 0.2 g. (0.0062 mole.)

and no CO in excess of that generated from the COX₂.

The liquid remaining in the second reaction vessel (55.5 g.) was analysed in a similar fashion to that in the previous experiment. The sample (16.6 g.) contained 1 g. C₂Cl₆ 3.3 g. CCl₃COCl and 9.086 g. CCl₃COCl and again there was an apparent loss of volatile halides.

Experiment type C.

Starting Materials

CCl₃COCl 112.5 g. (0.62 mole.)  
ClF₃ 30g. (0.32 mole.)

Products

0.924 eq. of X₂ + COX₂ were detected containing approximately

Cl 26.8 g. (0.76 mole.)  
F 3.2 g. (0.16 mole.)

60 g. of material remained in the second reaction vessel.
From these experiments we can state that the reaction between \( \text{ClF}_3 \) (32 g.) and \( \text{CCl}_3\text{COOH} \) (111.5 g.) produced.

\[
\begin{align*}
\text{C}_2\text{Cl}_6 & \quad 2.5 \text{ g.} \quad (0.011 \text{ mole.}) \\
\text{CCl}_4 & \quad 1.5 \text{ g.} \quad (0.0098 \text{ mole.}) \\
\text{CCl}_3\text{F} & \quad 6.9 \text{ g.} \quad (0.050 \text{ mole.}) \\
\text{CCl}_2\text{F}_2 & \quad 0.1 \text{ g.} \quad (0.00083 \text{ mole.}) \\
\text{CClF}_3 & \quad 0.1 \text{ g.} \quad (0.00096 \text{ mole.}) \\
\end{align*}
\]

\( \text{CO}_2 \) (from alkaline scrubber after correction for that from \( \text{COX}_2 \)) 5.1 g. (0.19 mole.)

By gas analysis 3.4 g. (0.077 mole.)

\( \text{COX}_2 \) containing

\[
\begin{align*}
\text{(CO)} & \quad 0.5 \text{ g.} \quad (0.019 \text{ mole.}) \\
\text{(Cl)} & \quad 0.8 \text{ g.} \quad (0.023 \text{ mole.}) \\
\text{(F)} & \quad 0.3 \text{ g.} \quad (0.015 \text{ mole.}) \\
\end{align*}
\]

halogen containing

\[
\begin{align*}
\text{(Cl)} & \quad 26.0 \text{ g.} \quad (0.73 \text{ mole.}) \\
\text{(F)} & \quad 2.9 \text{ g.} \quad (0.15 \text{ mole.}) \\
\end{align*}
\]

halogen as \( \text{CCl}_3\text{COX} \) carried over into alkaline sulphite scrubber

\[
\begin{align*}
\text{(Cl)} & \quad 6.2 \text{ g.} \quad (0.18 \text{ mole.}) \\
\text{(F)} & \quad 4.6 \text{ g.} \quad (0.24 \text{ mole.}) \\
\end{align*}
\]

A mixture of \( \text{CCl}_3\text{COF} \) and \( \text{CCl}_3\text{COCl} \) containing appreciable amounts of the acid fluoride 76.5 g.

\[ \text{Oxygen} \quad 0.1 \text{ g.} \quad (0.0031 \text{ mole.}) \]
Experiment to determine degree of substitution of CCl₃ group in CCl₃COOH

Starting Materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight (g)</th>
<th>Mole (0.16 mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClF₃</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>CCl₃COOH</td>
<td>104.5</td>
<td>(0.64 mole)</td>
</tr>
</tbody>
</table>

A reaction of type A was carried out at 100° for 3 hours.

Products

The alkaline sulphite scrubber contained

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight (g)</th>
<th>Mole (0.25 mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>9.0</td>
<td>(0.25 mole)</td>
</tr>
<tr>
<td>F⁻</td>
<td>7.6</td>
<td>(0.40 mole)</td>
</tr>
<tr>
<td>CO₂</td>
<td>21.0</td>
<td>(0.48 mole)</td>
</tr>
</tbody>
</table>

Halogenated methanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight (g)</th>
<th>Mole (0.032 mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>CCl₃F</td>
<td>1.6</td>
<td>(0.011 mole)</td>
</tr>
<tr>
<td>CCl₂F₂</td>
<td>0.3</td>
<td>(0.0025 mole)</td>
</tr>
<tr>
<td>CClF₃</td>
<td>0.2</td>
<td>(0.0019 mole)</td>
</tr>
</tbody>
</table>

Halogenated ethanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight (g)</th>
<th>Mole (0.062 mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂Cl₆</td>
<td>14.8</td>
<td></td>
</tr>
</tbody>
</table>

The residue in the reaction vessels (55.5 g. of solid) was analysed as follows. A sample of the crude acid (16.5 g.) and 0.5 g. of anhydrous ZnCl₂ were heated to 150° in a 100 ml. flask equipped with dropping funnel, reflux CO₂/EtOH condenser and CaCl₂ tube. Redistilled benzotrichloride (20 g. 0.14 mole.) was added and the mixture kept at this
temperature for a further 30 minutes. The solid CO₂ was removed from the cold finger and replaced by oil. Using the cold finger as a thermometer well the acid chlorides were distilled until the distillation temperature rose to 126°C. (CCl₃COCl b.p. 118°C) when 3.5 g. had distilled. The trap containing the acid chlorides was fitted with a dropping funnel, reflux CO₂/EtOH condenser and CaCl₂ tube and anhydrous MeOH (1 ml.) added. After the initial vigorous reaction occurred the mixture was heated to 160°C. and then left overnight. The crude esters were poured onto water, separated and washed with water (4 x 20 ml.) and dried (MgSO₄). The crude product was distilled under a static vacuum to give 2 g. of mixed esters for chromatographic analysis (see that section for details) which showed the presence of only CCl₃COOMe and Me₂CO₃. Authentic CF₃COOMe and CCl₃COOMe were prepared by the same process.

A second sample (6.4632 g.) was dissolved in water and the precipitate of C₂Cl₆ filtered off (1.5509 g.) and the filtrate made up to 100 ml. for Cl⁻ and F⁻ estimations.

There were found for the whole 55.5 g. 

\[
\begin{align*}
\text{Cl}^- & \quad 0.0085 \text{ eq.} \\
\text{F}^- & \quad 0.0023 \text{ eq.} \\
& \quad 0.0108 \text{ eq.}
\end{align*}
\]
By gas chromatography there were detected 0.000058 eq. of \( \text{Me}_2\text{CO}_3 \). Thus it is seen that most of the halogen must be present as \( \text{CCl}_3\text{COX} \). Using this information we have present in the 55.5 g. of reaction residues:

\[
\begin{align*}
\text{C}_2\text{Cl}_6 & \quad 13.3 \text{ g.} \\
\text{CCl}_3\text{COCl} & \quad 1.5 \text{ g.} \\
\text{CCl}_3\text{COF} & \quad 0.4 \text{ g.} \\
\text{CCl}_3\text{COOH} & \quad 40.3 \text{ g.}
\end{align*}
\]

The connecting tubes etc. yielded 1.5 g. \( \text{C}_2\text{Cl}_6 \). The exit gases contained 0.2 g. of \( \text{O}_2 \). From previous experiments of types B and C we can say that after 3 hours reaction the following had been formed:

COX containing
\[
\begin{align*}
\text{(CO)} & \quad 0.7 \text{ g.} & (0.026 \text{ mole.}) \\
\text{(Cl)} & \quad 0.8 \text{ g.} & (0.023 \text{ mole.}) \\
\text{(F)} & \quad 0.6 \text{ g.} & (0.029 \text{ mole.})
\end{align*}
\]

halogen containing
\[
\begin{align*}
\text{(Cl)} & \quad 3.7 \text{ g.} & (0.105 \text{ mole.}) \\
\text{(F)} & \quad 0.7 \text{ g.} & (0.037 \text{ mole.})
\end{align*}
\]

Gas analysis indicated the presence of

\[
\begin{align*}
\text{CO}_2 & \quad 6.7 \text{ g.} & (0.15 \text{ mole.}) \\
\text{O}_2 & \quad 0.1 \text{ g.} & (0.0031 \text{ mole.}) \\
\text{CO} & \quad 0.2 \text{ g.} & (0.0071 \text{ mole.})
\end{align*}
\]

Hence the products from the action of \( \text{ClF}_3 \) (15 g. 0.16 mole) on \( \text{CCl}_3\text{COOH} \) (104.5 g. 0.64 mole.) for 3 hours are:

\[
\begin{align*}
\text{C}_2\text{Cl}_6 & \quad 14.8 \text{ g.} & (0.062 \text{ mole.}) \\
\text{CCl}_4 & \quad 4.9 \text{ g.} & (0.032 \text{ mole.})
\end{align*}
\]
CCI

F

CCl3F

1.6 g. (0.011 mole.)

CCl2F2

0.3 g. (0.0025 mole.)

CClF3

0.2 g. (0.0019 mole.)

CO2 (from alkaline scrubber after correction for that from COX2) 19.8 g. (0.45 mole.) (By gas analysis. 6.7 g. (0.15 mole.))

COX2 containing

( CO

0.7 g. (0.026 mole.)

( Cl

0.8 g. (0.023 mole.)

(F

0.6 g. (0.029 mole.)

halogen containing

( Cl

3.7 g. (0.105 mole.)

(F

0.7 g. (0.037 mole.)

halogen as CCl3COX or HX

Cl

4.5 g. (0.13 mole.)

F

6.4 g. (0.34 mole.)

CCl3COF

1.5 g. (0.0091 mole.)

CCl3COCl

0.4 g. (0.0022 mole.)

CCl3COOH

40.3 g. (0.25 mole.)

Oxygen

0.1 g. (0.0031 mole.)

CO

0.2 g. (0.0071 mole.)

Experiment to determine effect of number of reaction vessels

The experiments types B and C gave results that had a rather strange variation with time. In order to investigate this phenomenon an experiment of type B was carried out using a single reaction vessel of larger
capacity (300 ml.) instead of the two in series.
The reaction (type B) was carried out in 10 hours and
products resulting from the reaction between the ClF₃
(57 g. 0.61 mole.) and the CCl₃COOH (200 g. 1.22 mole.)
were C₂Cl₆ (8.5 g. 0.037 mole.), recovered acid
(91 g. 0.56 mole.) and CO₂, CO₂, O₂ and CO as
represented graphically (Diagram 2 & 3).
26. S.W. Green  Symposium of Vapour Phase Chromatography page R191
   London  Butterworths Scientific Publications 1956
