CHAPTER II

EXPERIMENTAL
I. INTRODUCTION

The experimental work consists of preparation of deuterated o,m,p-fluorobromo and o,m,p-fluorochloro benzenes, purification of the deuterated and undeuterated samples by gas-liquid chromatography and recording Raman as well as infrared absorption spectra. The method of deuteration, testing the extent of deuteration and gas-chromatographic purification of the samples are discussed below, together with the details of obtaining the spectra.

II. PREPARATION AND DEUTERATION OF COMPOUNDS

1. Undeuterated Compounds:

   o,m,p-fluorobromo benzenes were obtained from Koch and Light Laboratories Ltd., Colnbrook, England and o,p-fluorochloro benzenes were obtained from Schuchardt, Munich, Germany.

   m-fluorochloro benzene was prepared\(^{(1)}\) in the laboratory starting with m-chloroaniline. The solution of m-chloroaniline in HCl was treated with nitrous acid. The resulting m-chloro diazonium chloride when treated with fluoboric acid, gave diazonium fluoborate. This decomposes at 130°C to give nitrogen, boron trifluoride and m-fluorochloro benzene. The chemical reactions involved in the process are given below:

   \[ \text{m-ClC}_6\text{H}_4\text{NH}_2 + \text{HCl} \rightarrow \text{m-ClC}_6\text{H}_4-(\text{NH}_2)^{-}+\text{H}^+\text{Cl}^- \rightarrow \text{OHNO} \]

   \[ - \text{H}_2\text{O} \]

   m-chloroaniline hydrochloride.
\[ \text{m-ClC}_6\text{H}_4-(\text{NH}_2)-\text{N}=\text{O}^+\text{Cl}^- \xrightarrow{\text{H}_2\text{O}} \text{m-ClC}_6\text{H}_4\text{N}^+ = \text{N} - \text{Cl}^- \]

**m-chlorophenyl nitroso ammonium chloride**  
**m-chlorophenyl diazonium chloride**

+ \( \text{HBF}_4 \)  
\[ \xrightarrow{\text{Heat}} \text{m-ClC}_6\text{H}_4\text{N}^+ = \text{N-BF}_4^- \]

**m-chlorophenyl diazonium fluoborate**  
**m-fluorochloro benzene**

2. Deuteration:

For exchange of hydrogen with deuterium, anhydrous DCl\(^{(2)}\) gas was bubbled through the sample in the presence of anhydrous AlCl\(_3\) acting as catalyst.

\[
\text{DCl} + \text{AlCl}_3 \xrightarrow{\text{Heat}} \text{D}^+\text{AlCl}_4^- 
\]

The reaction was carried out in the apparatus shown in Fig.1. About 2 ml of sample was taken in the clean sample tube S and to this, 300 milligrammes of finely powdered anhydrous AlCl\(_3\) was added. The sample tube S was clamped in its place in the system. The trap T was filled with solid carbondioxide-acetone mixture and the temperature of the trap was maintained at -86°C. 5 ml of acetyl chloride was taken in the flask F which was connected to the trap T by cone and socket arrangement. 1.25 ml of heavy water (99.9 per cent w/w D\(_2\)O) was taken in dropping funnel D which was fitted to the flask F.
APPARATUS FOR THE DEUTERATION BY DCl GAS

FIG. 1.
Heavy water was added drop by drop to acetyl chloride. DCl gas thus obtained from the instantaneous reaction between acetyl chloride and heavy water was made free from traces of heavy water and acetyl chloride in trap T.

\[ \text{CH}_3\text{COCl} + \text{D}_2\text{O} \rightarrow \text{CH}_3\text{COOD} + \text{DCl} \]

The purified gas was bubbled through the sample in presence of the catalyst AlCl₃. The dropping of heavy water was so adjusted that 1.25 ml lasted for about one and half hours. When heavy water was consumed completely, the residue of acetyl chloride in flask F was replaced by 5 ml of fresh acetyl chloride and 1.25 ml fresh heavy water was filled in dropping funnel. This was repeated four times, i.e. DCl corresponding to 5 ml of D₂O was bubbled through the sample.

The extent of isotopic enrichment was checked by observing the proton resonance spectrum as well as infrared spectrum of the sample. It was seen that after using about 5 ml D₂O the sample was deuterated to about 70 per cent. The bubbling of DCl gas was continued till no further deuteration was achieved.

The contents of the bulb were then transferred to a distillation bulb filled with anhydrous sodium carbonate (to remove the acid present in the sample). The distillation bulb was evacuated and sealed. Then it was slowly heated at the sample end and the distilled sample was collected at the other end of the system.

Another exchange process for the deuteration of o,m,p-fluorobromo benzenes and p-fluorochloro benzene was similar to that
employed by Best and Wilson (3) for p-dibromo benzene and bromo benzene but for a slight alteration in temperature to suit the requirements of these compounds. Three grammes of the para compounds were shaken with 96 per cent (W/W) \( D_2SO_4 \) (99.5 per cent D) for 8 hours and three grammes of o,m-fluorobromo benzenes were shaken with 89 per cent (W/W) \( D_2SO_4 \) (99.5 per cent D) for 8 hours at 85°C. The exchange process was repeated four times. The samples were purified by vacuum distillation as described earlier. The yield was poorer compared to the DCl method.

Considering both, the extent of isotopic enrichment and the yield of enriched sample, the method of deuteration by DCl gas was found to be more favourable. The big disadvantage of the \( D_2SO_4 \) method was that the compounds used to get charred and while trying to avoid the charring by reducing temperature and diluting con. \( D_2SO_4 \) by \( D_2O \), it was observed that deuteration was slow.

As the deuteration progressed, the integrated intensity of the nuclear magnetic resonance pattern of the undeuterated compound decreased. The process of deuteration was continued till no further deuteration was achieved. Neat liquids were used for recording the NMR spectra of all the twelve compounds. The final nuclear magnetic resonance spectrum obtained for one of the compounds, p-fluorochloro benzene, is given in Fig.2 to indicate the extent of deuteration. It can be seen from these that the concentration of tetradeutero compounds are much higher than the lower species in all the cases. The extent of deuteration of the samples used for obtaining spectra and the abundance of the isotopic species for all the molecules are given in Table 1.
FIG. 2. NUCLEAR MAGNETIC RESONANCE SPECTRA OF 1) $p$-$C_6H_4FCl$ 2) $p$-$C_6D_4FCl$.

(AREAS UNDER DOTTED CURVES REPRESENT INTEGRATED ABSORPTION INTENSITIES)
Table 1. Abundance of Isotopic Species in the Deuterated Compounds.

<table>
<thead>
<tr>
<th></th>
<th>Para</th>
<th></th>
<th>Meta</th>
<th></th>
<th>Ortho</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F,Br</td>
<td>F,Cl</td>
<td>F,Br</td>
<td>F,Cl</td>
<td>F,Br</td>
<td>F,Cl</td>
</tr>
<tr>
<td>Percentage of deuteration</td>
<td>93</td>
<td>97</td>
<td>98</td>
<td>90</td>
<td>96</td>
<td>98</td>
</tr>
<tr>
<td>Mono deutero compounds</td>
<td>0.12</td>
<td>0.01</td>
<td>0.00</td>
<td>0.36</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>Dideutero compounds</td>
<td>2.54</td>
<td>0.51</td>
<td>0.23</td>
<td>4.86</td>
<td>0.88</td>
<td>0.23</td>
</tr>
<tr>
<td>Trideutero compounds</td>
<td>22.53</td>
<td>10.95</td>
<td>7.53</td>
<td>29.16</td>
<td>14.16</td>
<td>7.53</td>
</tr>
<tr>
<td>Tetradutero compounds</td>
<td>75.51</td>
<td>88.53</td>
<td>92.21</td>
<td>65.61</td>
<td>84.94</td>
<td>92.21</td>
</tr>
</tbody>
</table>

Note: The concentration of the completely undeuterated species is 0.01 per cent or less. It can be seen from these that the concentration of tetradeutero compounds are much higher than the lower species in all the cases.

III. PURIFICATION BY GAS LIQUID CHROMATOGRAPHY

Initial infrared spectral studies showed that some of the deuterated as well as undeuterated compounds contained impurities, mainly the other isomers for a given species. This made the unequivocal assignments of weaker bands very difficult and hence all the impure compounds were purified by preparative gas chromatography.

For the analysis of o,m,p-fluorobromo, and o,m,p-fluorochloro benzenes and their deuterated analogues, both silicon grease and polyethylene glycol columns were tried at various temperatures and flow rates, using hydrogen flame ionisation detector. It was observed that the polyethylene glycol column was more efficient in the
separation of various components in the sample. The gaschromatographic conditions for the analysis and for the separation are given in Table 2.

Table 2. Gaschromatographic Conditions.

<table>
<thead>
<tr>
<th></th>
<th>For Analysis</th>
<th>For Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sampling size</td>
<td>0.5 µl</td>
<td>75 µl</td>
</tr>
<tr>
<td>2. Flow rate of N₂ at N.T.P.</td>
<td>25 ml/min.</td>
<td>25 ml/min.</td>
</tr>
<tr>
<td>3. Phase</td>
<td>Polyethylene glycol (10 per cent on chromosorb)</td>
<td>Polyethylene glycol (20 per cent on chromosorb)</td>
</tr>
<tr>
<td>4. Length of column</td>
<td>6'</td>
<td>9'</td>
</tr>
<tr>
<td>5. Diameter of the column</td>
<td>1/4&quot;</td>
<td>1/4&quot;</td>
</tr>
<tr>
<td>6. Detector</td>
<td>Flame ionisation</td>
<td>Thermal conductivity cell</td>
</tr>
<tr>
<td>7. Temp. and retention time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A) For fluorobromo benzenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Meta</td>
<td>105°C, 12.0'</td>
<td></td>
</tr>
<tr>
<td>(b) Para</td>
<td>105°C, 14.5'</td>
<td>115°C, 24.0'</td>
</tr>
<tr>
<td>(c) Ortho</td>
<td>105°C, 17.5'</td>
<td>115°C, 29.0'</td>
</tr>
<tr>
<td>(B) For fluorochloro benzenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Meta</td>
<td>85°C, 11.0'</td>
<td></td>
</tr>
<tr>
<td>(b) Para</td>
<td>85°C, 13.0'</td>
<td>90°C, 32.0'</td>
</tr>
<tr>
<td>(c) Ortho</td>
<td>85°C, 17.0'</td>
<td></td>
</tr>
</tbody>
</table>

* Samples were pure and hence no further purification was attempted.

The gaschromatographic analysis showed that all meta compounds were pure giving only one peak in gaschromatogram. The ortho
compounds were also pure except $\text{o-C}_6\text{D}_4^\text{FBr}$ which contained a small amount of $\text{m-C}_6\text{D}_4^\text{FBr}$, about 30 per cent of $\text{p-C}_6\text{D}_4^\text{FBr}$, 45 per cent of $\text{o-C}_6\text{D}_4^\text{FBr}$ and 20 per cent of unknown impurity. In case of para compounds, both the deuterated and undeuterated compounds contained 1-5 per cent of ortho isomer.

The impure samples were injected in the gas chromatographic preparative unit under the conditions mentioned in Table 2. The outcoming gas was condensed in a clean trap during the time the required fraction came out of the column; otherwise it was trapped in a separate trap. The traps were kept cooled all the time with solid carbon dioxide-acetone mixture. They were operated manually because small peaks due to impurities were very close to the main peak of interest.

The gaschromatograms of all the pure and impure samples as well as purified samples are shown in Figs. 3-5. It is seen that $\text{o-C}_6\text{D}_4^\text{FBr}$ which contained only about 45 per cent of $\text{o-C}_6\text{D}_4^\text{FBr}$ could be enriched to about 98 per cent and all the para compounds were found to be very pure after purification.

IV. SPECTRA.

A Perkin Elmer Model 621 double beam spectrophotometer equipped with double grating was used for recording infrared absorption spectra in the region 4000-200 cm$^{-1}$. A model 21 equipped with a grating interchange was also used for getting some of the spectra.
FIG. 3. GASCHROMATOGRAMS FOR PURE SAMPLES
(Y AXIS - $10^7$, $10^8$ OR $10^9$ AMPERES FULL SCALE).
FIG. 4. GASCHROMATOGRAMS (Y AXIS - $10^{-7}$, $10^{-8}$ OR $10^{-9}$ AMPERES FULL SCALE).
FIG. 5. GASCHROMATOGRAMS (Y AXIS – $10^{-7}$, $10^{-8}$ OR $10^{-9}$ AMPERES FULL SCALE)
The instruments were calibrated in different regions using atmospheric bands due to water vapour and carbon dioxide. The infrared absorption spectra were obtained for the purified undeuterated, deuterated and partially deuterated compounds in liquid state using .025 mm cell and thin films to avail of the complete information. The solution spectrum of m-C₆H₄FCl in CS₂ and the vapour phase spectrum m-C₆H₄FCl were recorded in the region 900-800 cm⁻¹.

The Raman spectra were recorded using a Spex Model 1400 Raman Spectrophotometer employing double monochromator and a photomultiplier detector followed by an electrometer, amplifier and recorder. The instrument was calibrated using emission lines of neon before recording the spectra and appropriate corrections were made. The exciting sources were 6328 Å He-Ne and 5145 Å Ar⁺ laser lines. The samples were filled in 50 mm long and 1.5 mm o.d. pyrex capillary tubes to half its capacity and both the ends were sealed. For getting the spectra the sample tube was mounted horizontally with its axis perpendicular to the incident laser beam and spectrograph slit. The light scattered at 90° to the incident radiation and to the axis of the tube was focussed on the slits of monochromator. The amount of the sample required was only about 0.02 ml. As the samples could not be prepared in large quantities, this technique was a big help to get complete Raman data including the measurements of depolarisation ratios of all the bands. To verify the correctness of the depolarisation measurements, under identical conditions, the depolarisation ratio was measured on the 458 cm⁻¹
FIG. 6. RAMAN SPECTRUM OF CARBON TETRACHLORIDE.
CCl\textsubscript{4} band. The two spectra with analyser at 0\textdegree\ and 90\textdegree\ are shown in Fig.6 for the CCl\textsubscript{4}. The depolarisation ratio was found to be 0.0032 which is quite satisfactory when compared with the earlier result\textsuperscript{(4)}.

V. SUMMARY

The present studies have given the preparation of the deuterated o,m,p-fluorochloro and fluorobromo benzenes. Conditions for preparative gaschromatographic purification of these compounds have been fixed. The extent of deuteration has been measured by NMR spectra. Infrared spectra of the deuterated compounds have been obtained on a Perkin Elmer Model 621 spectrophotometer in the range 4000–200 cm\textsuperscript{-1}. Raman spectra and depolarisation ratios are measured on Spex 1400 spectrophotometer with 6328 Å He-Ne and 5145 Å Ar\textsuperscript{+} laser lines. The spectra have been obtained for these compounds for the first time.
REFERENCES


