Investigation of some Group Three Halides
with various Donor Molecules
including a Thermodynamic Study of Carbonyl Bromide
and some Aluminium Halides

A thesis submitted by
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in candidature for the degree of Doctor of Philosophy
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Thanks are also due to the Science Research Council for providing a research grant.

DEDICATION

To my parents, and to everybody who has helped me along the way.
ABSTRACT

The interaction between boron tribromide (bromide, chloride) and benzene derivatives (benzene, m-xylene, mesitylene, hexamethylbenzene) has been studied using the techniques of cryoscopy, vapour pressure measurement, proton magnetic resonance and Raman spectroscopy. No evidence was found to support previous assertions of weak complex formation in solution.

The reactions between carbonyl halides (bromide, chloride) and Group Three halides (bromide, aluminium chloride, bromide, iodide) have been studied. No complexes could be isolated, in contrast to the system COCl₂/AlCl₃ studied previously. No reaction was found using boron halides, but with aluminium halides rapid and extensive halogen exchange occurred at ambient temperatures. Aluminium halides also catalysed the decomposition of carbonyl bromide:

\[ \text{COBr}_2(\ell) = \text{CO}(g) + \text{Br}_2(g) [+ \text{Br}_2(\ell)] \]

The enthalpy of hydrolysis of carbonyl bromide was measured by adiabatic solution calorimetry:

\[ \text{COBr}_2(\ell) + n\text{H}_2\text{O} \rightarrow \text{CO}_2(g) + [2\text{H}_3\text{Br}._{(n-1)}\text{H}_2\text{O}](1) \]

\[ \Delta H^\circ \text{ hydrolysis} = -49.06 \pm 0.16 \text{ kcal mol}^{-1} \]

\[ [-203.36 \pm 0.67 \text{ kJ mol}^{-1}] \]
From this was derived

$$\Delta H^\circ_{298} \text{COBr}_2(1) = -34.70 \pm 0.21 \text{ kcal mol}^{-1} \left[ -145.18 \pm 0.68 \text{ kJ mol}^{-1} \right]$$

differing significantly from previous values. Estimates have been made of thermodynamic functions for carbonyl iodide.

The standard enthalpies of formation of aluminium bromide and aluminium iodide have been determined as

$$\Delta H^\circ_{298} \text{AlBr}_3(c) = -118.4 \pm 0.6 \text{ kcal mol}^{-1} \left[ -495.2 \pm 2.4 \text{ kJ mol}^{-1} \right]$$

$$\Delta H^\circ_{298} \text{AlI}_3(c) = -67.1 \pm 0.6 \text{ kcal mol}^{-1} \left[ -230.9 \pm 2.4 \text{ kJ mol}^{-1} \right]$$

by isoperibol calorimetry of the reactions

$$\text{AlX}_3(c) + [3\text{NaCl} + n\text{NaOH}]'aq \rightarrow [\text{NaAl(OH)}_4] + 3\text{NaCl}$$

$$+ 3\text{NaX} + (n-4)\text{NaOH}'aq$$

$$\text{AlCl}_3(c) + [3\text{NaX} + n\text{NaOH}]'aq \rightarrow [\text{NaAl(OH)}_4] + 3\text{NaCl}$$

$$+ 3\text{NaX} + (n-4)\text{NaOH}'aq$$

where X = Br or I. In addition,

$$\Delta H^\circ_{298} \text{NaAl(OH)}_4 \cdot 15,000 \text{ H}_2\text{O} = -409.9 \pm 0.4 \text{ kcal mol}^{-1}$$

$$\left[ -1715.0 \pm 1.6 \text{ kJ mol}^{-1} \right]$$

Infra-red studies on the complex $\text{POCl}_3 \cdot \text{Cl}_3(c)$ have confirmed its structure as dative covalent, with bonding from oxygen to boron. On running the infra-red spectrum at room temperature, there is considerable dissociation of the complex, and also reaction with the potassium bromide windows. Determination of the degree of dissociation has shown that there is only negligible association in the vapour.
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Appendix Three*-

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PART ONE

THE INTERACTION BETWEEN BORON TRIFLUORIDE

AND BENZENE DERIVATIVES
INTRODUCTION

Previous work\(^1,2\) has suggested the presence of weak solute-solvent complexing in benzene solutions of boron tribromide and boron tri-iodide. In each case, the symmetric stretching mode, \(\nu_1\) (273 cm\(^{-1}\) Br\(_3\), 195 cm\(^{-1}\) I\(_3\)) of the boron trihalide appeared as a strong band in the infra-red spectrum. Since the selection rules predict Raman activity only for this mode, it was suggested that deformation of the boron trihalide was allowing the band to become active.

\(^{11}\)\(^B\) nuclear magnetic resonance of the boron tribromide/benzene system showed a residual high-field shift at infinite dilution of 0.43 p.p.m. (relative to pure boron tribromide) after correcting for the bulk diamagnetic susceptibility of the system, again suggesting weak interaction. It was proposed that the principal orientation of boron was above or below the plane of the aromatic ring, as indicated in the following diagram:

\[\text{Diagram showing orientation of boron in solution.}\]
The average distance between the aromatic ring and the boron atom was estimated to be 4.7 Å.

However, the same workers state that the phase diagrams for boron tribromide + benzene and boron tri-iodide + benzene showed no sign of complex formation.

The object of the present work was to seek further evidence for complex formation, using the following techniques:

(1) Cryoscopy, and determination of phase diagrams.
(2) Vapour Pressure Measurement.
(3) Proton Magnetic Resonance.
(4) Raman Spectroscopy.

Boron trichloride and boron tri-iodide were studied with the following aromatic compounds: benzene, m-xylene, mesitylene and hexamethylbenzene. The electron-donating methyl group should increase the Lewis basicity of the aromatic ring.

(1) **PHASE DIAGRAMS**

The apparatus was tested using the known chloroform/mesitylene system, and then the mixtures

- boron tribromide/mesitylene,
- boron tribromide/m-xylene,
- and boron tribromide/hexamethylbenzene

were studied.
Experimental

Apparatus:

The cryometer used (diagram 1) has been described in detail elsewhere. Temperature was measured using a miniature platinum resistance thermometer (Degussa Hanau) connected across one arm of a Wheatstone bridge, and calibrated using the freezing points of purified (see next paragraph) chlorobenzene (-45.2°C) and chloroform (-63.5°C) (diagram 2). Readings were accurate to ± 0.1°C. Stirring was achieved by means of a solenoid-activated, reciprocating, chromium-plated, iron cylinder.

Chemicals:

Chlorobenzene (May and Baker) was dried over 4 Å molecular sieves and distilled at atmospheric pressure (b.p. 131.5°C, literature 131.7°C).

Chloroform (May and Baker) was shaken with water to remove added alcohol, dried over 4 Å molecular sieves, and distilled (b.p. 61.2°C, literature 61.2°C).

Mesitylene (B.D.H. Ltd.) was dried over 4 Å molecular sieves and distilled (b.p. 164.7°C, literature 164.7°C).

M-xylene (B.D.H. Ltd.) and hexamethylbenzene (Koch-Light) were used as supplied commercially, with stated purities of at least 99% and 93% respectively.
CRYOSCOPIC APPARATUS

CELL

rubber cap

air jacket

PLATINUM RESISTANCE THERMOMETER

STIRRER

glass—coated iron
Boron tribromide (Koch-Light) was purified by shaking with mercury to remove any free bromine, and then distilled at atmospheric pressure, the portion boiling at \( 91 \pm 1^\circ\text{C} \) being retained, (literature b.p. \(^4\) 91.3\(^\circ\text{C}\).

**Procedure:**

One component was placed in the cryometer, and successive aliquots of the second component added through the side-arm. Moisture sensitive boron tribromide was always loaded in the cryometer in a dry-box, the side-arm covered with a self-sealing rubber cap, and the hydrocarbon aliquots added through the cap using a repeater syringe (Jencons Ltd.), weighed before and after each addition. The quantity of boron halide used was determined by post-experiment hydrolysis with water, separation of the hydrocarbon, and titration for bromide with 0.1N silver nitrate solution, using eosin indicator.

The mixture was frozen using a toluene/liquid nitrogen slush bath (ca. 94\(^\circ\text{C}\)). The freezing point was taken when the temperature remained almost constant for approximately one minute, or longer, due to the latent heat of fusion evolved. Where supercooling occurred, the temperature fell well below the freezing point, and then rose sharply as crystallisation commenced, falling again when equilibrium had been reached. The freezing point was taken as the maximum temperature reached after crystallisation\(^6\).
Results and Discussion

Chloroform + Mesitylene

The results of a single experiment are given in Table 1.

<table>
<thead>
<tr>
<th>P.R.T. Resistance (Ohms ± 0.1 Ohm)</th>
<th>Freezing Point (°C ± 0.1°C)</th>
<th>Mole Fraction % Chloroform</th>
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<tbody>
<tr>
<td>75.8</td>
<td>-63.5</td>
<td>100.0</td>
</tr>
<tr>
<td>73.1</td>
<td>-70.9</td>
<td>89.5</td>
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<tr>
<td>72.8</td>
<td>-71.5</td>
<td>87.3</td>
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<tr>
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<td>-73.5</td>
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<td>79.2</td>
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The freezing points for pure chloroform and pure mesitylene agree very well with literature values of
FREEZING POINT — COMPOSITION CURVE
FOR CHLOROFORM/MESITYLENE

DIAGRAM 3

FREEZING POINT °C

MOLE FRACTION ° CHLOROFORM

20 40 60 80 100
-63.5°C and -52.7°C respectively.

The phase diagram (diagram 3) shows a well-defined peak at 50 mole % chloroform, indicating a 1:1 complex with a congruent melting point. In effect, this corresponds to two eutectic phase diagrams linked together, namely, for chloroform + complex and complex + mesitylene. The diagram agrees well with previous results.

**Boron Tribromide + Mesitylene**

On mixing boron tribromide and mesitylene, both of which were colourless, a very pale lemon-yellow colour appeared, which deepened considerably on freezing the mixture.

In all, six experiments were carried out, the results of which are given in Table 2.

The results show very poor reproducibility below approximately 50 mole % boron tribromide (diagram 4). The reason for this is not entirely clear. One possible explanation is that supercooling, which was particularly marked in this area, resulted in the true freezing point not always being reached, upon commencement of crystallisation. Crystals of mesitylene, being in excess, would tend to separate, so that by the time equilibrium was reached the liquid present would be richer in boron tribromide, and the freezing point correspondingly lower. Hence the correct freezing point would never be attained.
### Table 2

**Freezing Points of Boron Tribromide/Butyldiene Mixtures**

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>P.R.T. Resistance (Ohm ± 0.1 Ohm)</th>
<th>Freezing Point (°C ± 0.1°C)</th>
<th>Mole Fraction % Boron Tribromide</th>
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<td>-81.6</td>
<td>36.8</td>
</tr>
<tr>
<td>4</td>
<td>68.4</td>
<td>-82.2</td>
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<td>32.9</td>
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<td>68.9</td>
<td>-81.6</td>
<td>32.7</td>
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<tr>
<td>3</td>
<td>70.5</td>
<td>-77.7</td>
<td>29.8</td>
</tr>
</tbody>
</table>
FREEZING POINT—COMPOSITION CURVE
FOR BORON TRIBROMIDE/MESITYLENE

DIAGRAM 4

FREEZING POINT °C

MOLE FRACTION % BORON TRIBROMIDE
TABLE 2 (CONTINUED)

<table>
<thead>
<tr>
<th>EXPERIMENT NUMBER</th>
<th>P.R.T. RESISTANCE (OHM ± 0.1 OHM)</th>
<th>FREEZING POINT (°C ± 0.1°C)</th>
<th>MOLE FRACTION % BORON TRIBROMIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>69.3</td>
<td>-80.5</td>
<td>29.4</td>
</tr>
<tr>
<td>5</td>
<td>71.6</td>
<td>-75.0</td>
<td>28.2</td>
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<td>4</td>
<td>69.9</td>
<td>-79.1</td>
<td>23.0</td>
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<td>2</td>
<td>70.7</td>
<td>-77.1</td>
<td>26.7</td>
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<td>72.5</td>
<td>-72.5</td>
<td>24.7</td>
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<tr>
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<td>72.4</td>
<td>-72.6</td>
<td>24.5</td>
</tr>
<tr>
<td>3</td>
<td>72.0</td>
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<td>71.4</td>
<td>-75.3</td>
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<td>73.5</td>
<td>-69.8</td>
<td>21.9</td>
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<td>74.0</td>
<td>-63.4</td>
<td>19.7</td>
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<td>72.2</td>
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<td>-71.3</td>
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<td>75.5</td>
<td>-64.5</td>
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<td>75.6</td>
<td>-64.2</td>
<td>12.3</td>
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<td>3</td>
<td>76.5</td>
<td>-62.0</td>
<td>12.0</td>
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<td>3</td>
<td>76.6</td>
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<td>3</td>
<td>76.6</td>
<td>-62.0</td>
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<td>4</td>
<td>76.0</td>
<td>-63.0</td>
<td>8.9</td>
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<td>3</td>
<td>77.3</td>
<td>-59.6</td>
<td>8.9</td>
</tr>
<tr>
<td>3</td>
<td>77.3</td>
<td>-59.6</td>
<td>7.5</td>
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<tr>
<td>4</td>
<td>76.8</td>
<td>-61.1</td>
<td>6.8</td>
</tr>
<tr>
<td>-</td>
<td>79.2</td>
<td>-54.6</td>
<td>0.0</td>
</tr>
</tbody>
</table>
The true freezing point is thus taken as the highest value obtained for any given composition, when a reasonably smooth curve is obtained.

A plateau is clearly discernible between approximately 33-43 mole % boron tribromide, but there is no evidence for a peak due to complex formation. The plateau is probably due to a miscibility gap\(^7,8\), containing, at equilibrium, two solids in equilibrium with the remaining liquid. [On complete solidification, a heterogeneous mixture of the two solids would presumably be obtained]. By applying the Phase Rule to this equilibrium\(^7,8\), we obtain, for three phases and only two components, one degree of freedom. This is taken up by the pressure of the system, assumed constant. This means that whatever the composition of the mixture within this range, the temperature of freezing must remain constant. A similar incongruency was found in the boron tri-iodide/benzene phase diagram\(^2\).

**Boron Tribromide + m-Xylene**

Again, a yellow colour was observed, but only in the solid phase.

The results of a single run are given in Table 3.

The literature\(^4\) freezing point for m-xylene is \(-47.4^\circ C\). The freezing point-composition curve (diagram 5) shows a simple eutectic at \(-79^\circ C\), where the composition is 47\% boron tribromide, 53\% m-xylene. There is no miscibility gap as for
FREEZING POINT—COMPOSITION CURVE FOR BORON TRIBROMIDE/m-XYLENE

FREEZEING POINT
°C

MOLE FRACTION \( \alpha^9 \) BORON TRIBROMIDE
<table>
<thead>
<tr>
<th>P.R.T. RESISTANCE (ohm's $\pm 0.1$ ohm)</th>
<th>FREEZING POINT ($^{\circ}$C $\pm 0.1 ^{\circ}$C)</th>
<th>MOLE FRACTION % BORON TRIBROMIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>82.7</td>
<td>-46.0</td>
<td>100.0</td>
</tr>
<tr>
<td>74.6</td>
<td>-67.0</td>
<td>66.0</td>
</tr>
<tr>
<td>73.0</td>
<td>-71.1</td>
<td>60.8</td>
</tr>
<tr>
<td>72.8</td>
<td>-71.8</td>
<td>56.4</td>
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<tr>
<td>72.1</td>
<td>-73.5</td>
<td>52.6</td>
</tr>
<tr>
<td>71.0</td>
<td>-76.4</td>
<td>49.3</td>
</tr>
<tr>
<td>70.3</td>
<td>-73.2</td>
<td>46.3</td>
</tr>
<tr>
<td>72.7</td>
<td>-71.8</td>
<td>41.4</td>
</tr>
<tr>
<td>74.8</td>
<td>-66.2</td>
<td>35.7</td>
</tr>
<tr>
<td>82.0</td>
<td>-47.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 3
FREEZING POINTS OF BORON TRIBROMIDE/m-XYLENE MIXTURES

boron tribromide/mesitylene, and no evidence for complex formation.

**Boron Tribromide + Hexamethylbenzene**

A similar phase diagram could not be obtained, due to the very low solubility of solid hexamethylbenzene in boron tribromide i.e. the presence of a wide miscibility gap. All solutions prepared at room temperature and cooled, gradually precipitated hexamethylbenzene to give saturated solutions of approximate composition 1 mole % hexamethylbenzene, 99 mole %
tribromide, and freezing at $-47.6^\circ C$.

On mixing hexamethylbenzene (a white solid) with boron tribromide (a colourless liquid), an orange colour appeared in the solutions obtained.
(2) **VAPOUR PRESSURE MEASUREMENTS**

The systems studied were:

- Boron tribromide + benzene
- Boron tri-iodide + benzene
- Boron tribromide + mesitylene.

**Experimental**

**Apparatus**:

All the compounds were handled on a vacuum line capable of achieving pressures of $10^{-4}$ torr or better (diagram 6). Mixing of the compounds, and all vapour pressure measurements, took place in a section of the line completely free from grease, thereby avoiding any absorption of the grease or reaction with boron tribromide. Under these conditions, best vacuum seals were obtained by using taps of the "Uni-form" type (Glass Precision Engineering Co. Ltd.), and "O-ring" joints (J. Young (Scientific Glassware) Ltd.). Thus the compounds were exposed only to Teflon, glass and mercury vapour (from the manometer). Vapour pressures were determined using a mercury manometer, consisting of two parallel glass tubes, approximate diameter 2 cm, connected by a capillary tube. The mercury was carefully degassed before use by pumping for several hours while warming gently. The difference in height of the two mercury columns was measured using a cathetometer. Pressures were usually reproducible to $\pm 1$ torr.
DIAGRAM 6  VACUUM SYSTEM FOR VAPOUR PRESSURE MEASUREMENTS

To Pump

Benzene

Mercury Manometer

Mixing Vessel

Boron Tribromide

Greaseless Tap
Chemicals:

Distilled boron tribromide, b.p. 91°C (literature 91.5°C) was redistilled into its container on the vacuum line, where it was stored over mercury to remove any free bromine formed. It was degassed by repeated freezing and pumping. Before each run, the sample used was distilled and trapped at ca. -80°C (solid carbon dioxide - acetone slush bath), at which temperature any hydrogen bromide impurity would be pumped off (vapour pressure ~ 500 torr). It was then condensed into the mixing vessel, and its purity checked by measurement of its vapour pressure at known temperatures:

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Experimental V.p. (torr)</th>
<th>Lit. Value (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>12.8</td>
<td>37</td>
<td>35</td>
</tr>
<tr>
<td>20</td>
<td>52</td>
<td>54</td>
</tr>
</tbody>
</table>

A supply of pure boron tri-iodide was already available in the laboratory, with established purity 93-99%.

Commercial samples of benzene and mesitylene (B.D.H. Ltd.) were distilled (b.p. 80.0°C and 164.7°C respectively, literature values 80.1°C and 164.7°C), and dried and stored over grade 4Å molecular sieves (B.D.H. Ltd.). Each was degassed by repeated freezing and pumping. The purity was also checked by measurement of vapour pressure.
<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Experimental V.P. (torr)</th>
<th>Lit. Value (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>25</td>
<td>26.3</td>
</tr>
<tr>
<td>12.8</td>
<td>52</td>
<td>52.5</td>
</tr>
<tr>
<td>20.5</td>
<td>79</td>
<td>76.7</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>2</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Procedure:

A quantity of boron trihalide was either condensed into the mixing vessel, (3Br3) or loaded in a dry-box and then connected to the vacuum line and degassed (Bi3). Aliquots of benzene or mesitylene were then distilled in, the amount added being determined by weighing the container before and after each addition. The mixture was now isolated from the pump, and allowed to come to equilibrium at the temperature selected for the pressure measurements. Readings were usually taken below room temperature to avoid thermostating the manometer. To achieve this, either an ice bath (0 ± 1°C) or a p-xylene/liquid nitrogen slush bath (13 ± 1°C) was used. In the case of boron tribromide + mesitylene, consistent readings were only obtained when the mixture was well stirred. The reason for this is not known. To achieve mixing, a magnetic stirrer and glass-coated follower were used, which meant however that the mixture could not be thermostated, and all readings had to be taken at room temperature.
The quantity of boron halide used was determined by post-experiment hydrolysis and titrimetric analysis. At the end of each run, the mixture was frozen in liquid nitrogen, and the mixing vessel cut off using a hot spot. The mixture was then analysed argentimetrically, as described previously (page 16), for halide.

Results and Discussion

Boron Tribromide + Benzene

A colourless solution resulted from mixing boron tribromide and benzene, which remained colourless on freezing, in contrast to the other systems studied.

Four experiments were performed, and the results shown in Table 4.

The results from experiment 1 were in very poor agreement with the rest, and were discarded in constructing the pressure - composition curves (diagram 7). These show a positive deviation from Raoul's Law:

\[ P = N_A p_A + N_B p_B \]

- \( N_A \) = Mole fraction component A
- \( p_A \) = Partial pressure component A
- \( P \) = Observed pressure.
DIAGRAM 7
VAPOUR PRESSURE OF
BORON TRIBROMIDE / BENZENE

VAPOUR PRESSURE (TORR)

MOLE FRACTION % BORON TRIBROMIDE

Raoult's Law

13°C

0°C
<table>
<thead>
<tr>
<th>EXPERIMENT NUMBER</th>
<th>VAPOUR PRESSURE (Torr ± 1 Torr)</th>
<th>MOLE FRACTION % BORON TRIBROMIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$0^\circ C ± 1^\circ C$</td>
<td>$13^\circ C ± 1^\circ C$</td>
</tr>
<tr>
<td>1</td>
<td>19</td>
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</tr>
<tr>
<td>2</td>
<td>19</td>
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<td>3</td>
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<td>3</td>
<td>27</td>
<td>49</td>
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<td>1</td>
<td>41</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>29</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>29</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
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<td>32</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>23</td>
<td>52</td>
</tr>
</tbody>
</table>

TABLE 4
VAPOUR PRESSURES OF BORON TRIBROMIDE/BENZENE MIXTURES
This implies that the major contribution to interaction between boron tribromide and benzene in the liquid phase comes from Van der Waal's forces. An alternative representation is that the attraction between two molecules of the same component is greater than between two different molecules. If any significant complex formation occurred, a negative deviation would be expected.

Boron Tri-iodide + Benzene

Great difficulty was experienced in dissolving boron tri-iodide, even with vigorous stirring. Consequently, measurements were only possible at 13°C, and then only at concentrations below 30 mole % boron tri-iodide.

The solutions were colourless, and remained so on freezing.

The results of the single experiment are given in Table 5.

<table>
<thead>
<tr>
<th>VAPOUR PRESSURE OF BORON TRI-IODIDE + BENZENE</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAPOUR PRESSURE (TORR ± 1 TORR)</td>
</tr>
<tr>
<td>13°C ± 1°C</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>43</td>
</tr>
<tr>
<td>48</td>
</tr>
<tr>
<td>49</td>
</tr>
<tr>
<td>52</td>
</tr>
</tbody>
</table>
DIAGRAM 8

VAPOUR PRESSURE OF BORON TRIIODIDE / BENZENE

VAPOUR PRESSURE (TORR)

MOLE FRACTION % BORON TRIIODIDE
Despite the small number of points, and the fact that only one-third of the total composition range is covered, the pressure-composition curve (diagram 3) shows a clear positive deviation from Raoult's Law. Again, there is no support for complex formation.

**Boron Tribromide + Nenylene**

As in the cryoscopic experiments, a yellow colour, particularly pronounced in the solid phase, appeared on mixing the two components.

Because of the necessity for stirring to obtain consistent pressure measurements, readings were only taken at room temperature, 19°C. The results are shown in Table 6.

**TABLE 6**

<table>
<thead>
<tr>
<th>VAPOUR PRESSURE (Torr ± 1 Torr)</th>
<th>MOLE FRACTION % BORON TRIBROMIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>52 ± 1 Torr</td>
<td>100.0</td>
</tr>
<tr>
<td>37 ± 1 Torr</td>
<td>64.3</td>
</tr>
<tr>
<td>36 ± 1 Torr</td>
<td>61.7</td>
</tr>
<tr>
<td>33 ± 1 Torr</td>
<td>49.7</td>
</tr>
<tr>
<td>26 ± 1 Torr</td>
<td>35.0</td>
</tr>
<tr>
<td>25 ± 1 Torr</td>
<td>32.5</td>
</tr>
<tr>
<td>2 ± 1 Torr</td>
<td>0.0</td>
</tr>
</tbody>
</table>

As with the previous experiments, there is a positive deviation from Raoult's Law, and no evidence of complexing (diagram 9).
Diagram 9: Vapour Pressure of Boron Tribromide / Mesitylene

VAPOUR PRESSURE (TORR)

MOLE FRACTION % BORON TRIBROMIDE
(3) PROTON MAGNETIC RESONANCE

'H shifts were determined for mesitylene, and a 1:1 mixture of mesitylene and boron tribromide, using tetramethylsilane (T.M.S.) as internal standard. For comparison, the 1:1 mesitylene/chloroform spectrum was also run.

Experimental

Chemicals:

Mesitylene, chloroform and boron tribromide were purified as described previously (p. 29). Tetramethylsilane was used as obtained commercially (3.D.M. Ltd.).

Procedure:

All the spectra were run on a Varian HA 60-1L machine (60 MHz), locked on to the T.M.S. peak, with facilities for low temperature spectra using a liquid nitrogen/nitrogen gas flow for cooling.

The N.M.R. tubes were filled with sample in a dry-box (including small quantities of T.M.S. as an internal standard), and then sealed.

Spectra were obtained for all three samples at room temperature, and also at -40°C for mesitylene and mesitylene/boron tribromide.
Results and Discussion

### Table 7

Proton Magnetic Resonance Results

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>INTENSITY RATIO</th>
<th>PROTON</th>
<th>CHEMICAL SHIFT</th>
<th>SPLITTING PATTERN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Room temperature</td>
<td>-40°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hz</td>
<td>p.p.m.</td>
</tr>
<tr>
<td>C₆H₅(CH₃)₃</td>
<td>3</td>
<td>CH₃</td>
<td>128.7</td>
<td>2.145</td>
</tr>
<tr>
<td>+ Br₂</td>
<td>1</td>
<td>H</td>
<td>396.4</td>
<td>6.607</td>
</tr>
<tr>
<td>C₆H₅(CH₃)₃</td>
<td>3</td>
<td>CH₃</td>
<td>129.2</td>
<td>2.153</td>
</tr>
<tr>
<td>+ Br₂</td>
<td>1</td>
<td>H</td>
<td>396.8</td>
<td>6.613</td>
</tr>
<tr>
<td>C₆H₅(CH₃)₃</td>
<td>3</td>
<td>CH₃</td>
<td>130.0</td>
<td>2.167</td>
</tr>
<tr>
<td>+ CHCl₃</td>
<td>1</td>
<td>H</td>
<td>400.6</td>
<td>6.577</td>
</tr>
</tbody>
</table>

All shifts are relative to TMS, and accurate to ± 0.3 Hz (0.006 p.p.m.).

The separation between peaks due to splitting was ~ 0.6 Hz for each system.
The predicted spectrum for mesitylene is two peaks with very complex splitting, since all the couplings are long range, small, and of the same order. However, the chemical shifts and observed splitting in the present case are in good agreement with published spectra for pure mesitylene.\(^{11,12,13}\)

Before the shifts in the mixtures can be compared with those of pure mesitylene, allowance must be made for the variation in bulk magnetic susceptibility. This can be represented\(^{14}\) as "preferred orientations" of the molecules in the mixtures arising not from any chemical interaction but from the inherent magnetic anisotropy of the molecules not averaging out to zero when all possible molecule-molecule orientations are considered. The correction is made using the equation\(^{5,15,16}\)

\[
\delta_{\text{corrected}} = \delta_{\text{observed}} + \frac{2}{3} \pi (\chi_{\text{mixture}} - \chi_{\text{mesitylene}})
\]

where \(\delta = \text{shift in p.p.m.}\)

\(\chi = \text{volume susceptibility}\)

and\(^{5}\)

\[
\chi_{\text{mixture}} = N_A \chi_A + N_3 \chi_3
\]

The values used were

\[
\begin{align*}
\chi_{\text{mesitylene}} &= -0.652 \text{ c.g.s. units}^5 \\
\chi_{\text{BBr}_3} &= -0.900 \quad 1 \\
\chi_{\text{CHCl}_3} &= -0.731 \quad 5
\end{align*}
\]
The effect of the TMS in this respect can be neglected, since it is only slightly affected by changes in bulk magnetic susceptibility, and it is present in only very low concentrations.

After making the corrections, the shifts obtained (relative to pure mesitylene as zero) are:

TABLE 8
CORRECTED P.M.R. SHIFTS (MESITYLENE = 0)

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>PROTON</th>
<th>CHEMICAL SHIFT (P.P.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ROOM TEMPERATURE</td>
</tr>
<tr>
<td>MESITYLENE</td>
<td>CH₃</td>
<td>-0.24</td>
</tr>
<tr>
<td>+ Br₃</td>
<td>H</td>
<td>-0.25</td>
</tr>
<tr>
<td>MESITYLENE</td>
<td>CH₃</td>
<td>-0.06</td>
</tr>
<tr>
<td>+ CHCl₃</td>
<td>H</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Due to the corrections made, shifts are now accurate to only ± 0.01 p.p.m.

All shifts are now up-field, showing more shielding, as expected. Aromatic protons or substituents are normally strongly deshielded by the field produced by the ring current\textsuperscript{14,16}, which opposes the applied field within the aromatic ring, but reinforces it outside the ring. Hence an up-field shift
suggests a weaker ring current, which would occur if there was interaction between the $\pi$-electron system and the Lewis acid.

However, the shifts are always only very slight, indicating that any interaction must be extremely weak. Compare, for example, with the complexes of 1,3,5 trinitrobenzene with benzene and methylbenzenes$^{17}$, where shifts of $1.2 - 1.3$ p.p.m. are obtained for the ring protons. But negligible shifts are also obtained for solutions of iodine in benzene$^{18}$, where a weak charge-transfer interaction is also thought to occur$^{19}$.

Previous studies$^{1,5}$ on the shifts of the chloroform proton and $11^B$ of boron tribromide, both in mesitylene solution, gave values for 1:1 mixtures of $-1.1$ p.p.m. and $-0.60$ p.p.m. respectively, relative to pure chloroform and pure boron tribromide. The small values again suggest only weak interaction, though stronger than indicated by the present work. This is probably due to the change in shielding of the Lewis acid atom, cited directly above the $\pi$-electron cloud, being more pronounced than the indirect shielding of the ring substituents.

The identical shifts obtained at room temperature and $-40^\circ\text{C}$ for mesitylene/boron tribromide suggest little or no temperature dependence for any interaction. This is rather surprising, since the shift obtained would be a weighted average of the shifts for "complexed" and "free" molecules (assuming rapid exchange). [See, for example, reference 14, p.100]. One would expect an increasing proportion of molecules to be complexed as the temperature was lowered, with a corresponding increase in shift.
Raman Spectroscopy

The Raman spectrum of an approximately 1:1 mixture of boron tribromide and benzene was run in the region 0-300 cm\(^{-1}\), while the sample was kept frozen, in order to detect the possible presence of lattice bands attributable to relative motion of molecules in the solid (see, for example, reference 20). Because of the large masses of the molecules involved, such lattice modes would be expected at very low frequencies.

**Experimental**

Spectra were run using a Carey 81 instrument, with a 50 mW Helium-Neon laser, and 6328Å exciting line.

The sample was placed in a flat-ended capillary, subsequently sealed. This was surrounded by a wall of plasticine to act as an insulating jacket, frozen by immersion in liquid nitrogen, and placed in the laser beam. Periodic visual checks were made to ensure that the sample remained solid.

**Results and Discussion**

Only two bands were obtained, at 153 cm\(^{-1}\) and 230 cm\(^{-1}\), both strong in intensity. These are attributable to the \(\nu_4\) (in-plane bend) and \(\nu_1\) (symmetric stretch) modes of boron tribromide, which occur at 150 cm\(^{-1}\) and 273 cm\(^{-1}\) in liquid boron tribromide\(^{21,22}\). Benzene has no absorption in this region\(^{23}\).
The absence of any further bands indicates that lattice bands must be so weak as to be indistinguishable from background noise.
While the results obtained eliminate the existence of strongly-bonded complexes between boron trihalides and benzene derivatives, the possibility of weak contact charge-transfer bonding remains open.

The positive vapour pressure deviations from Raoult's Law, and the failure to find any discontinuities due to complexing in the phase diagrams suggest that the bonding energy must be extremely small, even by charge-transfer standards (for example, benzene/iodine is quoted as \(-1.32 \text{ kcal/mol} [-5.52 \text{ kJ/mole}]\) and benzene/trinitrobenzene as \(-1.71 \text{ kcal/mol} [-7.15 \text{ kJ/mole}]\)). A parallel can be drawn with the benzene/iodine system (see, for example, the reviews in references 19 and 27), where the bulk properties of the solutions show no deviations, but charge-transfer complexing is well established by other methods, such as infra-red and ultra-violet spectroscopy, spectrophotometry, X-ray crystallography, etc. Also, as already mentioned, there is no measurable shift in the benzene \(^1\)H resonance on dissolving iodine.

Further support for loose complexing comes from the yellow colours observed when freezing many mixtures of boron tribromide and methylbenzenes. Absorption in the visible spectrum is a well-known phenomenon associated with charge-transfer complexes, caused by transitions between energy levels.
associated with the charge-transfer bond. Indeed, the closely related systems aluminium bromide/benzene or methylbenzenes have been shown to form 1:1 and 2:1 solid complexes, all of which are various shades of yellow.$^{29,30}$

Two approaches which might provide more evidence of complexing are the use of dipole moments and of ultra-violet spectral measurements of solutions of boron trihalides in benzenes. Both require further investigation. Many charge-transfer complexes, even when formed by molecular species each with very small individual dipoles, have been shown to exhibit appreciable dipole moments$^{31}$ (e.g. iodine/benzene). A determination$^{32}$ of the dipole moment of boron tribromide in benzene yielded a value of 0.194 e.s.u. Since very low values are unreliable it was inferred that the boron tribromide was planar. However, in view of some of the other evidence, this needs re-investigating, along with other systems, in case the low value represents a real deviation from zero.
PART TWO

INTERACTION OF GROUP THREE HALIDES

WITH CARBONYL HALIDES
INTRODUCTION

Although reactions of boron and aluminium halides with organic carbonyls (and other organic ligands) have been extensively studied because of their importance in Friedel-Crafts type syntheses, with one exception very little work has been done on their reaction with carbonyl halides.

The exception is the system aluminium chloride/carbonyl chloride (phosgene). The first reference to this is in a paper by Band, who claimed the existence of several solid complexes varying from $\text{Al}_2\text{Cl}_6\cdot5\text{COC}_2\text{H}_4$ to $2\text{Al}_2\text{Cl}_6\cdot\text{COC}_2\text{C}_2$. In the light of later work, this paper seems very unreliable. Germann and co-workers carried out extensive studies on the solutions, which contributed considerably to the formulation of acid-base theories for solvent systems. Aluminium chloride/phosgene solutions were believed to contain ionic species, such as $\text{CCl}_3^+$ or $\text{CO}_2^+$ cations and $\text{AlCl}_4^-$ anions, and the solid complexes obtainable from these solutions were also thought to be ionic. Subsequently, Huston has shown that the exchange rate of radioactive chlorine for very dilute (less than 2 equivalent fraction per cent) aluminium chloride solutions in phosgene is very slow, exchange half-lives varying between 12 and 60 hours at $0^\circ\text{C}$. This slow exchange would be extremely improbable if ionic species were involved. Huston also showed the exchange to be homogeneous. In a later paper, however, he modified this view to allow for the appearance of ions at
higher concentrations, the exact concentration at which ions first appear in the solution being dependent on temperature. (Approximately 10 equivalent fraction per cent at -21°C, 2 at 0°C and 0.3 at 25°C).

More recently, Jones and Wood⁴¹ and Christe⁴² have shown that only the 1:1 complex exists at ambient temperatures, this being a white, easily dissociated solid, melting point 25°C.

Both sets of workers overcame extreme experimental difficulties caused by the reactivity of the complex to obtain its infra-red spectrum. Although there are some wide discrepancies between the two sets of band assignments, both papers agree on the dative covalent nature of the complex, with co-ordination through the oxygen to aluminium.

\[ \text{Cl} \quad \text{C=O} \quad \text{Al} \quad \text{Cl} \]

Christe confirmed the 1:1 aluminium chloride/phosgene complex by measurement of vapour pressure - composition curves at 0°C and 25°C, when both a negative deviation from Raoult's Law and a sharp break at a 1:1 mole ratio were found. However, with boron trichloride/carbonyl chloride, he found a positive
deviation from Raoult's Law, and no evidence for a complex. This is rather surprising, since boron trichloride is generally accepted to be a stronger Lewis acid than aluminium chloride\(^{43,44}\).

Literature data on systems involving bromide is very sparse. A. von Bartal\(^{45}\) claimed that aluminium bromide reacted with excess phosgene according to the equation

\[
\text{AlBr}_3 + 3\text{COCl}_2 = \text{AlCl}_3 + 3\text{COClBr}.
\]

With the aluminium bromide in excess, however, at 100°C aluminium dichlorobromide, AlBrCl\(_2\), was supposed to be formed as a brick-red solid, melting at 142-143°C. Identification of this substance was based on analysis. The red colour seems rather surprising in view of the fact that both aluminium chloride and aluminium bromide are white. In a much later paper\(^{46}\), Corbett and Gregory repeated the experiment, and found that the red colour was due to free bromine. Also, the crystals obtained resembled an annealed mixture of aluminium chloride and aluminium bromide rather than any mixed halide phase involving AlBrCl\(_2\); no analytical data were given. Aluminium dichlorobromide is known, however, from the reaction of hydrogen chloride on aluminium bromide\(^{46,47}\).

The objects of the present work were:

(1) In view of the failure of Christe\(^{42}\) to find a complex between boron trichloride and carbonyl chloride, to investigate the system boron tribromide/carbonyl bromide. Boron tribromide
is a better Lewis acid than boron trichloride due to the smaller degree of $\pi$-bonding involved in the molecule, leading to a smaller reorganisation energy for the transition $3sp^2 \rightarrow 3sp^3$ required on complexing$^{48,49,50}$. Carbonyl bromide, despite being thermodynamically much less stable than phosgene with respect to the dissociation

$$\text{COX}_2(1) = \text{CO}(g) + X_2(1) \text{ or } (g) \text{ [See Part 3]}$$
might be expected to behave as a better donor because of the lower electronegativity of bromine compared with chlorine$^{51}$. There is the added advantage that possible halogen exchange would be unimportant. Techniques employed were infra-red spectroscopy of gaseous mixtures and solid mixtures, and the $^{113}$S magnetic resonance of liquid mixtures.

(ii) To re-investigate the reaction between aluminium bromide and phosgene, and also the other combinations:

- Aluminium chloride/carbonyl bromide
- Aluminium bromide/carbonyl bromide
- Aluminium iodide/carbonyl chloride

with a view not only to establishing the products of exchange reactions, but also determining any complex formation, both at room temperature and below.
Techniques employed were:-
(a) Mixing the two components, both at room temperature and low temperatures, pumping off volatile products, then weighing and analysing the residues.
(b) Infra-red spectroscopy of the vapours from the mixtures.

In both (i) and (ii), infra-red and Raman spectra of both solutions and residues would have been invaluable. However, sufficiently inert materials suitable for fabricating infra-red cells were not available (compare reference 41, where the complex aluminium chloride/carbonyl chloride is stated to attack sodium chloride, potassium bromide, silver chloride and polythene). Infra-red spectra of the residues yielded only bands too broad and too weak to be assigned. Measurement of Raman spectra was attempted, but each time strong fluorescence obscured any bands. This was possibly due to bromine being present in very low concentrations, since it is well known that minute quantities of coloured impurities can cause strong fluorescence.
EXPERIMENTAL

Apparatus and Procedure

All the compounds were handled on a modification of the grease-free vacuum line described in Part One (p. 27) (diagram 10). Volatile compounds were stored in the grease-free containers, A and B, from which samples could be distilled into the respective U-tubes and then into the mixing tube, C. This mixing tube was fitted with a greaseless tap and attached to the line via a greaseless joint, so that it could be readily detached and weighed. Having obtained the required mixture, one of the storage containers could then be replaced by an infra-red cell or N.M.R. tube as required. The relatively involatile, solid, aluminium halides were loaded into the mixing tube in a dry-box, and the mixing tube then attached to the line and evacuated.

For infra-red gas phase spectra, a cell specially designed and constructed in the department was used (diagram 11). The cell, path-length 10 cm, was fitted with potassium bromide windows, held on and sealed by Viton 'O-rings' and metal screw caps. It was also fitted with a "Uniform" greaseless tap (Glass Precision Engineering Co. Ltd.), and with an 'O-ring' joint for attachment to the vacuum line. It was capable of holding a vacuum of ca. $10^{-4}$ torr. For filling with the vapour
Diagram 10

Vacuum System for Carbonyl Halides

Group Three Halides

To Pump

T Greaseless Tap
from a reaction mixture, the cell and mixing vessel were both evacuated, and then closed to the pump. The taps connecting the two were opened, and the system allowed to come to equilibrium. After shutting the taps and pumping away excess vapour, the cell could usually be removed from the line simply by sliding the joint apart, despite the vacuum inside. In a few instances, it was necessary to shrink the 'O-rings' of the joint, using a little liquid nitrogen, in order to pull it apart. To run the spectrum of a gaseous mixture of boron tribromide and carbonyl bromide, the cell was attached to the line in place of the mixing vessel. Each of the components, stored in vessels A and B, was distilled into its respective U-trap, where they were thermostated such that the two vapour pressures were nearly identical, and of a suitable value to obtain reasonable peak heights in the spectra. The boron tribromide was kept at room temperature (approximately 20°C) and the carbonyl bromide at approximately -5°C (ice/salt bath), where both have vapour pressures in the region 50 torr. The vapours were then allowed to mix, and the cell filled.

The spectrum of a solid boron tribromide/carbonyl bromide mixture was obtained by using the cold cell shown in diagram 12. A 1:1 mixture of the vapours, prepared as described above, was sprayed through the fine nozzle on to the caesium iodide plate.
Diagram 12  Low Temperature  Infra-Red Cell

Diagram:
- Line & Sample
- KBr Plate
- Copper Holder
- CsI Plate
- To Vacuum Line
Caesium iodide was used due to its superior resistance to thermally-induced strain compared with most common window materials. The plate was sited in a copper holder cooled by liquid nitrogen. After spraying on the mixture, the plate could be rotated by means of the greased joint at the top of the apparatus so as to align it with the potassium bromide windows. Care had to be taken that the greased joint did not seize due to the extreme cold. Best mobility was obtained using Apiezon N grease (May and Baker). Another problem encountered in humid weather was that of water and carbon dioxide condensing on the outside of the potassium bromide plates due to the cooling of the apparatus, and spurious bands were obtained in the spectra at approximately 3500 cm\(^{-1}\) and 1600 cm\(^{-1}\), (water) and 665 cm\(^{-1}\) (carbon dioxide). The one doubt about the principle of the method might be that, for weak complexes where there is interaction in the solid but not the gas phase, spraying a gaseous mixture on to a cold plate gives not a mixed crystal, but a mixture of the individual crystals. However, using a similar method for bromine/benzene, Person\(^{54}\) showed that only the mixed crystal was formed, and complexing was observed.

All infra-red spectra described above were run on a Perkin-Elmer 337 instrument, giving a resolution of approximately \(\pm 5\) cm\(^{-1}\).
Infra-red spectra of the residues from aluminium halide/carbonyl halide reactions were attempted as nujol mulls and dry powders, between potassium bromide plates. These spectra were run on a Perkin-Elmer 325 instrument. However, the bands obtained were always too broad and weak to be of use in identifying the residues.

Raman spectra of solutions and solids were attempted on both Cary 81 (helium/neon laser, 6328Å exciting line) and Spex Ramalog (ionised argon laser, 5147Å exciting line) instruments, but all samples fluoresced so strongly as to completely obscure any bands. The samples were made up by filling thick-walled capillary tubes (with flattened bases of thinner glass) in a dry-box situated in a fume cupboard, then freezing, and sealing off the tubes.

$^{11}B$ nuclear magnetic resonance for boron tribromide/carbonyl bromide and pure boron tribromide was carried out on a Perkin-Elmer R10 instrument (60 MHz). Two N.M.R. tubes, each containing a sealed capillary of boron trifluoride etherate, BF$_3$.OEt$_2$, as external reference, and fitted with a greaseless joint, were attached to the vacuum line and filled respectively with pure boron tribromide and an approximately 1:1 mixture of boron tribromide/carbonyl bromide. They were then sealed, and the spectra run. Shifts were measured accurately to ±3 p.p.m.
For studying the reactions of aluminium halides and carbonyl halides, the mixing vessel was evacuated, weighed, loaded with aluminium halide in a dry-box, then re-evacuated and re-weighed. Carbonyl halide was distilled in, and the mixing vessel re-weighed. The system was then thermostated if required. After pumping off carbonyl halide at low temperature, usually \(-45 \pm 10^\circ C\) (chlorobenzene slush bath), the mixing vessel was re-weighed to see if there was any addition in weight corresponding to complex formation. Comparison with the method of preparation\(^{39}\) and dissociation pressures\(^{42}\) quoted for aluminium chloride/carbonyl chloride showed the unlikelihood of decomposing any complex formed by pumping away excess carbonyl halide at \(-45^\circ C\). After pumping to dryness at room temperature the residue was weighed, hydrolysed, and analysed as follows:

Excess sodium hydroxide solution (concentration not critical) was placed in the mixing vessel above the tap, and the vessel stoppered. The tap was slowly opened to allow gradual hydrolysis of the residue. After shaking to dissolve the residue completely, the hydrolysate was made up to a standard volume in slightly acid solution (HClO\(_3\)). The addition of acid was to prevent the slow precipitation of various aluminium/hydroxide species which occurs in alkaline solution on standing, and which are very difficult to redissolve. The hydrolysis
itself had to be carried out in alkaline medium because aluminium bromide, unlike aluminium chloride, hydrolyses only extremely slowly at pH \( \leq 7 \). Total halide concentration was determined by Volhard's method, involving the precipitation of silver halide from nitric acid solution with excess 0.1N silver nitrate, filtering, and back-titrating the excess silver nitrate with 0.1N ammonium thiocyanate, using ferric indicator. Chloride was determined by first removing bromide by oxidation to bromine with potassium iodate in acid solution, followed by boiling. Excess iodate was removed by reduction with phosphorous acid, \( \text{H}_3\text{PO}_3 \), and boiling off the iodine so formed. The chloride solution remaining was then titrated by Volhard's method as above, the bromide present being obtained by difference. Aluminium was determined gravimetrically by precipitation as the 8-hydroxyquinolate ("oxinate"), \( \text{Al}(\text{C}_6\text{H}_8\text{O}_3) \), in ammonium acetate buffer (reference 56, p. 383 and 516). The precipitate was collected in a sintered glass crucible (porosity No. 4), washed, dried at 120°C, and weighed.

**Chemicals**

Carbonyl bromide was prepared according to the method of Schumacher and Lenher, by the reaction of carbon tetrabromide with concentrated sulphuric acid (specific gravity 1.83) at 150-170°C. The carbon tetrabromide was heated just to melting
in a dry, nitrogen-filled atmosphere, and the sulphuric acid added dropwise from a funnel. After all the sulphuric acid had been added, the mixture was heated to 150-170°C, when all the volatile products of the reaction distilled off, and were condensed using a cold finger filled with an ice/salt mixture. The distillate was collected in a flask cooled in a solid carbon dioxide/acetone slush bath. The dark-brown distillate contained, apart from carbonyl bromide, considerable quantities of free bromine, hydrogen bromide, and assorted sulphur compounds. The apparatus was open to the atmosphere via a drying bottle (concentrated sulphuric acid) to allow for the escape of carbon monoxide also formed in the reaction.

The bromine was removed by the very slow addition of mercury while shaking and cooling the liquid. [This process must be carried out very carefully, since the large heat of reaction between mercury and bromine can easily lead to decomposition of the carbonyl bromide]

\[ \text{COBr}_2(l) \rightarrow \text{CO}(g) + \text{Br}_2(l) + \text{(g)} \]

The mercuric bromide formed "tailed off" to give a coating on the wall of the flask, while the liquid turned from dark brown to pale yellow.

The carbonyl bromide was distilled off at atmospheric pressure, the portion boiling between 61-65°C being retained.
The last traces of bromine were removed by the careful addition of small quantities of antimony powder, while cooling, and a further distillation at reduced pressure yielded colourless carbonyl bromide (boiling point at atmospheric pressure 64.5 ± 0.5°C, literature value 64-65°C). The yield for the preparation varied between 20-40% of theoretical based on the equation

\[ \text{C}_3\text{Br}_4 + [\text{O}] \rightarrow \text{COBr}_2 + \text{Br}_2. \]

Carbonyl bromide is extremely poisonous, so all distillations were carried out in a well-ventilated fume cupboard, and the apparatus was open to the atmosphere only via a concentrated sulphuric acid washbottle (to exclude moisture) and a washbottle of concentrated alkali to decompose any carbonyl bromide vapour:

\[ 2\text{NaOH} + \text{COBr}_2 \rightarrow 2\text{NaBr} + \text{CO}_2 + \text{H}_2\text{O} \]

The carbonyl bromide was introduced into the vacuum line, degassed by repeated freezing and pumping, and stored in the dark at -196°C (liquid nitrogen). When a sample was required, it was fractionated through -45°C (chlorobenzene slush bath) to a trap at -94°C (toluene slush bath), at which temperature any hydrogen bromide impurity would be pumped away (vapour pressure approximately 500 torr).
The purity of the carbonyl bromide was tested by hydrolysing a sample with alkali, as described for aluminium halides above, and titrating by Volhard's method. A typical result, using a 0.339g sample made up to 200 ml solution was

\[
\text{Br (found)} \quad 84.6\% \text{ by mass} \\
\text{Br (calculated)} \quad 85.1\% \text{ by mass}
\]

To test for the presence of free bromine, potassium iodide was added to a slightly acid post-hydrolysis solution, followed by a drop of starch solution. The absence of any immediate blue colour due to starch-iodine complex showed the iodine concentration to be less than \(2 \times 10^{-5}\) M, corresponding to a bromine content in carbonyl bromide of less than one half of one per cent.

Commercial carbonyl chloride (Matheson Co. Ltd.), supplied in a cylinder under pressure, with stated purity 99.0\% minimum, was further purified by fractionation as for carbonyl bromide. The cylinder was connected to the vacuum line by a length of reinforced polythene tubing, the joint either end being made vacuum tight by application of "Torrseal" resin (Varian Ltd).

Boron tribromide was purified as described previously (p. 29).
Commercial aluminium chloride and aluminium bromide (3.D.H. Ltd.), with minimum stated purities 98% and 99% respectively, were vacuum sublimed several times each, the first few times from a mixture with finely-divided aluminium powder to remove water and free halogen. A minimum of heating had to be used for these sublimations, because on heating at low pressures, the reaction

$$2\text{Al}(s) + \text{AlX}_3(s) \rightarrow 3\text{AlX}(g)$$

tends to occur\(^{59}\). On condensing, the monohalide disproportionates to the trihalide and aluminium again, resulting in a transfer of aluminium metal to the final product.

After sublimation, both trihalides were white, crystalline solids, though the tribromide darkened slightly after several months even though stored in the dark. The purities were tested by alkaline hydrolysis followed by halide and aluminium determination as described above. The results were

- \(\text{AlCl}_3\)
  - Cl\(\text{(found)}\) 79.1% by mass
  - Cl\(\text{(calc.)}\) 79.7% by mass
  - Al\(\text{(found)}\) 20.3% by mass
  - Al\(\text{(calc.)}\) 20.3% by mass

- \(\text{AlBr}_3\)
  - Br\(\text{(found)}\) 83.8% by mass
  - Br\(\text{(calc.)}\) 83.9% by mass
  - Al\(\text{(found)}\) 10.2% by mass
  - Al\(\text{(calc.)}\) 10.1% by mass

Attempts to purify commercial aluminium iodide (Alfa Inorganics; no stated purity) by sublimation resulted only in
further decomposition to aluminium and iodine. Likewise, preparation from the elements according to the method of Watt and Hall\(^6\) resulted only in discoloured product. Probably this was due to the difficulty in the method, which involved subliming iodine through heated aluminium granules, of packing the aluminium extremely tightly. Only one-third of the quoted weight of aluminium per unit volume of apparatus could be achieved. Therefore, the commercial product, supplied as a pink powder compared with the white colour of pure aluminium iodide, was used directly, since analysis showed the purity to be better than 99\%, despite the discolouration.

\[
\text{AlI}_3 \\
I(\text{found}) 93.2\% \text{ by mass} \quad \text{Al(\text{found}) 7.0\% by mass} \\
I(\text{calc.}) 93.4\% \text{ by mass} \quad \text{Al(\text{calc.}) 6.6\% by mass}
\]
RESULTS

Boron Tribromide + Carbonyl Bromide

On mixing boron tribromide and carbonyl bromide, a colourless solution resulted, which turned very slowly brown on standing in the light for several hours, due to decomposition of carbonyl bromide. The rate of appearance of bromine colour was about the same as for pure carbonyl bromide under the same conditions.

The gas phase spectra of boron tribromide, carbonyl bromide, and an approximate 1:1 gaseous mixture of the two are shown in diagrams 13, 14 and 15 respectively, and the frequencies listed in table 9.

All frequencies are ± 5 cm⁻¹.

The spectra of boron tribromide and carbonyl bromide agree very well with published spectra⁶¹,⁶², except for the presence of a ν₃ fundamental (1362 cm⁻¹) of sulphur dioxide⁶³, present as an impurity from the preparation. The intensity of this band indicates that the sulphur dioxide was present in only small concentrations, and indeed after the first few samples the band disappeared (compare, for example, with the carbonyl bromide/boron tribromide spectrum, diagram 15).
### Table 9

**Gas Phase Infra-red Frequencies of Boron Tribromide/Carbonyl Bromide**

<table>
<thead>
<tr>
<th>Assignment (Ref. 61)</th>
<th>Carbonyl Bromide cm⁻¹</th>
<th>Carbonyl Bromide/Boron Tribromide cm⁻¹</th>
<th>Boron Tribromide cm⁻¹</th>
<th>Assignment (Ref. 62)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 ν₂</td>
<td>3633 m</td>
<td>3632 w</td>
<td></td>
<td>2 ν₃⁽¹⁰ο⁾</td>
</tr>
<tr>
<td>υ₂</td>
<td>1822 s</td>
<td>1822 s</td>
<td></td>
<td>2 ν₃⁽¹¹ο⁾</td>
</tr>
<tr>
<td>3 υ₅ + υ₄</td>
<td>1730 m</td>
<td>1715 w</td>
<td>1715 m</td>
<td>2 υ₁ + υ₅⁽¹¹ο⁾</td>
</tr>
<tr>
<td>2 υ₄</td>
<td>1510 m</td>
<td>-</td>
<td>1375 w</td>
<td>υ₁ + υ₃⁽¹⁰ο⁾</td>
</tr>
<tr>
<td>2 υ₅ + υ₄</td>
<td>1480 m</td>
<td>-</td>
<td>1373 m</td>
<td>υ₁ + υ₃⁽¹¹ο⁾</td>
</tr>
<tr>
<td>SO₂ impurity</td>
<td>1352 s</td>
<td>-</td>
<td></td>
<td>υ₂ + υ₄⁽¹⁰ο⁾</td>
</tr>
<tr>
<td>2 υ₁ + υ₅</td>
<td>1214 w</td>
<td>-</td>
<td>1132 m</td>
<td>υ₁ + υ₃⁽¹⁰ο⁾</td>
</tr>
<tr>
<td>υ₄ + υ₁</td>
<td>1160 m</td>
<td>1093 m</td>
<td>1093 s</td>
<td>υ₃ + υ₄⁽¹¹ο⁾</td>
</tr>
<tr>
<td>2 υ₆</td>
<td>1018 w</td>
<td>-</td>
<td>1000 w</td>
<td>υ₃ + υ₄⁽¹⁰ο⁾</td>
</tr>
<tr>
<td>υ₃ + υ₄</td>
<td>918 w</td>
<td>-</td>
<td>910 w</td>
<td>2 υ₁ + υ₂⁽¹¹ο⁾</td>
</tr>
<tr>
<td>υ₁ + υ₅</td>
<td>786 vs</td>
<td>784 vs</td>
<td>855 vs</td>
<td>υ₃⁽¹⁰ο⁾</td>
</tr>
<tr>
<td>υ₄</td>
<td>741 vs</td>
<td>742 vs</td>
<td>818 vs</td>
<td>υ₃⁽¹¹ο⁾</td>
</tr>
<tr>
<td>υ₄ - υ₃</td>
<td>560 w</td>
<td>575 w</td>
<td>574 m</td>
<td>υ₃ - υ₁⁽¹⁰ο⁾</td>
</tr>
<tr>
<td>υ₆</td>
<td>512 m</td>
<td>512 w</td>
<td>540 m</td>
<td>υ₃ - υ₁⁽¹¹ο⁾</td>
</tr>
<tr>
<td>υ₁</td>
<td>427 m</td>
<td>423 m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The spectrum of the 1:1 mixture is clearly a superimposition of the two component spectra, whereas if there was any association in the gas phase, shifts or changes in relative intensity would be expected in some of the bands, accompanied possibly by new bands attributable to a B—O bond. Compare, for example, with aluminium chloride/carbonyl chloride, where a band assigned to a shifted C=O stretch appeared in the region 1600-1700 cm⁻¹ ⁴¹,⁴².

Similar conclusions are reached from consideration of the spectra of the solids (diagrams 16, 17, 18; table 10). Although many of the bands show temperature shifts relative to the gas phase spectra, there are no shifts in the 1:1 mixture relative to the pure components. This strongly suggests that no complex exists even at low temperatures (less than -100°C).

The ¹¹B nuclear magnetic resonance spectra again lend no support to the possibility of association. Samples of pure boron tribromide and 1:1 boron tribromide/carbonyl bromide both gave low-field shifts of 39 ± 3 p.p.m. relative to boron trifluoride etherate. No corrections for changes in bulk magnetic susceptibility have been attempted, since these would be insignificant relative to the limits of accuracy of the measurements.
### Table 10
SOLID INFRARED FREQUENCIES FOR CARBONYL BROMIDE/BORON TRI-BROMIDE

<table>
<thead>
<tr>
<th>ASSIGNMENT</th>
<th>CARBONYL BROMIDE cm⁻¹</th>
<th>CARBONYL BROMIDE/BORON TRI-BROMIDE</th>
<th>BORON TRI-BROMIDE cm⁻¹</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 ν₂</td>
<td>3570 w</td>
<td>1790 s</td>
<td>1685 m</td>
<td>1683 m</td>
</tr>
<tr>
<td>ν₂</td>
<td></td>
<td>1792 s</td>
<td>1600 m</td>
<td>1602 m</td>
</tr>
<tr>
<td>2 ν₄</td>
<td>1500 vw</td>
<td></td>
<td>1403 m</td>
<td>1403 m</td>
</tr>
<tr>
<td>2 ν₅ + ν₄</td>
<td>1430 m</td>
<td>1420 sh</td>
<td>1360 m</td>
<td>1365 m</td>
</tr>
<tr>
<td>SO₂ impurity</td>
<td>1330 vw</td>
<td></td>
<td>1255 m</td>
<td>1252 m</td>
</tr>
<tr>
<td>2 ν₁ + ν₅</td>
<td>1210 w</td>
<td></td>
<td>1112 m</td>
<td>1108 m</td>
</tr>
<tr>
<td>ν₄ + ν₁</td>
<td>1140 m</td>
<td></td>
<td>1070 s</td>
<td>1067 s</td>
</tr>
<tr>
<td>2 ν₆</td>
<td>1018 w</td>
<td></td>
<td>983 w</td>
<td>984 w</td>
</tr>
<tr>
<td>ν₃ + ν₄</td>
<td>890 w</td>
<td></td>
<td>936 w</td>
<td>933 w</td>
</tr>
<tr>
<td>ν₁ + ν₅</td>
<td>(300–700 vs)</td>
<td></td>
<td>900 m</td>
<td>900 m</td>
</tr>
<tr>
<td>ν₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ ν₆</td>
<td>660 m</td>
<td>665 m</td>
<td>485 w</td>
<td>485 w</td>
</tr>
<tr>
<td>ν₁</td>
<td>420 w</td>
<td>425 sh</td>
<td>465 w</td>
<td>465 w</td>
</tr>
</tbody>
</table>
DIAGRAM 16

INFRA-RED SPECTRUM OF BORON TRIBROMIDE (SOLID)

TRANSMITTANCE %

WAVENUMBER CM⁻¹

2000

3000
INFRA-RED SPECTRUM OF
CARBONYL BROMIDE (SOLID)

DIAGRAM 17

TRANSMITTANCE %

WAVENUMBER CM⁻¹

1000 2000 3000
Diag. 18

Solid phase infrared spectrum of boron tribromide/carbonyl bromide.
Aluminium Bromide + Carbonyl Bromide

On condensing a large excess (mole ratio ca. 5:1) of carbonyl bromide on to aluminium bromide, a white solid mixture resulted whilst maintained at -196°C, indicating the absence of bromine. On allowing the mixture to warm, the carbonyl bromide melted, and the aluminium bromide floated to the surface of the liquid. The aluminium bromide slowly dissolved, but as it did so effervescence and the formation of a brown colour were both clearly visible at the solid/liquid interface. By the time room temperature had been reached, all the solid had dissolved, and the colour had spread to give a uniformly dark-brown solution. On pumping this solution at -45°C, where pure carbonyl bromide has a vapour pressure of ca. 10 torr\(^5\), a dark brown solid resulted, which obviously still contained considerable quantities of free bromine. Therefore, the temperature was gradually raised, while still pumping, till a white solid remained. This proved to be aluminium bromide, recovered almost quantitatively, two experiments giving respectively 98.5% and 97.0% of the starting weight. This is in sharp contrast to the preparation of aluminium chloride/carbonyl chloride complex\(^4\), where on pumping off excess carbonyl chloride at approximately 10 torr, the 1:1 complex remained.

Although the aluminium bromide/carbonyl bromide mixture
DIAGRAM 19  INFRA-RED SPECTRUM OF VAPOUR FROM

ALUMINIUM BROMIDE / CARBONYL BROMIDE

TRANSMITTANCE

%  

WAVENUMBER CM⁻¹
turned dark-brown within minutes while warming to room temperature, a reference sample of pure carbonyl bromide, kept at room temperature under otherwise similar conditions, remained colourless. Evidently the aluminium bromide catalysed the decomposition of carbonyl bromide, a conclusion supported by the presence of a new, strong, band in the infra-red spectrum of the vapour from the mixture (diagram 19). Centred at 2150 ± 10 cm⁻¹, with well-defined P and R branches and rotational fine structure, this band is attributable to carbon monoxide.⁶³

Even when maintained at -45°C, a freshly prepared mixture still turned brown, though much more slowly than at room temperature.

**Aluminium Chloride + Carbonyl Bromide**

Several experiments were performed, with aluminium chloride: carbonyl bromide ratios ranging from 2:1 to 1:30. On allowing some mixtures to slowly warm up from -196°C, the reaction appeared visually identical to the aluminium bromide/carbonyl bromide system, with solid floating on the carbonyl bromide, and gradually dissolving, accompanied by effervescence and formation of bromine, to give a dark-brown solution. The appearance of bromine colour was extremely rapid, reaching its maximum intensity in well below five minutes when hand-heat was applied to bring the system to room temperature quickly.
Even when maintained at \(-45^\circ C\), bromine was still formed, but only very slowly. On pumping to dryness, also at \(-45^\circ C\), the residue showed a weight increase far less than that predicted for a 1:1 complex. Since the residue was brown, the weight increase was probably due, at least in part, to bromine, which at \(-45^\circ C\) is a solid with vapour pressure only \(\approx 1\) torr\(^4\). This was confirmed by the appearance of brown vapour on warming the residue to room temperature. The result was:

Starting wt. AlCl\(_3\) = 0.0605 g
Final wt. residue = 0.0654 g

Hence, even at these low temperatures and pressures, there is no evidence for an isolable complex.

Two solutions, both containing a large excess of carbonyl bromide, were allowed to stand at room temperature for several hours, then pumped to dryness (when a white solid remained) and analysed. Results were:

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>(0.33 \times 10^{-3}) (\text{g. atom} )</td>
<td>(0.73 \times 10^{-3}) (\text{g. atom} )</td>
</tr>
<tr>
<td>Cl</td>
<td>(0.40 \times 10^{-3}) (\text{g. atom} )</td>
<td>(0.71 \times 10^{-3}) (\text{g. atom} )</td>
</tr>
<tr>
<td>Br</td>
<td>(0.46 \times 10^{-3}) (\text{g. atom} )</td>
<td>(1.62 \times 10^{-3}) (\text{g. atom} )</td>
</tr>
<tr>
<td>Wt. residue (calc)</td>
<td>0.0662 g.</td>
<td>0.1757 g.</td>
</tr>
<tr>
<td>Wt. residue (found)</td>
<td>0.0599 g.</td>
<td>0.1758 g.</td>
</tr>
<tr>
<td>Starting wt. AlCl(_3)</td>
<td>0.0465 g.</td>
<td>0.1244 g.</td>
</tr>
<tr>
<td>FREQUENCY cm⁻¹</td>
<td>ASSIGNMENT</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>3630 s</td>
<td>2 ν₂ CO₂</td>
<td></td>
</tr>
<tr>
<td>2150 s</td>
<td>2 CO</td>
<td></td>
</tr>
<tr>
<td>1922 w</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>1822 vs</td>
<td>ν₂ CO₂</td>
<td></td>
</tr>
<tr>
<td>1780 m</td>
<td>3 ν₅+ ν₄ CO₃Br₂</td>
<td></td>
</tr>
<tr>
<td>1660 w</td>
<td>2 ν₄ COCl₂</td>
<td></td>
</tr>
<tr>
<td>1590 m</td>
<td>2 ν₄ COCl₃Br</td>
<td></td>
</tr>
<tr>
<td>1505 m</td>
<td>2 ν₄ CO₃Br₂</td>
<td></td>
</tr>
<tr>
<td>1480 m</td>
<td>2 ν₅+ ν₄ CO₃Br₂</td>
<td></td>
</tr>
<tr>
<td>1405 vw</td>
<td>ν₁+ ν₄ COCl₂</td>
<td></td>
</tr>
<tr>
<td>1318 m</td>
<td>ν₁+ ν₄ COCl₃Br</td>
<td></td>
</tr>
<tr>
<td>1218 m</td>
<td>2 ν₁+ ν₅ CO₃Br₂</td>
<td></td>
</tr>
<tr>
<td>1165 m</td>
<td>ν₁+ ν₄ CO₃Br₂</td>
<td></td>
</tr>
<tr>
<td>1133 w</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>1094 w</td>
<td>ν₄+ ν₅ CO₃Br₂</td>
<td></td>
</tr>
<tr>
<td>1085 w</td>
<td>2 ν₆ COCl₃Br</td>
<td></td>
</tr>
<tr>
<td>1022 m</td>
<td>2 ν₆ CO₃Br₂</td>
<td></td>
</tr>
<tr>
<td>960 w</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>920 m</td>
<td>ν₃+ ν₄ CO₃Br₂</td>
<td></td>
</tr>
<tr>
<td>833 s</td>
<td>ν₁+ ν₅ COCl₃Br</td>
<td></td>
</tr>
<tr>
<td>851 m</td>
<td>ν₄ COCl₂</td>
<td></td>
</tr>
<tr>
<td>803 vs</td>
<td>ν₄ COCl₃Br</td>
<td></td>
</tr>
<tr>
<td>785 vs(sh)</td>
<td>ν₁+ ν₅ CO₃Br₂</td>
<td></td>
</tr>
<tr>
<td>745 vs</td>
<td>ν₄ CO₃Br</td>
<td></td>
</tr>
<tr>
<td>610 m</td>
<td>ν₁+ ν₃ CO₃Br₂</td>
<td></td>
</tr>
<tr>
<td>548 m</td>
<td>ν₆ COCl₃Br</td>
<td></td>
</tr>
<tr>
<td>522 s</td>
<td>ν₁ COCl₃Br</td>
<td></td>
</tr>
<tr>
<td>512 s</td>
<td>ν₆ CO₃Br</td>
<td></td>
</tr>
<tr>
<td>426 s</td>
<td>ν₁ CO₃Br</td>
<td></td>
</tr>
</tbody>
</table>
DIAGRAM 20  INFRA-RED SPECTRUM OF VAPOUR FROM

ALUMINIUM CHLORIDE / CARBONYL BROMIDE
Both residues correspond to $\text{AlX}_3$ only, and also clearly demonstrate that halogen exchange has occurred.

Further proof of exchange came from the infra-red spectrum of the vapour from a room temperature solution, when bands for carbonyl bromide, carbonyl chlorobromide and carbonyl chloride were all clearly visible. The assignments are given in table 11, and part of a spectrum obtained at lower pressure (by expanding vapour into a larger volume) is shown in diagram 20 (compare with diagrams 14 and 21).

The much lower intensity of carbonyl chloride bands compared to the others is presumably due to

(a) The large excess of carbonyl bromide over aluminium chloride in the starting materials.

(b) Complexing of carbonyl chloride with aluminium chloride, thus reducing its vapour pressure.

**Aluminium Bromide + Carbonyl Chloride**

Similar results were obtained, with the solid dissolving, and formation of carbon monoxide and bromine. This occurred very rapidly at room temperature, but much more slowly at $-45^\circ\text{C}$.

On pumping two solutions (both with a large excess of carbonyl chloride) to dryness, one at $-45^\circ\text{C}$, one at room temperature, the residues showed a decrease in weight compared
to the starting aluminium bromide, ruling out any simple, 1:1 complex formation. Results were:

-45°C: (Brown residue)

| Initial wt. AlBr₃ | = 0.1250 |
| Final wt. residue | = 0.1183 |

Room temperature: (White residue)

| Initial wt. AlBr₃ | = 0.2505 |
| Final wt. residue | = 0.1453 |

Analysis of the room temperature residue corresponded to AlX₃:

\[
\begin{align*}
\text{Al} & = 0.97 \times 10^{-3} \text{ g. atom} \\
\text{Cl} & = 2.72 \times 10^{-3} \text{ g. atom} \\
\text{Br} & = 0.25 \times 10^{-3} \text{ g. atom}
\end{align*}
\]

Wt. residue (calc.) = 0.1423 g.
Wt. residue (found) = 0.1453 g.

Infra-red spectra of the vapour from a room temperature solution again showed the presence of carbonyl chloride, carbonyl chlorobromide, carbonyl bromide and carbon monoxide, all in appreciable quantities (diagram 22; table 12). The gas phase spectrum of pure carbonyl chloride was run for comparison purposes (diagram 21), and gives good agreement with published spectra\(^{64,65}\).
DIAGRAM 21  INFRA-RED SPECTRUM OF
CARBONYL CHLORIDE (GAS)
DIAGRAM 22  INFRA-RED SPECTRUM OF VAPOUR FROM

ALUMINIUM BROMIDE / CARBONYL CHLORIDE
**TABLE 12**

**INFRA-RED FREQUENCIES OF VAPOUR FROM CARBONYL CHLORIDE/ALUMINIUM BROMIDE**

<table>
<thead>
<tr>
<th>FREQUENCY cm(^{-1})</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>3630 (\text{m})</td>
<td>2 (\nu_2) CO(_2)X</td>
</tr>
<tr>
<td>2140 (\text{m})</td>
<td>CO</td>
</tr>
<tr>
<td>1825 (\text{m})</td>
<td>(\nu_2) CO(_2)X</td>
</tr>
<tr>
<td>1680 (\text{m})</td>
<td>2 (\nu_4) COCl(_2)</td>
</tr>
<tr>
<td>1595 (\text{m})</td>
<td>2 (\nu_4) COClBr</td>
</tr>
<tr>
<td>1405 (\text{m})</td>
<td>(\nu_4 + \nu_4) COCl(_2)</td>
</tr>
<tr>
<td>1310 (\text{m})</td>
<td>(\nu_4 + \nu_4) COClBr</td>
</tr>
<tr>
<td>1160 (\text{m})</td>
<td>2 (\nu_1), 2 (\nu_6) COCl(_2)</td>
</tr>
<tr>
<td>1080 (\text{w})</td>
<td>2 (\nu_6) COClBr</td>
</tr>
<tr>
<td>1010 (\text{m})</td>
<td>(\nu_1 + \nu_5) COCl(_2)</td>
</tr>
<tr>
<td>970 (\text{w})</td>
<td>?</td>
</tr>
<tr>
<td>890 (\text{m})</td>
<td>(\nu_1 + \nu_5) COClBr</td>
</tr>
<tr>
<td>850 (\text{vs})</td>
<td>(\nu_4) COCl(_2)</td>
</tr>
<tr>
<td>805 (\text{vs})</td>
<td>(\nu_4) COClBr</td>
</tr>
<tr>
<td>780 (\text{s (sh)})</td>
<td>(\nu_1 + \nu_5) CO(_3)Br (_2)</td>
</tr>
<tr>
<td>745 (\text{s})</td>
<td>(\nu_4) CO(_3)Br (_2)</td>
</tr>
<tr>
<td>580 (\text{m})</td>
<td>(\nu_6) COCl(_2)</td>
</tr>
<tr>
<td>565 (\text{w (sh)})</td>
<td>(\nu_1) COCl(_2)</td>
</tr>
<tr>
<td>545 (\text{w})</td>
<td>(\nu_6) COClBr</td>
</tr>
<tr>
<td>520 (\text{m})</td>
<td>(\nu_1) COClBr</td>
</tr>
<tr>
<td>445 (\text{vw})</td>
<td>(\nu_5) COCl(_2)</td>
</tr>
<tr>
<td>425 (\text{vw})</td>
<td>(\nu_1) CO(_3)Br (_2)</td>
</tr>
</tbody>
</table>
Aluminium Iodide + Carbonyl Chloride

Mixing aluminium iodide and carbonyl chloride at -196°C, then allowing the mixture to warm, resulted in the white aluminium iodide slowly disappearing, presumably due to solution in the liquid carbonyl chloride though this was masked by the deposition of considerable quantities of iodine crystals. Effervescence was also observed.

Infra-red spectra of the vapour from the mixture showed only carbonyl chloride and carbon monoxide (diagram 23 shows the region 1300-400 cm⁻¹; table 13 gives the full frequencies). By comparison with aluminium chloride/carbonyl bromide and aluminium bromide/carbonyl chloride, this would seem to suggest that both carbonyl chloroiodide and carbonyl iodide are unstable at room temperature, decomposing to carbon monoxide, iodine and carbonyl chloride. (See also Part 3).
Diagram 23

Infra-Red Spectrum of Vapour from Aluminium Iodide / Carbonyl Chloride
<table>
<thead>
<tr>
<th>FREQUENCY cm⁻¹</th>
<th>ASSIGNMENT (REF. 64 and 65)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3630 m</td>
<td>2 $\nu_2$ COCl₂</td>
</tr>
<tr>
<td>3540 m</td>
<td>$\nu_2$ + 3 $\nu_1$ COCl₂</td>
</tr>
<tr>
<td>2150 s</td>
<td>CO</td>
</tr>
<tr>
<td>2070 m</td>
<td>$\nu_2$ + $\nu_5$ COCl₂</td>
</tr>
<tr>
<td>1823 vs</td>
<td>$\nu_2$ COCl₂</td>
</tr>
<tr>
<td>1680 s</td>
<td>2 $\nu_4$ COCl₂</td>
</tr>
<tr>
<td>1422 m</td>
<td>$\nu_1$ + $\nu_4$ COCl₂</td>
</tr>
<tr>
<td>1165 m</td>
<td>2 $\nu_1$, 2 $\nu_6$ COCl₂</td>
</tr>
<tr>
<td>1015 s</td>
<td>$\nu_1$ + $\nu_5$ COCl₂</td>
</tr>
<tr>
<td>845 vs</td>
<td>$\nu_4$ COCl₂</td>
</tr>
<tr>
<td>745 w</td>
<td>$\nu_3$ + $\nu_5$ COCl₂</td>
</tr>
<tr>
<td>530 s</td>
<td>$\nu_6$ COCl₂</td>
</tr>
<tr>
<td>567 s</td>
<td>$\nu_1$ COCl₂</td>
</tr>
</tbody>
</table>
DISCUSSION

Because of the high electronegativities of the halogens, carbonyl halides might be predicted to act as poor Lewis bases compared to other carbonyls, such as organic ketones\textsuperscript{41,66}. Such complexes as exist would be expected to be fairly unstable, a theory supported by the properties of the aluminium chloride/carbonyl chloride complex.

The present results on boron tribromide/carbonyl bromide give no evidence for complex formation, even at low temperatures, in accord with Christe's findings\textsuperscript{42} on the boron trichloride/carbonyl chloride system. Normally, boron halides are considered better Lewis acids than aluminium halides (e.g. with phosphoryl chloride\textsuperscript{67} and ethylacetate\textsuperscript{43}). Yet for carbonyl halides, while aluminium chloride forms an isolable complex with phosgene, and there must be interaction in the other systems to account for halogen exchange and catalytic decomposition of carbonyl bromide, boron trichloride forms no complex, and boron tribromide does not catalyse the same decomposition. (The boron tribromide/carbonyl chloride and boron trichloride/carbonyl bromide systems remain to be studied). This discrepancy is probably due\textsuperscript{42} to the need for boron to rehybridise from planar $sp_2$ to tetrahedral $sp^3$ on coordination, involving the loss of considerable $\pi$-bond energy
which has to be compensated by the formation of a new donor-acceptor bond. Thus if the boron-donor bond energy is less than the $\pi$-bond energy loss, no adduct would be expected. In the aluminium halides, however, the aluminium is already tetrahedrally coordinated, so the same problem does not arise.

As already stated, although no isolable complexes were found, some interaction in the systems aluminium bromide/carbonyl bromide, aluminium chloride/carbonyl bromide and aluminium bromide/carbonyl chloride must be assumed to account for the halogen exchange and the catalytic decomposition of carbonyl bromide. The speed of halogen exchange, as exemplified by

(a) the quick appearance of strong infra-red peaks for all three carbonyl halides,
(b) the rapid production of bromine,
is in contrast to the results of Huston$^{39,40}$. For solutions of similar concentrations to those used in the present work, he found half-lives for exchange between radioactive aluminium chloride and phosgene of 30 minutes or longer at 25°C. In the present work, quantitative comparisons are difficult and very approximate, because of the need for cooling the systems initially to obtain the mixtures, which then slowly warm to room temperature. On applying external heat, however, to
speed the attainment of room temperature, the bromine colour seemed to reach maximum intensity in the order of 5 minutes, suggesting a faster exchange rate. The reason is not known, but the fast rate suggests that exchange probably occurs through an ionic rather than covalent mechanism. For the concentration range involved, Huston postulated ionisation in the system aluminium chloride/carbonyl chloride.

The presence of appreciable quantities of all three carbonyl halides, even after standing for several hours, suggests that the exchange is an equilibrium process, involving several separate equilibria of the type:

\[
\begin{align*}
\text{AlCl}_3 + \text{CO}_2\text{Br}_2 & \rightarrow [\text{AlCl}_2/\text{AlBr}_3] + \text{COClBr} = \text{AlBr}_3 + \text{COCl}_2 \\
\text{CO} + \text{Br}_2 & \rightarrow [\text{AlCl}_2/\text{AlBr}_3] + \text{COCl}_2 + \text{CO}_2\text{Br}_2 + \text{COClBr}
\end{align*}
\]

In a closed apparatus, such as that used, equilibrium would be established, but in an open system the escape of carbon monoxide would pull the equilibria over. Even so, von Bartel's claim that only the reaction

\[
\text{AlBr}_3 + 3\text{COCl}_2 \rightarrow \text{AlCl}_3 + 3\text{COClBr}
\]

takes place seems a vast oversimplification. Likewise, his claim, based on halide analysis, that with excess aluminium
bromide, aluminium chlorobromide is formed quantitatively also seems dubious. The nature of the aluminium halides in solution, and on pumping off carbonyl halides, cannot be judged from the results available. From the variation in analytical data, however, there must be a mixture of aluminium halides, whether the simple aluminium chloride/aluminium bromide mixture or involving chemically distinguishable mixed halides. In this connection, the failure to obtain any useful Raman or infra-red spectra is unfortunate. Corbett and Gregory's assertion\(^45\) that the residue from aluminium bromide/phosgene is an annealed mixture of aluminium chloride/aluminium bromide is merely qualitative, with no apparent experimental backing.

The possibility remains that complexes may be formed at temperatures lower than \(-45^\circ\)C, at which temperatures halogen exchange and carbonyl bromide decomposition might be sufficiently slow to enable complex isolation. This is most likely with carbonyl chloride, which is liquid down to \(-104^\circ\)C\(^4\), whereas carbonyl bromide solidifies at a higher temperature, estimated at \(-70\) to \(-30^\circ\)C, (although the exact freezing point is not known) and there would be difficulty in pumping off any excess. Even if complexes were isolated at such temperatures, their study would of course present great problems due to the need to maintain them at all times at the same low temperatures to avoid decomposition.
PART THREE

THERMOCHEMICAL PROPERTIES

OF CARBONYL BROMIDE

[See also


(1970) 2 697,

a reprint of which is included at the end of this thesis].
INTRODUCTION

Three papers have been published\(^6\),\(^9\),\(^7\) on the equilibrium

\[
\text{CO}(g) + \text{Br}_2(g) \rightleftharpoons \text{COBr}_2(g)
\]

reporting equilibrium constants for temperatures ranging from 293K to 456K. Since

\[
\frac{d}{d(1/T)} \ln K_p = \frac{\Delta H^\circ}{R}
\]

the enthalpy of reaction and hence the standard enthalpy of formation for carbonyl bromide could be derived. Wagman et al.\(^7\) used Trautz's (1915) results\(^6\) to obtain \(\Delta H^\circ_{\text{COBr}_2(g)} = -23.0\) kcal mol\(^{-1}\) \([-96.2\) kJ mol\(^{-1}\)], while Cox and Filcher\(^7\) quote a "best" value of \(-20.1\) kcal mol\(^{-1}\) \([-84.1\) kJ mol\(^{-1}\)] derived from Schmächer and Bergmann's\(^7\) work (1931). Reerink's results\(^6\) (1923) lead to an intermediate value of \(-20.9\) kcal mol\(^{-1}\) \([-87.4\) kJ mol\(^{-1}\)].

In the absence of any further experimental data, and in view of the spread of values, it was decided to redetermine \(\Delta H^\circ\) employing a different, calorimetric, approach. The reaction studied was

\[
\text{COBr}_2(1) + \text{nH}_2\text{O}(1) \rightarrow \text{CO}_2(1) + [2\text{HBr}(\text{n-1}) \text{H}_2\text{O}](1)
\]

at 293.15K and one atmosphere pressure, for which the enthalpy change is denoted as \(\Delta H_{\text{hyd}}\). By using water already saturated
with carbon dioxide for the hydrolysis, all the carbon
dioxide produced in the reaction can be considered as in its
standard (gaseous) state. Since the enthalpies of formation
of all the other reactants and products are well known,
measurement of \( \Delta H_{\text{hyd}} \) allows \( \Delta H^0_2 \text{COBr}_2(1) \) to be calculated.

Preliminary studies showed the reaction to be slow,
0.3339 g of carbonyl bromide in 200 ml of water taking ca
forty minutes to dissolve completely. Since carbonyl bromide
and water are immiscible, and shaking speeded up the reaction,
the rate of hydrolysis is probably controlled by the surface
area of the two liquids in contact. Analysis of the hydroly-
sate gave 99.5% of the calculated bromide, indicating that the
reaction goes to completion. In view of the slowness of
reaction, the use of an adiabatic solution calorimeter was
considered essential.
**EXPERIMENTAL**

**Chemicals**

The carbonyl bromide was from the same batch used previously (p. 63) [Analysis: Br (found) 84.6% by mass, Br (calcd) 85.1% by mass].

Distilled water was saturated with carbon dioxide by adding a few lumps of dry ice to a flask of water which was then placed in a thermostated bath at 298K to equilibrate.

**Calorimeter**

The calorimeter was basically similar to that described in Part 4 (p. 131), but modified to operate adiabatically. Comprehensive details are already available. The principle differences from the constant-temperature-environment calorimeter described in the next chapter were:

(a) The calorimeter was immersed in a water jacket, the temperature of which was automatically controlled such that the temperature difference between the inside of the calorimeter and the jacket was maintained at a constant, pre-set, level (ca 0.05 ± 0.002 degrees). The design of the automatic adiabatic control was the same, with minor modifications, as that employed in the Gallenkamp Adiabatic Bomb Calorimeter.
(b) As part of the adiabatic control unit, the glass Dewar shown in diagram 26 (p. 132) contained two additional thermistors.

(c) A Scalamp galvanometer (1400 Ω) was used in place of the chart recorder as the out-of-balance detector in the thermistor bridge for measuring the temperature inside the calorimeter. Readings of the thermistor resistance were taken every minute.

The only modifications in the present work of the apparatus and procedure given in reference 73 were due to the fact that reproducible results were only obtained on eliminating all contact between carbonyl bromide and grease. The reason is not known certainly, but one possible explanation is absorption of carbonyl bromide vapour by the grease. This was supported by discrepancies of up to 10% in the quantity of carbonyl bromide used as determined by weighing and comparison with the results of post-hydrolysis bromide analysis. To overcome this:

(i) The ampoule design was changed slightly (diagram 24) to enable sealing under vacuum. The narrowed, thickened portion facilitated sealing at a well-defined point, which meant that the ampoule volume could be determined beforehand by weighing first empty then filled to the constriction with water. A blank calorimeter run showed that the effect of heating the ampoule during sealing, and the enthalpy of ampoule breaking, were both negligible.
DIAGRAM 24  COBr₂ AMPOULE
(11) No grease was used in the calorimeter head. Tests showed that the two flanges of the glass Dewar were waterproof if held firmly together by a circular wire clip, and then lightly greased on the outside rim only. Nor was any grease used on the joint connecting the ampoule to the ampoule holder.

Before and after using the calorimeter for carbonyl bromide, its performance was checked by measuring the enthalpy of neutralization of tris(hydroxymethyl)aminomethane (THAM), (B.D.H. Aristar grade; 99.9% minimum purity), in excess aqueous 0.1% hydrochloric acid. Results were

Before: $-7.11 \text{ kcal mol}^{-1}$ [-29.75 kJ mol$^{-1}$]
After: $-7.11 \text{ kcal mol}^{-1}$ [-29.75 kJ mol$^{-1}$]

Previous THAM results$^7$ for this calorimeter gave a mean for ten runs of $-7.11 \text{ kcal mol}^{-1}$ [-29.75 kJ mol$^{-1}$] with a standard deviation of the mean of 0.005 kcal mol$^{-1}$ [0.02 kJ mol$^{-1}$]. The H$_2$O:THAM mole ratio varied from 1155 to 2227. These results compare with literature values of

<table>
<thead>
<tr>
<th>DILUTION (H$_2$O:THAM RATIO)</th>
<th>$\Delta H^\circ \text{ kcal mol}^{-1}$</th>
<th>$\Delta H^\circ \text{ kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gunn$^7$</td>
<td>373 - 1120</td>
<td>$-7.107 \pm 0.001$</td>
</tr>
<tr>
<td>Sunner and Wadso$^7$</td>
<td>1138 - 1462</td>
<td>$-7.111 \pm 0.001$</td>
</tr>
<tr>
<td>Ojelund and Wadso$^7$</td>
<td>1320 - 1390</td>
<td>$-7.112 \pm 0.002$</td>
</tr>
<tr>
<td>Hill et. al.$^7$</td>
<td>1170 - 1574</td>
<td>$-7.109 \pm 0.001$</td>
</tr>
</tbody>
</table>
Procedure

After its volume had been determined, a dried ampoule was attached, via an adaptor, to the greaseless vacuum line described previously (p. 53), in place of the mixing vessel. The pressure was slowly reduced to minimise the danger of fracturing the fragile glass bulbs, and the ampoule tested for its ability to hold a pressure $\leq 10^{-4}$ torr. Carbonyl bromide was then condensed in by cooling the lower bulb in a solid carbon dioxide/acetone bath ($-80^\circ$C). [The bulbs were found to crack at liquid nitrogen temperatures]. With the $-80^\circ$C bath still in position, the ampoule was sealed at the constriction, using as small a torch flame as possible. At $-80^\circ$C, the low vapour pressure of acetone combined with the carbon dioxide gas evolved was sufficient to avoid ignition of the acetone. The carbonyl bromide was allowed to warm to room temperature, and the completion of the seal tested by the ability of the system above the constriction to hold pressures $\leq 10^{-4}$ torr.

The ampoule was removed from the vacuum line, attached to the holder by platinum wire, and placed in position, together with the other inserts, in the glass Dewar. After pipetting in 200 ml of carbon dioxide-saturated water, the Dewar was lowered into the adiabatic jacket and allowed to equilibrate.
The quantity of carbonyl bromide used was determined by analysis after the reaction and calibration. 10 ml samples from the 200 ml total were titrated for bromide against 0.1M silver nitrate solution, using eosin indicator.
RESULTS

On breaking ampoules of carbonyl bromide into water, the heavier carbonyl bromide sank to the bottom, where it was broken into small globules by the stirring. Effervescence was observed at the carbonyl bromide - water interfaces due to the production of carbon dioxide gas.

The graph for a typical reaction (No. 3 in Table 14) is shown in diagram 25. The calibration graph is similar except that the heating period corresponding to the reaction period is linear rather than curved because the electric heater supplies heat at a uniform rate, whereas in the reaction the rate of heating decreases as the amount of carbonyl bromide decreases.

Assuming the heat capacity of the solution remains unchanged throughout (a valid assumption for very dilute solutions such as those used)

\[ \frac{\Delta H_{\text{reaction}}}{\Delta T_{\text{reaction}}} = \frac{\Delta H_{\text{calibration}}}{\Delta T_{\text{calibration}}} \]

\[ \Delta H_{\text{calibration}} = (\text{Power through heater}) \times (\text{heating time}) \]

whence

\[ \Delta H_{\text{reaction}} = \frac{P \times t}{4184 \times m \times \Delta T_{\text{calibration}}} \]
DIAGRAM 25  REACTION TRACE FOR 
COBr₂ CALORIMETRY

Thermistor Resistance (Ω)

Time of ampoule breaking

R₁

R₂

Time (Minutes)

4560

4600

90

80

70

60

50

40

30

20

10

0
where \( P = \) Power through heater (\( \text{IxV joules} \))
\( t = \) Heating time
\( m = \) No. moles CO\(_2\) used
\( \Delta T = \) Temperature rise

\( 4184 = \) Conversion factor, joules to kcal.

It can be readily shown (reference 73, p.221) that, to an accuracy of 99.9\%, for a thermistor

\[
\frac{\Delta T}{\Delta T_{\text{reaction}}} = \frac{\log R_{\text{reaction}}}{\log R_{\text{calibration}}} = \log \frac{R_1}{R_2}
\]

where \( R_1 = \) Resistance corresponding to temperature before reaction

\( R_2 = \) " " " " after reaction.
\( R_3 = \) " " " " before calibration.
\( R_4 = \) " " " " after calibration.

Since under adiabatic conditions the rate of heat loss can be assumed constant (compare the similar slopes for fore- and after-periods in diagram 25), the resistances \( R_2 \) and \( R_4 \) corresponding to the temperatures after reaction and after calibration can be determined simply by extrapolating the relevant after-periods back to the times of ampoule breaking and switching on the heater respectively.
Table 14 gives the results for nine determinations of

$$\text{An hyd:}$$

$$\text{H}_2\text{O}(1) + \text{COBr}_2(1) \xrightarrow{\text{An hyd}} \text{CO}_2(\text{g}) + [2\text{HBr}.(n-1)\text{H}_2\text{O}](1)$$

<table>
<thead>
<tr>
<th>RUN NUMBER</th>
<th>NO. MOLES COBr₂ USED (x 10³)</th>
<th>-ΔH.obs (kcal mol⁻¹)</th>
<th>-ΔH.corr (kcal mol⁻¹)</th>
<th>n (MOLE RATİON)</th>
<th>-ΔH hyd (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.382</td>
<td>49.01</td>
<td>0.05</td>
<td>5587</td>
<td>48.96</td>
</tr>
<tr>
<td>2</td>
<td>1.028</td>
<td>49.06</td>
<td>0.12</td>
<td>10777</td>
<td>43.94</td>
</tr>
<tr>
<td>3</td>
<td>1.194</td>
<td>49.49</td>
<td>0.11</td>
<td>9277</td>
<td>49.33</td>
</tr>
<tr>
<td>4</td>
<td>1.154</td>
<td>48.37</td>
<td>0.09</td>
<td>9524</td>
<td>48.28</td>
</tr>
<tr>
<td>5</td>
<td>1.197</td>
<td>43.56</td>
<td>0.11</td>
<td>9233</td>
<td>43.45</td>
</tr>
<tr>
<td>6</td>
<td>1.359</td>
<td>49.16</td>
<td>0.10</td>
<td>8141</td>
<td>49.06</td>
</tr>
<tr>
<td>7</td>
<td>1.779</td>
<td>49.63</td>
<td>0.05</td>
<td>6224</td>
<td>49.62</td>
</tr>
<tr>
<td>8</td>
<td>2.056</td>
<td>49.61</td>
<td>0.06</td>
<td>4384</td>
<td>49.56</td>
</tr>
<tr>
<td>9</td>
<td>0.450</td>
<td>49.61</td>
<td>0.30</td>
<td>24615</td>
<td>49.31</td>
</tr>
</tbody>
</table>

The column headed ΔH corre gives the corrections applied to the observed enthalpies of reaction to allow for some carbonyl bromide being present as vapour. The latent heat of vaporization, ΔH vap, and the vapour pressure, P, of carbonyl bromide are both known at 293K53 [7.4 kcal mol⁻¹ and 190 torr respectively], and by measuring the volume, V, of the
ampoule (neglecting the small volume of CO\textsubscript{3}\textsubscript{r\textsubscript{2}}(l)), the correction becomes

\[ \Delta H_{\text{corr}} = \frac{\Delta H_{\text{vap}}}{m} \times \frac{P \times V}{R \times 298.15} \times V \times 10^{-5} \frac{\text{kcal mol}^{-1}}{m} \]

where \( V \) = Volume in ml of ampoule.

\( m \) = No. moles CO\textsubscript{3}r\textsubscript{2} used

\( R \) = Gas constant, \( 1.99 \times 10^{-3} \text{ kcal K}^{-1}\text{mol}^{-1} \)

or \( 62.360 \times 10^{3} \text{ ml torr K}^{-1}\text{mol}^{-1} \)

In calculating \( \Delta H_{\text{hyd}} \), thermal effects arising from the decreased solubility of carbon dioxide with the small temperature rise during reaction, and also from the mixing of CO\textsubscript{2}(aq) and K\textsubscript{Br}(aq) were ignored. Nor was account taken of the increase in pressure due to the carbon dioxide produced.

From Table 14, a mean value of

\[ \Delta H_{\text{hyd}} = -49.06 \pm 0.16 \text{ kcal mol}^{-1} \]

\([ -205.36 \pm 0.67 \text{ kJ mol}^{-1} ] \]

is obtained. The uncertainty interval is calculated as \( \pm \) one standard deviation of the mean, \[ \left[ \frac{\sum d^2}{n \cdot (n-1)} \right]^{\frac{1}{2}} \]

following the recommendations of Rossini\textsuperscript{79}. 
DISCUSSION

Standard Enthalpy of Formation of Carbonyl Bromide

From the equation for the hydrolysis of carbonyl bromide, it is apparent that the standard enthalpy of formation, $\Delta H_f^0$, of carbonyl bromide is given by

$$\Delta H_f^0 \text{COBr}_2(1) = \Delta H_f^0 \text{CO}_2(g) + 2\Delta H_f^0 \text{HBr in } \frac{1}{3}(n-1)\text{H}_2\text{O}$$

$$-\Delta H_f^0 \text{H}_2\text{O} - \Delta H \text{hyd.}$$

Using accepted values,$^71$

$$\Delta H_f^0 \text{CO}_2(g) = -94.05 \pm 0.01 \text{ kcal mol}^{-1} [-393.51 \pm 0.04 \text{ kJ mol}^{-1}]$$

$$\Delta H_f^0 \text{H}_2\text{O}(1) = -28.315 \pm 0.001 \text{ kcal mol}^{-1} [-118.3 \pm 0.004 \text{ kJ mol}^{-1}]$$

$$\Delta H_f^0 \text{HBr in } \frac{1}{3}(n-1)\text{H}_2\text{O} = -29.01 \pm 0.01 \text{ kcal mol}^{-1} [-121.38 \pm 0.04 \text{ kJ mol}^{-1}]$$

(mean value between $n = 5000$ and $n = 25000$)

this gives

$$\Delta H_f^0 \text{COBr}_2(1) = -34.70 \pm 0.21 \text{ kcal mol}^{-1} [-145.1 \pm 0.83 \text{ kJ mol}^{-1}]$$

Using Schumacher and Lenher's$^53$ value of 7.4 kcal mol$^{-1}$ (no errors assignable) for the latent heat of vaporization, this gives

$$\Delta H_f^0 \text{COBr}_2(g) = -27.3 \text{ kcal mol}^{-1} [-114.2 \text{ kJ mol}^{-1}]$$

differing markedly from the values derived by equilibrium studies$^{63,69,70}$. The reason for this is not known definitely, but in view of the differences between equilibrium constants
for similar temperatures quoted in the three papers, one possibility is that true equilibrium was not achieved in some or all of the experiments. This would be in accord with the fact that the decomposition of carbonyl bromide (and hence presumably the attainment of equilibrium) is known to be very slow.

Thermodynamic Functions for Carbonyl Halides

Overend and Evans\(^6\) calculated the statistical thermodynamic functions for carbonyl bromide from infra-red frequency measurements, using the harmonic oscillator/rigid rotor approximations.\(^8\) This gave

\[
S^0_{COBr_2(g)} = 293.15\text{K} = 73.82 \text{cal K}^{-1}\text{mol}^{-1}
\]

Using the following values\(^9\)

\[
\begin{align*}
S^0_C (\text{graphite}) &= 1.3609 \text{cal K}^{-1}\text{mol}^{-1} \\
\frac{1}{2} S^0 O_2(g) &= 24.502 \text{cal K}^{-1}\text{mol}^{-1} \\
S^0 Br_2(l) &= 36.4 \text{cal K}^{-1}\text{mol}^{-1} \\
S^0 Br_2(g) &= 53.639 \text{cal K}^{-1}\text{mol}^{-1}
\end{align*}
\]

the standard entropy of formation of carbonyl bromide is derived

\[
\Delta S^0_f \text{ COBr}_2(g) = 11.6 \text{cal K}^{-1}\text{mol}^{-1} \text{[standard state Br}_2(l)\text{]} \\
-10.7 \text{cal K}^{-1}\text{mol}^{-1} \text{[standard state Br}_2(g)\text{]}
\]

From \(\Delta H^0_f\) and \(\Delta S^0_f\),

\[
\Delta H^0_f \text{ COBr}_2(g) = -30.7 \text{ kcal mol}^{-1}
\]
These values are compared with those for carbonyl fluoride and carbonyl chloride in table 15.

**TABLE 15**

**THERMODYNAMIC FUNCTIONS FOR COX₂(g)**

<table>
<thead>
<tr>
<th></th>
<th>COF₂</th>
<th>COCl₂</th>
<th>COBr₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H^0)_k cal mol⁻¹</td>
<td>151.7</td>
<td>52.3</td>
<td>27.3</td>
</tr>
<tr>
<td>(\Delta S^0)_k kcal mol⁻¹</td>
<td>143.0</td>
<td>48.9</td>
<td>30.7</td>
</tr>
<tr>
<td>(\Delta S^0)_k cal k⁻¹mol⁻¹</td>
<td>12.4</td>
<td>11.4</td>
<td>-11.6 (10.7)</td>
</tr>
</tbody>
</table>

The reason for deriving the entropy of formation of carbonyl bromide from both liquid and gaseous bromine can be seen from table 15. An apparently anomalous value for the standard entropy of formation is due to the condensed standard state of bromine; as shown, a steady progression is obtained using the value for bromine gas.

**Carbonyl Iodide**

It is interesting at this stage to consider how table 15 might be extended to include carbonyl iodide, COI₂. There are no reports in the literature of its preparation, and the results in Part Two (p. 94) suggest it is very unstable even at -45°C. Molecular models using 'planar' carbon are easily made, and there is no reason to assume adverse structural features; hence consideration of its thermodynamic stability is appropriate.
The first need is for an estimate of $\Delta H^0$ for carbonyl iodide. Although many bond-energy schemes have been devised to assess $\Delta H^0(g)^{72}$, none of them is appropriate in the present example because no "correction parameters" are available to allow for two halogen atoms being bonded to the same carbonyl group, a situation unique to the carbonyl halides. As an example, the values for $\Delta H^0(g)$ calculated (without correction factors) from the schemes of Laidler$^{72,82}$, Allen$^{72,83}$ and Cox$^{84}$ are compared with the experimental values in table 16.

**Table 16**

$\Delta H^0 COX_2(g)$, Estimated from Bond-Energy Schemes

<table>
<thead>
<tr>
<th></th>
<th>$COF_2$</th>
<th>$COCl_2$</th>
<th>$COBr_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>151.7</td>
<td>52.3</td>
<td>27.3</td>
</tr>
<tr>
<td>Laidler$^{72,82}$</td>
<td>119.3</td>
<td>38.2</td>
<td>15.0</td>
</tr>
<tr>
<td>Allen$^{72,83}$</td>
<td>102.7</td>
<td>31.3</td>
<td>8.4</td>
</tr>
<tr>
<td>Cox$^{84}$</td>
<td>115.5</td>
<td>37.5</td>
<td>11.5</td>
</tr>
</tbody>
</table>

In view of the small differences in C=O bond lengths$^{85}$ in going from $COF_2$ to $COBr_2$, as shown in table 17, (compare with $COH_2$ or $CO(CH_3)_2$ for example), a reasonable starting point would seem to be the assumption of a constant bond energy for the carbonyl group.
From the cycle

\[
\text{C}(g) + \text{O}(g) + 2\text{X}(g) \xleftarrow{\Sigma \text{Dissociation Energies}} \text{COX}_2(g)
\]

\[\Delta H^\circ_{\text{atomization}} = \Delta H^\circ_{\text{f}}\]

\[\text{C(graphite)} + \frac{1}{2}\text{O}_2(g) + \text{X}_2(\text{standard state})\]

\[\Delta H^\circ_{\text{f}} \text{COX}_2(g) = \Delta H_{\text{atomization}} - 2\overline{D}(\text{C-X}) - \overline{D}(\text{C=O})\]

where

\(\overline{D}(\text{C-X})\) is the mean bond dissociation energy for the \(\text{C-X}\) bond,

and \(\overline{D}(\text{C=O})\) is defined by the relation

\[\overline{D}(\text{C=O}) = \text{Dissociation Energies} - 2\overline{D}(\text{C-X})\]

Using values from reference 71,

\[\Delta H_{\text{atomization}}\]

\[
\begin{array}{ccc}
X & F & 263.60 \text{ kcal mol}^{-1} \\
& Cl & 289.01 \text{ kcal mol}^{-1} \\
& Br & 284.32 \text{ kcal mol}^{-1}
\end{array}
\]
The values of $\Delta(C-X)$ used were those for $CX_4(g)^{71}$, since, despite the change in hybridisation of the carbon atom (which would be expected to have only a small effect$^{84}$), of all the simple organic halides the bond lengths$^{85}$ in $CX_4$ came closest to those in $COX_2$ (table 18).

**Table 18**

**CX$_4$ bond lengths and mean bond dissociation energy**

<table>
<thead>
<tr>
<th>Bond length (nm)</th>
<th>$\Delta(C-X)$ kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CF_4(g)$</td>
<td>$0.1323 \pm 0.0005$</td>
</tr>
<tr>
<td>$CCl_4(g)$</td>
<td>$0.1766 \pm 0.0003$</td>
</tr>
<tr>
<td>$CBr_4(g)$</td>
<td>$0.1942 \pm 0.0003$</td>
</tr>
</tbody>
</table>

Using the values for $\Delta(C-X)$ in table 18,

$\Delta(C=O)\ COF_2 = 136$ kcal mol$^{-1}$  
$\Delta(C=O)\ COCl_2 = 185$ kcal mol$^{-1}$  
$\Delta(C=O)\ COBr_2 = 182$ kcal mol$^{-1}$

in accord with the initial assumption.

Despite the approximate and empirical nature of the method, the good agreement obtained justifies extending it to carbonyl iodide, where

\[
\text{Ar atomization} = 231.9 \text{ kcal mol}^{-1}
\]

\[
\Delta(C=O) = 185 \text{ kcal mol}^{-1} \text{ from above.}
\]

Unfortunately, data for $CI_4$ are not available, so $\Delta(C-X)$ has to be extrapolated from values for $CH_3I$ and $CH_2I_2$ by comparison with the other halides (table 19).
TABLE 19
MEAN C-X BOND DISSOCIATION ENERGY FOR CH\textsubscript{4-n}

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^0$ kcal mol(^{-1})</th>
<th>TOTAL DISSOCIATION ENERGY kcal mol(^{-1})</th>
<th>$\overline{D}$ (C-X) kcal mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBr(_4)</td>
<td>19</td>
<td>259.3</td>
<td>64.7</td>
</tr>
<tr>
<td>CBr(_3)</td>
<td>4</td>
<td>299.6</td>
<td>67.7</td>
</tr>
<tr>
<td>CH(_2)Br(_2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH(_3)Br</td>
<td>-3.4</td>
<td>362.7</td>
<td>63.1</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>-24.6</td>
<td>312.2</td>
<td>73.1</td>
</tr>
<tr>
<td>CICl(_3)</td>
<td>-24.7</td>
<td>335.3</td>
<td>73.6</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>-22.1</td>
<td>355.7</td>
<td>80.6</td>
</tr>
<tr>
<td>CH(_3)Cl</td>
<td>-19.3</td>
<td>376.0</td>
<td>81.4</td>
</tr>
<tr>
<td>CI(_4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH(_2)I(_2)</td>
<td>27.0</td>
<td>299.6</td>
<td>52.6</td>
</tr>
<tr>
<td>CH(_3)I</td>
<td>3.1</td>
<td>350.0</td>
<td>55.4</td>
</tr>
</tbody>
</table>

(Relevant values for $D$(C-H) taken from Laidler\textsuperscript{72} and Cox\textsuperscript{84})

This gives $\overline{D}$(C-I) ca 50 kcal mol\(^{-1}\)

from which

$\Delta H^0$ COI\(_2\)(g) = -3 \pm ca 5 kcal mol\(^{-1}\)

\([-13 \pm 20 \text{ kJ mol}^{-1}\)]
Using Kubaschewski and Evans' procedure for the estimation of entropies

\[ S_{298}^0 \text{COI}_2(g) = 39.0 + 0.34M - 6.2 \times 10^{-4} M^2 \] (cal K\(^{-1}\)mol\(^{-1}\))

where \( M = \) Molecular weight COI\(_2\), 231.81

leads to

\[ S_{298}^0 \text{COI}_2(g) = 86 \text{ cal K}^{-1}\text{mol}^{-1} \]

whence

\[ \Delta S_f^0 \text{COI}_2(g) = 32 \text{ cal K}^{-1}\text{mol}^{-1} \]

[-2 cal K\(^{-1}\)mol\(^{-1}\) if standard state of iodine is taken as gas]

and

\[ \Delta G_f^0 \text{COI}_2(g) = -13 \pm 10 \text{ kcal mol}^{-1} \]

Clearly, however, carbonyl iodide would be expected to exist as a condensed phase in its standard state. By comparison with the other carbonyl halides, the latent heat of vaporization is likely to be ca 8 kcal mol\(^{-1}\) \([\text{COF}_2 \text{ ca 4 kcal mol}^{-1} \text{ COCl}_2 6 \text{ kcal mol}^{-1}, \text{ CBr}_3 7.4 \text{ kcal mol}^{-1}]\). The entropy of vaporization for molecular compounds is usually close to the Trouton figure of 22 cal K\(^{-1}\)mol\(^{-1}\), giving

\[ \Delta H_f^0 \text{COI}_2 (1) \text{ ca } -11 \text{ kcal mol}^{-1} \]

\[ \Delta S_f^0 \text{COI}_2 (1) \text{ ca } 10 \text{ cal K}^{-1}\text{mol}^{-1} \]

\[ \Delta G_f^0 \text{COI}_2 (1) \text{ ca } -14 \text{ kcal mol}^{-1} \]
**Dissociation Equilibria**

In view of the great variation in stabilities for the carbonyl halides, it is interesting to compare the equilibrium constants at 293.15 K for the dissociation

\[
\text{COX}_2(g \text{ or } l) \rightleftharpoons \text{CO}(g) + \text{X}_2(\text{s-s})
\]

The necessary data are given in table 20.

**TABLE 20**

**ENTHALPY, ENTROPY AND FREE ENERGY OF DISSOCIATION**

**FOR CARBONYL HALIDES**

<table>
<thead>
<tr>
<th></th>
<th>ΔH diss. kcal mol(^{-1})</th>
<th>ΔS diss. cal K(^{-1})mol(^{-1})</th>
<th>ΔG diss. kcal mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF(_2)(g)</td>
<td>125.3</td>
<td>33.7</td>
<td>115.2</td>
</tr>
<tr>
<td>COCl(_2)(g)</td>
<td>25.9</td>
<td>32.7</td>
<td>16.1</td>
</tr>
<tr>
<td>COBr(_2)(g)</td>
<td>0.9</td>
<td>9.8</td>
<td>-2.1</td>
</tr>
<tr>
<td>(1)</td>
<td>8.3</td>
<td>31.8</td>
<td>-1.2</td>
</tr>
<tr>
<td>COI(_2)(g)</td>
<td>-23</td>
<td>-11</td>
<td>-20</td>
</tr>
<tr>
<td>(1)</td>
<td>-8</td>
<td>11</td>
<td>-19</td>
</tr>
</tbody>
</table>

From these values, the equilibrium constants, \(K_p\), for dissociation are derived as

- \(\text{COF}_2(g)\): \(4.7 \times 10^{-85}\)
- \(\text{COCl}_2(g)\): \(1.6 \times 10^{-12}\)
- \(\text{COBr}_2(g)\): \(34.4\)
  (1): \(7.6\)
- \(\text{COI}_2(g)\): \(4 \times 10^{14}\)
  (1): \(8 \times 10^{13}\)
PART FOUR

THERMOCHEMICAL PROPERTIES

OF

ALUMINIUM HALIDES
INTRODUCTION

Though the literature contains several determinations of the standard enthalpy of formation of aluminium chloride, the values for aluminium bromide and aluminium iodide have been much less thoroughly investigated, and rely mostly on fairly old work. Table 21 lists the literature data.

**Table 21**

**LITERATURE VALUES FOR THE ENTHALPIES OF FORMATION OF ALUMINIUM HALIDES**

<table>
<thead>
<tr>
<th>AUTHORS</th>
<th>REFERENCES</th>
<th>YEAR</th>
<th>(-\Delta H_f(c)) kcal mol(^{-1})</th>
<th>(\text{AlCl}_3)</th>
<th>(\text{AlBr}_3)</th>
<th>(\text{AlI}_3)</th>
<th>TEMP.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berthelot</td>
<td>87, 71</td>
<td>1873</td>
<td>a</td>
<td>170.6</td>
<td>126.8</td>
<td>77.6</td>
<td>293</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b</td>
<td>-</td>
<td>124.6</td>
<td>75.9</td>
<td>293</td>
</tr>
<tr>
<td>Klemm and Tanke</td>
<td>63, 90</td>
<td>1931</td>
<td>c</td>
<td>167</td>
<td>121</td>
<td>71</td>
<td>293</td>
</tr>
<tr>
<td>Klemm and Jacobi</td>
<td>89</td>
<td>1932</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Siemonsen</td>
<td>91</td>
<td>1951</td>
<td>d</td>
<td>167.5</td>
<td>-</td>
<td>-</td>
<td>293</td>
</tr>
<tr>
<td>Dear and Eley</td>
<td>95, 81, 95</td>
<td>1954</td>
<td>e</td>
<td>-</td>
<td>-</td>
<td>75.2</td>
<td>293</td>
</tr>
<tr>
<td>Corbett and Gregory</td>
<td>92, 95</td>
<td>1954</td>
<td>f</td>
<td>-</td>
<td>-</td>
<td>73.7</td>
<td>293</td>
</tr>
<tr>
<td>Coughlin</td>
<td>93</td>
<td>1953</td>
<td>g</td>
<td>163.57</td>
<td>-</td>
<td>-</td>
<td>293</td>
</tr>
<tr>
<td>Gross and Hayman</td>
<td>94</td>
<td>1967</td>
<td>h</td>
<td>163.50</td>
<td>-</td>
<td>-</td>
<td>293</td>
</tr>
</tbody>
</table>

* The nature of the crystal structures is irrelevant to the present work. "AlX₃" is used only as an abbreviation for "aluminium halide", and is not intended to suggest that the crystals consist of AlX₃ units.
(a) Calculated using Berthelot's values for the enthalpies of solution in water at 232 K,

- \( \text{AlCl}_3(c) \) \(-75.3 \text{ kcal mol}^{-1} \)
- \( \text{AlBr}_3(c) \) \(-85.3 \text{ kcal mol}^{-1} \)
- \( \text{AlI}_3(c) \) \(-89.0 \text{ kcal mol}^{-1} \)

and \( \Delta H^0_\beta \text{Al}^{3+}(aq) \) and \( \Delta H^0_\beta X^-(aq) \) from reference 71, assuming

\( \text{AlX}_3(c) \xrightarrow{H_2O} \text{Al}^{3+}(aq) + 3X^-(aq) \)

[after the JANAF tables].

(b) Berthelot also measured the enthalpies of solution:

- \( \text{AlBr}_3(c) + [3\text{KCl.nH}_2\text{O}](1) \xrightarrow{} -86.9 \text{ kcal mol}^{-1} \)
- \( \text{AlCl}_3(c) + [3\text{KBr.nH}_2\text{O}](1) \xrightarrow{} -75.0 \text{ kcal mol}^{-1} \)
- \( \text{AlI}_3(c) + [3\text{KCl.nH}_2\text{O}](1) \xrightarrow{} -89.1 \text{ kcal mol}^{-1} \)
- \( \text{AlCl}_3(c) + [3\text{KI.nH}_2\text{O}](1) \xrightarrow{} -76.6 \text{ kcal mol}^{-1} \)

where \( n = \text{cm} \cdot 1000 \). From these results, using the value for \( \Delta H^0_\beta \text{AlCl}_3(c) \) from Gross and Hayman, and assuming (after Berthelot) that the resultant solutions for each pair (i) and (ii) are identical,

\[ \Delta H_\beta \text{AlBr}_3(c) = \Delta H(ii) - \Delta H(i) + 3 \left[ \Delta H_\beta \text{KBr}(aq) - \Delta H_\beta \text{KCl}(aq) \right] + \Delta H^0_\beta \text{AlCl}_3(c) \]

and similarly for aluminium iodide.
(c) Klemm and Tanke measured the enthalpies of solution:
\[ \Delta H^{\text{sol}}_n \]
\[ \text{AlCl}_3(\text{c}) + [3\text{KCl} \cdot 100 \text{MCl}](1) \rightarrow -71.7 \text{ kcal mol}^{-1} \]
\[ \text{AlCl}_3(\text{c}) + [3\text{KBr} \cdot 100 \text{MCl}](1) \rightarrow -71.8 \text{ kcal mol}^{-1} \]
\[ \text{AlCl}_3(\text{c}) + [3\text{KI} \cdot 100 \text{MCl}](1) \rightarrow -72.3 \text{ kcal mol}^{-1} \]
\[ \text{AlBr}_3(\text{c}) + [3\text{KCl} \cdot 100 \text{MCl}](1) \rightarrow -85.5 \text{ kcal mol}^{-1} \]
\[ \text{AlI}_3(\text{c}) + [3\text{KCl} \cdot 100 \text{MCl}](1) \rightarrow -89.9 \text{ kcal mol}^{-1} \]

where \( n \) represents a large, unspecified, excess. Using literature values\(^90\) for the enthalpy of reaction
\[ \text{Al}(\text{c}) + [n \cdot 100 \text{MCl}](1) \underset{\Delta H_{\text{Al}}}{\longrightarrow} [\text{AlCl}_3(n-3) \cdot 100 \text{MCl}](1) + \frac{3}{2} \text{H}_2(\text{g}) \]

they obtained \( \Delta H_{\text{f}} \) \( \text{AlX}_3 \) as
\[ \Delta H_{\text{f}} \text{AlX}_3(\text{c}) = \Delta H_{\text{sol}} + \Delta H_{\text{Al}} - 3 \Delta H_{\text{fCl}}(\text{aq}) -3\Delta H_{\text{fKX}}(\text{aq}) + 3\Delta H_{\text{fKCl}}(\text{aq}) \]

(d) Siemonsen used solution calorimetry similar to (c).
(e) Dear and Eley measured the enthalpy of solution of aluminium iodide in water \([-91.4 \pm 1.5 \text{ kcal mol}^{-1}\]), then followed the same procedure as in (a).
(f) Corbett and Gregory measured the enthalpy of reaction
\[ \text{AlI}_3(\text{c}) + 3\text{HCl}(\text{g}) \rightarrow \text{AlCl}_3(\text{c}) + 3\text{HI}(\text{g}) \]
Knowing the other enthalpies of formation, \( \Delta H_{\text{f}} \text{AlI}_3(\text{c}) \) was evaluated.
Coughlin measured the enthalpy of solution of aluminium chloride and aluminium in 4M hydrochloric acid, similar to (c).

Gross and Haysen used combustion calorimetry to measure directly the enthalpy of formation of aluminium chloride

\[
\text{Al}(s) + \frac{3}{2} \text{Cl}_2(g) \rightarrow \text{AlCl}_3(s)
\]

Despite the seeming measure of agreement, there are several reasons why many of the values are open to doubt:

1. On dissolving aluminium halides in water or acid, hydrolysis results in the formation of considerable acid mist above the solutions, this being more marked for the bromide and iodide than the chloride (see references 87 and 88). This is bound to affect the accuracy of calorimetric results, especially early work where only one or two experiments were performed by each worker to determine enthalpies of solution.

2. The hydrolysis, particularly for the bromide and iodide, is slow (see also Part Two, p. 61), while all the calculations assume that the final state is attained almost instantaneously.

3. The enthalpy of hydrolysis might be expected to depend on the aluminium halide to water ratio. Indeed, for aluminium chloride, the enthalpy of dilution has been shown to be appreciable and negative over a large concentration range, due to hydrolysis. This is in contrast to most common electrolytes, which have only small enthalpies of dilution, positive to
ca 1M, and negative in more dilute solution.

(4) The assumption is made in some methods that solution yields simple, equated $\text{Al}^{3+}$ and $\text{Al}^{-}$ ions. In fact, the situation is very complicated, for the nature of aluminium halides in solution is very sensitive to both pH and concentration changes, and the literature contains many papers postulating species such as $[\text{Al}(\text{OH})(\text{H}_{2}\text{O})_{5}]^{2+}$ (98, 99, 100, 106), $\text{Al}_{2}(\text{CH})_{5}\text{Cl} (102)$, $[\text{Al}(\text{H}_{2}\text{O})_{n}(\text{CH})_{2}]^{4+} (101)$, $[\text{Al}(\text{CH})\text{Cl}_{2}]_{2} (103)$ etc. in neutral or acid solution. Only for very dilute solutions at high or low pH does the situation seem at all clear-cut; for dilute solutions in strong acid ($\text{pH} \lesssim 2$) the cation $\text{Al}(\text{H}_{2}\text{O})_{6}^{3+}$ is predominant$^{100}$, while for dilute solutions in alkali ($\text{pH} \approx 13$) the anion $\text{Al}(\text{OH})_{4}^{-}$ is exclusively present$^{104}$, 105.

The relevance of these points can be demonstrated by comparing the literature values for the enthalpies of solution of aluminium halides in water (table 22).

For aluminium chloride, these values compare with an enthalpy of solution in 4.360M hydrochloric acid of $-72.51 \pm 0.05$ kcal mol$^{-1}$ (303K)$^{93}$, whereas for simple solution and complete dissociation to $\text{Al}^{3+} + 3\text{Cl}^{-}$, the effect of the hydrochloric acid would be expected to be only slight.
It has also been shown\(^ {112} \) that the enthalpy of formation (and hence the enthalpy of solution) of aluminium chloride in hydrochloric acid is a linear function of the acid molality, with a spread of \(-7.6 \text{ kcal mol}^{-1}\) from \(m = 0\) to \(m = 5\).

In view of the uncertainty, it was decided to redetermine the enthalpies of formation of aluminium bromide and iodide by measuring the enthalpies of solution in aqueous alkali, quantities not previously determined. The method used was to measure the enthalpy of solution of aluminium bromide (or iodide) in 0.1 M sodium hydroxide solution containing sodium.
chloride, and the enthalpy of solution of aluminium chloride in alkali containing sodium bromide (or iodide)

(1) $\text{AlX}_3(c) + n\text{NaOH} + 3\text{NaCl}(aq) \xrightarrow{\text{AH}_1} [\text{NaAl(OH)}_4 + 3\text{NaCl} + 3\text{NaX} + (n-4)\text{NaOH}](a_l)$

(2) $\text{AlCl}_3(c) + n\text{NaOH} + 3\text{NaX}(a_l) \xrightarrow{\text{AH}_2} [\text{NaAl(OH)}_4 + 3\text{NaCl} + 3\text{NaX} + (n-4)\text{NaOH}](a_l)$

whence

$$\Delta H^o_{\text{AlX}_3(c)} = \Delta H_2 - \Delta H_1 + 3\Delta H^o_{\text{NaX}(a_l)} - 3\Delta H^o_{\text{NaCl}(a_l)} + \Delta H^o_{\text{AlCl}_3(c)}.$$ 

Besides the fact that aluminium is present in only one form, this method has the advantage over other solution methods that the acid mist formed above the solution is greatly reduced.
EXPERIMENTAL

Chemicals

The same stocks of aluminium halides were used as described in Part Two (p. 65).

Analar grade (BDH Ltd) sodium chloride, sodium bromide and sodium iodide (stated purities 99.9%, 99% and 99.5% minimum respectively) were dried in an oven at 120°C before use.

0.1003 sodium hydroxide (BDH volumetric solution) was used directly.

Apparatus

Preliminary experiments showed the reactions to be extremely rapid, suited to constant-temperature-environment (CTE) calorimetry.

The calorimeter was an all-glass Dewar type (diagram 26), which has been used successfully in the Department for several years, and is fully described elsewhere113, 114. Since a typical experiment involves long periods of waiting for equilibration, experiments were performed in overlapping pairs using two separate calorimeters. Minor modifications to the original design and the procedure for using the calorimeters are well described by Coley115.

Temperature changes were monitored by an F53 thermistor (Standard Telephone and Cable Ltd.) connected as one arm of a
DIAGRAM 26  C.T.E. CALORIMETER
wheatstone bridge, and with a resistance change of ca 180 Ω per degree at 25°C. The only modification of Coley's procedure was that the out-of-balance bridge potential was registered by a chart recorder (Bryans Ltd; model 27000) in place of a galvanometer. It can readily be shown (Appendix One, p.187) that the displacement from zero shown by the recorder is linear with respect to changes in thermistor resistance, and by suitable adjustment of the recorder sensitivity, resistances could be read off directly from a scale of 1 Ω = 1 cm of chart paper.

The sample was contained in a thin-walled glass ampoule, made with two small, very thin, glass bulbs, one above the level of sample in the ampoule and one below, such that on breaking the two bulbs calorimeter liquid could flow through the ampoule to ensure complete mixing. The ampoule was filled with aluminium halide in a dry-box, being weighed before and after filling. The ampoule of aluminium halide was broken into 200 ml of 0.100N sodium hydroxide containing sodium chloride or sodium bromide (sodium iodide).

Calibration was achieved by an electric heater of measured power (ca one watt), consisting of a spiral of wire sited in a thin-walled glass well filled with light oil of good thermal conductivity.

The system was returned to the bath temperature (25.00 ± 0.01°C) between reaction and calibration by the addition of
small pieces of solid carbon dioxide into the cooling tube.

Procedure

From Part Three, p. 110,

\[
\Delta H = \frac{f \times P \times t}{4184} \times \frac{M}{w} \times \frac{\ln \frac{R_1}{R_2}}{\ln \frac{R_3}{R_4}}
\]

\[
f = \frac{R_{\text{obs}}}{R_{\text{exp}}} \times \text{to allow for resistance of leads}
\]

\[
M = \text{Molecular weight of sample.}
\]

\[
w = \text{Weight of sample used.}
\]

The resistance-time plots for pre- and post-reaction, and pre- and post-calibration, periods can be regarded as linear for times less than ca ten minutes (Appendix Two, p. 189).

As the reaction was quick (complete in under 0.5 min.), the values for the resistances before and after reaction, \( R_1 \) and \( R_2 \), could be obtained by extrapolating the straight fore- and after-periods to the time of ampoule breaking. In drawing the line for the after-period, the typical "overshoot" which occurred for ca one minute immediately following the reaction, was ignored. During this time, the system was not at equilibrium, the temperature of the calorimetric liquid being higher than that of the glass, due to the former being stirred and having a much better thermal capacity.

However, electrical heating during calibration took ca four minutes, and allowance had to be made for the heat lost during this period when extrapolating the fore- and after-
periods. This was achieved by Dickinson's "equal areas" method\textsuperscript{115, 116, 117}. In the present circumstances, this is simplified by the linear form of the resistance-time plot during the heating period (ignoring the times needed for equilibration on switching the heater on and off, which are both small and also tend to cancel each other). $R_3$ and $R_4$ are obtained by extrapolating the fore- and after-periods to the time corresponding to the halfway point between the intersections of the linear heating period with the extended fore- and after-periods (see Appendix Three and diagram 27).

The performance of the two calorimeters was checked periodically using the enthalpy of neutralization of THAM, as described in Part Three, p.\textsuperscript{107}. The results were

<table>
<thead>
<tr>
<th>1st Calorimeter</th>
<th>2nd Calorimeter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. THAM (g)</td>
<td>$\Delta H$ (kcal mol$^{-1}$)</td>
</tr>
<tr>
<td>1.1033</td>
<td>7.17</td>
</tr>
<tr>
<td>1.0246</td>
<td>7.03</td>
</tr>
<tr>
<td>1.0596</td>
<td>8.05</td>
</tr>
<tr>
<td>1.0757</td>
<td>7.03</td>
</tr>
<tr>
<td>1.0567</td>
<td>7.11</td>
</tr>
<tr>
<td>1.0554</td>
<td>7.16</td>
</tr>
<tr>
<td>0.9293</td>
<td>7.13</td>
</tr>
</tbody>
</table>

Ignoring run 3 for set 1, which lies outside three standard deviations from the mean, this gives
<table>
<thead>
<tr>
<th>1st Calorimeter</th>
<th>2nd Calorimeter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean</strong> = -7.11 kcal mol(^{-1})</td>
<td><strong>Mean</strong> = -7.12 kcal mol(^{-1})</td>
</tr>
<tr>
<td><strong>Standard deviation</strong> = 0.021 kcal mol(^{-1})</td>
<td><strong>Standard deviation</strong> = 0.015 kcal mol(^{-1})</td>
</tr>
<tr>
<td>of the mean kcal mol(^{-1})</td>
<td>of the mean kcal mol(^{-1})</td>
</tr>
</tbody>
</table>
RESULTS

In all the reactions, the solid aluminium halide dissolved rapidly. In all cases, despite the alkali, some acid mist was formed above the solution in the calorimeter, this being most pronounced for aluminium bromide. However, the mist quickly dissolved, and had no apparent effect on the reaction trace. Analyses of the end products for halide confirmed that very little, if any, halide was lost.

\[ \text{AlBr}_3 + \text{NaOH/NaCl} \]

(i) Br (found) $1.46 \times 10^{-3}$ g. atom (ii) Br (found) $1.60 \times 10^{-3}$ g. atom
Br (calc) $1.47 \times 10^{-3}$ g. atom Br (calc) $1.62 \times 10^{-3}$ g. atom
99.3% 98.6%

\[ \text{AlI}_3 + \text{NaOH/NaCl} \]

(i) I (found) $1.42 \times 10^{-3}$ g. atom (ii) I (found) $1.22 \times 10^{-3}$ g. atom
I (calc) $1.43 \times 10^{-3}$ g. atom I (calc) $1.23 \times 10^{-3}$ g. atom
99.3% 99.2%

\[ \text{AlCl}_3 + \text{NaOH/NaI} \]

(i) Cl (found) $2.65 \times 10^{-3}$ g. atom (ii) Cl (found) $2.54 \times 10^{-3}$ g. atom
Cl (calc) $2.70 \times 10^{-3}$ g. atom Cl (calc) $2.56 \times 10^{-3}$ g. atom
98.1% 99.2%

The results are given in tables 23-26.
\[ \ce{Al3r_3(s) + [nNaOH + 3NaCl](aq) \rightarrow nNaAl(OH)_4 + 3NaBr + 3NaCl + (n-4)NaOH(aq)} \]

### TABLE 23

**ENTHALPY OF REACTION FOR**

Run one in the 1st Calorimeter is greater than three standard deviations from the mean, and was hence ignored.

**Mean** = \(-101.46\) kcal mol\(^{-1}\) \((-424.50\) kJ mol\(^{-1}\)]

**Standard deviation of the mean** \(= \sqrt{\frac{6.39}{12 \times 11}} = 0.22\) kcal mol\(^{-1}\) \((0.92\) kJ mol\(^{-1}\)]

**Standard deviation from the mean** \(= \sqrt{\frac{6.39}{11}} = 0.77\) kcal mol\(^{-1}\) \((3.22\) kJ mol\(^{-1}\)]
**TABLE 24**

**ENTALPY OF REACTION FOR**

\[
\text{AlCl}_3(\text{o}) + 3\text{NaOH} + 3\text{Na}_3\text{r}](\text{aq}) \xrightarrow{\Delta H^\circ_{\text{R}}} \text{NaAl(OH)}_4 + 3\text{NaCl} \\
+ 3\text{Na}_3\text{r} + (n-4)\text{NaOH}(\text{aq})
\]

<table>
<thead>
<tr>
<th>1st CALORIMETER</th>
<th>2nd CALORIMETER</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>wt. AlCl_3 g</strong></td>
<td><strong>wt. AlCl_3 g</strong></td>
</tr>
<tr>
<td>0.1175</td>
<td>0.0478</td>
</tr>
<tr>
<td>0.1090</td>
<td>0.0605</td>
</tr>
<tr>
<td>0.0916</td>
<td>0.1202</td>
</tr>
<tr>
<td>0.0602</td>
<td>0.0929</td>
</tr>
<tr>
<td>0.0831</td>
<td>0.0799</td>
</tr>
<tr>
<td></td>
<td>0.1103</td>
</tr>
</tbody>
</table>

Mean = -84.40 kcal mol^{-1} [-353.14 kJ mol^{-1}]

Standard deviation of the mean = \(\sqrt{\frac{5.87}{11 \times 10}}\) = 0.23 kcal mol^{-1} [0.96 kJ mol^{-1}]

Standard deviation from the mean = \(\sqrt{\frac{5.87}{10}}\) = 0.77 kcal mol^{-1} [3.22 kJ mol^{-1}]
TABLE 25
ENTHALPY OF REACTION FOR

\[
\text{AlI}_3(aq) + (n\text{NaOH}+3\text{NaCl})_{aq} \rightarrow \text{NaAl(OH)}_4+3\text{NaI}+3\text{NaCl} + (n-4)\text{NaOH}_{aq}
\]

<table>
<thead>
<tr>
<th>1st CALORIMETER</th>
<th>2nd CALORIMETER</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. AlI₃</td>
<td>n</td>
</tr>
<tr>
<td>g</td>
<td></td>
</tr>
<tr>
<td>0.0753</td>
<td>108.3</td>
</tr>
<tr>
<td>0.2527</td>
<td>32.3</td>
</tr>
<tr>
<td>0.2735</td>
<td>29.3</td>
</tr>
<tr>
<td>0.2351</td>
<td>34.7</td>
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<tr>
<td>0.2340</td>
<td>34.8</td>
</tr>
<tr>
<td>0.1630</td>
<td>49.5</td>
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</table>

Mean = \(-105.89\) kcal mol\(^{-1}\) [-443.04 kJ mol\(^{-1}\)]

Standard deviation of the mean = \(\sqrt{\frac{1.525}{11 \times 10}} = 0.12\) kcal mol\(^{-1}\) [0.50 kJ mol\(^{-1}\)]

Standard deviation from the mean = \(\sqrt{\frac{1.525}{10}} = 0.39\) kcal mol\(^{-1}\) [1.63 kJ mol\(^{-1}\)]
### Table 26

**Enthalpy of Reaction for**

\[
\begin{align*}
\text{AlCl}_3(c) + [n\text{NaOH} + 3\text{NaI}]_{aq} \xrightarrow{\Delta H^\circ} & [\text{NaAl(OH)}_4 + 3\text{NaI} + 3\text{NaCl} + (n-4) \\
& \quad \text{NaCl}]_{aq}
\end{align*}
\]

<table>
<thead>
<tr>
<th>1st CALORIMETER</th>
<th>2nd CALORIMETER</th>
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<td><strong>wt. AlCl\textsubscript{3}</strong></td>
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<td><strong>n</strong></td>
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<td><strong>(-\Delta H) \text{ kcal mol}^{-1})</strong></td>
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<tr>
<td><strong>Mean</strong></td>
<td>(-34.19 \text{ kcal mol}^{-1} )</td>
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<tr>
<td><strong>Standard deviation</strong></td>
<td>(\sqrt{\frac{10.26}{12 \times 11}} = 0.23 \text{ kcal mol}^{-1}[1.17 \text{ kJ mol}^{-1}])</td>
</tr>
</tbody>
</table>
THERMISTOR RESISTANCE (Ω)

TIME (MINUTES)

Diagram 27

Typical Al₂O₃ reaction trace

Table 25, 1st Calor., No. 4.

Ampoule Broken (R₁)

Recorder Setting Checked

R₂

Recorder Setting Changed
Diagram 27 (Cont.)

Thermistor Resistance (Ω)

Time (Minutes)

Heater Switched On

Heater Off

R₃

R₄

4929

4880

AIₓ₂ Calibration
DISCUSSION

Enthalpy of Formation of Aluminium Halides

From the introduction,
\[ \Delta H^0_{\text{f}} \text{AlX}_3(c) = \Delta H^0_{\text{f}}(2) - \Delta H^0_{\text{f}}(1) + 3\Delta H^0_{\text{f}} \text{NaX(aq)} \]
\[ -3\Delta H^0_{\text{f}} \text{NaCl(aq)} + \Delta H^0_{\text{f}} \text{AlCl}_3(c) \]

This ignores any contributions from

(i) Enthalpies of dilution arising from slight differences in concentration between the final products of reactions (1) and (2). The random spread of experimental results with regard to the weight of aluminium halide used shows these to be negligible.

(ii) Enthalpies of mixing of \( \text{NaX(aq)} \) + \( \text{NaCl(aq)} \) + \( \text{NaOH(aq)} \). These too might be expected to be very small, and would tend to cancel each other.

The ancillary data used in the calculations were from reference 81 unless otherwise stated:

\[ \Delta H^0_{\text{f}} \text{NaCl.736H}_2\text{O} = -97.265 \text{ kcal mol}^{-1} \]
\[ \Delta H^0_{\text{f}} \text{NaBr.607H}_2\text{O} = -86.140 \text{ kcal mol}^{-1} \]
\[ \Delta H^0_{\text{f}} \text{NaI.525H}_2\text{O} = -70.610 \text{ kcal mol}^{-1} \]
\[ \Delta H^0_{\text{f}} \text{AlCl}_3(c) = -168.80 \pm 0.20 \text{ kcal mol}^{-1} \] (from reference 94).
From which

\[ \Delta H_f^\circ Al_2O_3(c) = -118.4 \pm 0.6 \text{ kcal mol}^{-1} \]

\[ \Delta H_f^\circ Al_2O_3(c) = -118.4 \pm 0.6 \text{ kcal mol}^{-1} \]

**Enthalpy of Formation of Aqueous Sodium Aluminate**

From the equation

\[ AlCl_3(c) + [nNaOH+3NaX](aq) \xrightarrow{\Delta H_f^\circ(2)} \text{NaAl(OH)}_4+3NaCl + 3NaX + (n-4)NaOH(aq) \]

the standard enthalpy of formation of aqueous sodium aluminate can be obtained as

\[ \Delta H_f^\circ \text{NaAl(OH)}_4(aq) = \Delta H_f^\circ(2) + \Delta H_f^\circ AlCl_3(c) - 3\Delta H_f^\circ NaCl(aq) + 4\Delta H_f^\circ NaOH(aq) \]

Using the values given above in conjunction with

\[ \Delta H_f^\circ NaOH.555H_2O = -112.12 \text{ kcal mol}^{-1} \text{ (reference 81)} \]

leads to a value of

\[ \Delta H_f^\circ \text{NaAl(OH)}_4.15000 H_2O = -409.9 \pm 0.4 \text{ kcal mol}^{-1} \]

\[ \Delta H_f^\circ \text{NaAl(OH)}_4.15000 H_2O = -409.9 \pm 0.4 \text{ kcal mol}^{-1} \]

This compares with the value obtained from references 71 and 81 (origin not given) by adding \( \Delta H_f^\circ Na^+(aq) + \Delta H_f^\circ Al(OH)_4^-(aq) \) both at unit molality, of

\[ \Delta H_f^\circ \text{NaAl(OH)}_4.55.6H_2O = -413.5 \text{ kcal mol}^{-1} \]

\[ \Delta H_f^\circ \text{NaAl(OH)}_4.55.6H_2O = -413.5 \text{ kcal mol}^{-1} \]
PART FIVE

THE PHOSPHORYL CHLORIDE

- BORON TRICHLORIDE COMPLEX
INTRODUCTION

Although easily prepared and handled, the 1:1 complex between phosphoryl chloride and boron trichloride has been the source of much controversy in recent years, on two main fronts:

(1) The nature and interpretation of its infra-red spectrum
(2) The value for the enthalpy of dissociation,

\[ \text{POCl}_3 \cdot 3\text{Cl}_3(c) \rightleftharpoons \text{POCl}_3(g) + 3\text{Cl}_3(g). \]

(1) INFRA-RED SPECTRUM AND INTERPRETATION

Four possible structures could be conceived for the adduct:

(a) Coordination through oxygen to boron, \( \text{Cl}_3\text{PO} \rightarrow \text{BCl}_3 \)

(b) Coordination through chlorine to boron, \( \text{Cl}_2\text{POCl} \rightarrow \text{BCl}_3 \)

(c) As the extreme case of (b), an ionic structure involving the tetrachloroborate ion, \( [\text{POCl}_2]^+ [\text{BCl}_4]^- \).

(d) A combination of ionic and dative covalent bonding, \( [\text{POCl}_2 \cdot 3\text{Cl}_2]^+ \text{Cl}^- \)

Examples of both (a)\(^{118-121}\) and (b)\(^{122,123}\) are described in the literature, while the \( \text{BCl}_4^- \) ion is also well documented\(^{124}\). Conductimetric\(^{125}\) and \( ^{37}\text{Cl} \)-exchange\(^{126}\) experiments have shown...
that there is negligible ionization for solutions of the complex in boron trichloride, while in phosphoryl chloride solution there is appreciable ionization, the nature of which is not yet certain. Although ionization to (c) is more likely, (d) cannot be completely ruled out.  

Certain predictions can be made about the shifts expected in the infra-red spectrum of (a), (b), (c) and (d) relative to the frequencies in pure boron trichloride and pure phosphoryl chloride. In (a), (b) and (c), but not (d), the boron goes from $sp^2$ to $sp^3$ on complexing, which has the consequence of lowering the $3-Cl$ stretching frequencies ($995 \text{ cm}^{-1}$ and $956 \text{ cm}^{-1}$ in $^{10}B$ and $^{11}B$ boron trichloride respectively for the asymmetric stretching mode). In case (c), the characteristic $3Cl_4^-$ frequencies should be observed. With coordination through oxygen, as in (a) and possibly (d), a considerable lowering of the $P=O$ stretching mode is expected ($1290 \text{ cm}^{-1}$ in phosphoryl chloride), accompanied by a raising of the $P-Cl$ stretching modes ($595 \text{ cm}^{-1}$ (gas) or $531 \text{ cm}^{-1}$ (liquid) for the asymmetric mode, $490 \text{ cm}^{-1}$ (gas) or $485 \text{ cm}^{-1}$ (liquid) for the symmetric mode, in phosphoryl chloride). For (b) and (c) the opposite should occur, with a very slight increase in the $P=O$ stretching mode, and a marked decrease in the $P-Cl$ frequencies, similar to the situation occurring in the complexes of nitrosyl and acetyl halides. With (a) and (b), vibrations associated with the newly formed
PO-3 or PCl-3 bonds are expected. However, these should be only weak if the pattern of other boron-oxygen complexes is followed.

Three main groups of workers have published the infrared spectrum of $\text{POCl}_2\cdot\text{BCl}_3$. Waldington et al. used a nujol mull between sodium chloride or potassium bromide plates. They found a strong band at 1290 cm$^{-1}$, which they assigned to an unchanged P-O stretching frequency. Despite this, they postulated structure (a) on the basis of a weak band at 1190 cm$^{-1}$, which they assigned to a B-O stretching mode, and a large decrease in B-Cl stretching frequencies (700 cm$^{-1}$ and 657 cm$^{-1}$ for $^{10}\text{B}$ and $^{11}\text{B}$). In a second paper, an additional weak band at 1150 cm$^{-1}$ was assigned to an $^{11}\text{B}$-O stretching mode, and the 1190 cm$^{-1}$ band to $^{10}\text{B}$-O. The bands assigned to P-Cl stretching modes showed only very slight frequency shifts.

Gerrard et al. also concluded from a nujol mull (potassium chloride plates) that the P=O stretching frequency was unchanged on complexing. This, together with the presence of what was termed a "$\text{BCl}_4^-$" envelope in the 700 cm$^{-1}$ region led them to the conclusion that the ionic structure (c) was correct. They also claimed that a slight increase in the P-Cl stretching frequencies (583 cm$^{-1}$ and 490 cm$^{-1}$) was compatible with a change in hybridization from tetrahedral $\text{POCl}_3$ to planar $\text{POCl}_2^+$. No trace was found of the 1190 cm$^{-1}$
or 1150 cm\(^{-1}\) bands assigned by Waddington to 3-O stretching modes.

Goubeau et al.\(^{127}\) obtained the low-temperature infra-red spectrum and the room temperature Raman spectrum as part of a systematic investigation of POX\(_3\) : MX\(_3\) complexes (X = halogen, M = S, Al, Ga or In). At low temperatures, no 1290 cm\(^{-1}\) band was found, but a strong band at 1157 cm\(^{-1}\) was attributed to a stretching mode of P-O in the adduct. Strong bands at 713 cm\(^{-1}\) and 332 cm\(^{-1}\) were assigned to 3-O stretching and 3-O-P bending modes respectively. The asymmetric 3-Cl stretching modes were lowered to the region 727 – 795 cm\(^{-1}\), while the asymmetric and symmetric 3-Cl stretching modes showed a marked increase to 642 cm\(^{-1}\) and 505 cm\(^{-1}\) respectively. The room temperature Raman spectrum gave substantially analogous results. Goubeau concluded on the basis of these assignments that structure (a) was correct. He also stated, giving no details, that the conflicting results of Waddington and Gerrard were due to dissociation, hydrolysis and reaction with the cell windows.

In addition to the three main works mentioned, SenGupta\(^{132}\) obtained the infra-red spectrum of the adduct in carbon disulphide and cyclohexane solutions, when the spectra compared in their salient features with those of Waddington, but not with those of Goubeau i.e. P-O stretching mode at 1300 cm\(^{-1}\), 3-O band at 1200 cm\(^{-1}\).

The object of the present work was to try to resolve the
discrepancies between the various results, both by repeating some of the published work and by obtaining spectra using different experimental techniques. The conditions employed were:

(i) Gas phase infra-red.

(ii) Low temperature, solid phase infra-red.

(iii) Room temperature solid phase infra-red, obtained by subliming the adduct on to the windows of a gas cell.

(iv) Room temperature nujol mill.

(v) Room temperature solid phase Raman spectrum.

EXPERIMENTAL

Chemicals

Commercial boron trichloride (B.D.H. Ltd; minimum stated purity 98%) and phosphoryl chloride (B.D.H. Ltd; minimum stated purity 98%) were both further purified by fractional vacuum distillation through -45°C (chlorobenzene slush bath) to -94°C (toluene slush bath). The purity of samples of each were tested by chloride analysis (Volhard's method) following alkaline hydrolysis.

Results were

POCl₃

Cl (found) 63.9% by mass
Cl (calc) 63.3% by mass

BCl₃

Cl (found) 90.8% by mass
Cl (calc) 90.8% by mass
The 1:1 adduct was prepared by condensing an excess of boron trichloride on to phosphoryl chloride, allowing the two to mix at room temperature, then pumping off excess boron trichloride at -45°C. A white solid remained. A sample of the adduct was analysed for chloride:

Cl (found) 73.7% by mass
Cl (calc) 73.6% by mass.

Apparatus and Procedure

Gas phase spectra were obtained using the cell described previously (p. ), fitted with potassium bromide windows. 1:1 mixtures of gaseous phosphoryl chloride and boron trichloride were obtained by utilizing the vapour above the solid complex. Using the grease-free vacuum line described earlier (p. 53; diagram 10), a sample of the solid complex was placed in the mixing vessel, the line evacuated, and then isolated from the pump. With the remainder of the line, apart from the gas cell, saturated with vapour from the complex, the tap on the mixing vessel was shut to isolate the solid. Vapour was then allowed to fill the gas cell. This procedure ensured that the vapour in the cell was below saturation pressure, to avoid any sudden, slight, local cooling leading to condensation on the cell windows.

Room temperature spectra of the sublimed solid complex were obtained by making intentional use of the condensation
problem mentioned above. The gas cell was opened to vapour from the solid complex, which was maintained by hand-heat at a slightly higher temperature. With the gas cell saturated with vapour, the tap was shut, and the cell windows subjected to a flow of slightly-cooled air, when a thin film of solid condensed on the plates. With practice, the thickness of the film could be controlled by the degree of heating or cooling applied. After the spectrum had been run, the cell was re-connected to the vacuum line, all volatile products pumped off, and a further spectrum obtained.

Room temperature nujol mull spectra were obtained by grinding a sample of the adduct with a little nujol (dried over sodium wire) in a dry-box, and then spreading a thin film of the mull between potassium bromide plates. The spectrum was run as quickly as possible after making the mull (ca two minutes) and again periodically after leaving the plates + mull open to the atmosphere.

The low temperature (ca -100°C) spectra of the solid were obtained using the apparatus described previously (p. 56), by spraying vapour from the complex on to a liquid nitrogen-cooled caesium iodide plate.

All the infra-red spectra were run on a Perkin Elmer 337 machine.

The Raman spectrum of a sample of the solid, contained in a capillary tube, was obtained on a Carey 81 instrument (6328Å exciting line).
RESULTS AND DISCUSSION

Table 27 compares the bands found in the various infrared spectra, including for reference some literature spectra. In diagrams 23-35, the spectra are reproduced, in the region 1300-400 cm\(^{-1}\), for the following systems:

28 Phosphoryl chloride gas.
29 Boron trichloride gas.
30 1:1 gaseous mixture.
31 Solid adduct at low temperatures (ca -100\(^{\circ}\)C).
32 Sublimed solid adduct at room temperature.
33 The cell windows after the solid in 32 had been pumped off.
34 Nujol mull.
35 The nujol mull in 34 after standing for 45 minutes.

The spectra of gaseous phosphoryl chloride and gaseous boron trichloride agreed very well with published data (references 139 and 140 respectively). The spectrum of the gaseous mixture showed no deviations from a simple superimposition of the individual spectra, with no evidence for association.

In contrast, the spectrum of a 1:1 solid mixture at -100\(^{\circ}\)C showed almost total association. The P=O stretching mode of free phosphoryl chloride (1320 cm\(^{-1}\) in the gas, 1290 cm\(^{-1}\) in the liquid) was absent or very weak. A weak band was present at 1280 cm\(^{-1}\), but since this coincides with an overtone (2 x 635 cm\(^{-1}\)), it is impossible to say whether
DIAGRAM 28 INFRA-RED SPECTRUM OF POCI₃(g)
DIAGRAM 30  INFRA-RED SPECTRUM OF $\text{POCl}_3 / \text{BCl}_3$ (g)

TRANSMITTANCE %

WAVENUMBER CM$^{-1}$

1300  1100  900  700  500
Diagram 31: Low Temperature Infra-Red Spectrum of $\text{POCl}_3 \cdot \text{BCl}_3 (s)$
INFRA-RED SPECTRUM OF
POCl₃·BCl₃ (SUBLIMED SOLID)

DIAGRAM 32

TRANSMITTANCE %

WAVENUMBER CM⁻¹
DIAGRAM 33  INFRA-RED SPECTRUM OF KBr WINDOWS USED FOR DIAGRAM 32, AFTER PUMPING CELL
Diagram 35  Infra-red spectrum of POCl₃, BC₃, (Nujol mull) after standing for 45 minutes.
<table>
<thead>
<tr>
<th>POCl₃</th>
<th>BCl₃</th>
<th>POCl₃ + BCl₃</th>
<th>POCl₃ + 3Cl₂</th>
<th>Goubeau, Low Temperature (s)</th>
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<th>Sublimed Kidney, Solid</th>
<th>Mull</th>
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<th>Sublimed Kidney, Solid</th>
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of the POC\textsubscript{3}•BCl\textsubscript{3} complex, \(\text{cm}^{-1}\)

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<th>MULL (NUJOL MULL)</th>
<th>WADDINGTON (NUJOL MULL)</th>
<th>GERRARD (NUJOL MULL)</th>
<th>ASSIGNMENT</th>
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<td>1290 s</td>
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<td>2 (P=0 str.) adduct</td>
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<td>1190 m</td>
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<td>2 (\nu_3) (asy. str.) \textsubscript{10}BCl\textsubscript{3}</td>
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<td>1150 w</td>
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<td>2 (\nu_3) (asy. str.) \textsubscript{11}BCl</td>
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</table>

P-Cl

\(\nu_1\) (sym. str.) adduct

\(\nu_3\) (asy. str.) \textsubscript{10}BCl\textsubscript{3}(g) or \(\text{cm}^{-1}\) (1)

\(\nu_3\) (asy. str.) \textsubscript{11}BCl\textsubscript{3}(g) or \(\text{cm}^{-1}\) (1)

\(\nu_4 + \nu_5\) POC\textsubscript{3}(g)

\(\nu_4 + \nu_6\) POC\textsubscript{3}(g)
<table>
<thead>
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<th>BCl₃ (g)</th>
<th>POCl₃ + BCl₃ (g)</th>
<th>POCl₃·BCl₃</th>
<th>Goubeau, Low Temp. (s)</th>
<th>Solid, Sublimed Solid, After Pumping</th>
<th>Nujol Mull*</th>
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<td></td>
<td>700</td>
<td>s(br)</td>
<td></td>
</tr>
<tr>
<td>670 w</td>
<td></td>
<td></td>
<td></td>
<td>670 m</td>
<td>670 s</td>
<td></td>
</tr>
<tr>
<td>620 w</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>595 vs</td>
<td>595 s</td>
<td>590 m</td>
<td>595 w</td>
<td>590 s</td>
<td>585 s</td>
<td></td>
</tr>
<tr>
<td>490 s</td>
<td>485 m</td>
<td>490 m</td>
<td>490 m</td>
<td>485 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>475 s</td>
<td>485 m</td>
<td>475 m</td>
<td>475 m</td>
<td>480 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>455 s</td>
<td>455 m</td>
<td>455 m</td>
<td>455 m</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

s = strong intensity  v = very
m = medium intensity  br = broad
w = weak intensity    sh = shoulder
(CONTINUED)

<table>
<thead>
<tr>
<th>NUJOL MULL CH STANDING</th>
<th>WADDINGTON (NUJOL MULL)</th>
<th>GERRARD (NUJOL MULL)</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>773 s</td>
<td>(3-Cl str.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>743 s</td>
<td>(+ C-O str. ?)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>715 s</td>
<td>(adduct</td>
<td></td>
</tr>
<tr>
<td>700 m</td>
<td>700 v</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>670 w</td>
<td>670 m</td>
<td>s(br)</td>
<td>BCl₄⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BCl₄⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2 ν₃ PCl₃(g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(P-Cl ass. str.) adduct</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>585 s</td>
<td>583 s</td>
<td>590 v</td>
<td>ν₂(P-Cl ass. str.) PCl₃(g) or (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>490 m</td>
<td>(P-Cl ass. str.) adduct</td>
</tr>
<tr>
<td></td>
<td></td>
<td>490 m</td>
<td>ν₁(P-Cl ass. str.) PCl₃(g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>490 v</td>
<td>ν₂ 10BCl₃(g) or (1) + ν₁POCl₃(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>490 m</td>
<td>ν₂ 11BCl₃(g) or (1)</td>
</tr>
</tbody>
</table>

} = only one band observed  
asy. = asymmetric  
# = bands due to nujol omitted  
sy. = symmetric  
str. = stretching mode  
? = not assignable
the free P=O stretching mode was totally absent; its intensity was certainly greatly reduced. In its place, a new, strong, band appeared at 1130 cm\(^{-1}\), attributable to the stretching frequency of a P=O group acting as Lewis base. In addition, the 3-Cl asymmetric stretching modes (995 cm\(^{-1}\) and 955 cm\(^{-1}\) in free \(^{10}\)\(^{3}\)\(^{13}\)Cl\(_2\) and \(^{11}\)\(^{3}\)\(^{13}\)Cl\(_2\)) were shifted down to the 800-700 cm\(^{-1}\) region, though the broad, ill-defined, nature of the bands made precise assignments impossible. The P-Cl asymmetric stretching mode increased from 595 cm\(^{-1}\) to 635 cm\(^{-1}\), while the symmetric stretching mode also increased, from 430 cm\(^{-1}\) (gas) or 435 cm\(^{-1}\) (liquid) to 505 cm\(^{-1}\). These results agree well with those of Wartenberg and Goubeau\(^{127}\), the only discrepancies being that the completed P=O mode occurred ca 40 cm\(^{-1}\) lower (1130 cm\(^{-1}\)) than found by Goubeau (1167 cm\(^{-1}\)), and there was no sign of the weak 1067 cm\(^{-1}\) band found by Goubeau. In the present work, the bands were not sharp enough to assign a P=O stretching mode (c.f. Goubeau 713 cm\(^{-1}\)). The shifts observed in the low-temperature spectrum are compatible only with an oxygen-coordinated species, structure (a).

The room temperature spectra of the adduct, both as sublimed solid and nujol mull, were vastly more complicated than those obtained at low temperatures. The solid film spectrum in particular contained many more bands, some of which were attributable to dissociated vapour, present in the cell as
a result of the technique used. The complexed P=O stretching mode (1140 cm\(^{-1}\)) was still present, though with a much reduced intensity compared to the low temperature spectrum. In addition, however, strong bands for free phosphoryl chloride were also observed (1320 cm\(^{-1}\) gas, and 1290 cm\(^{-1}\) liquid), suggesting a large degree of dissociation. This was confirmed by the presence of both complexed and free \(\text{P}-\text{Cl}\) stretching frequencies (ca 750 cm\(^{-1}\) and 995/955 cm\(^{-1}\) respectively). The complexed stretching modes slowly moved, with time, to lower frequencies ca 700 cm\(^{-1}\). On attempting to pump all of the adduct out of the cell, all bands disappeared except for strong peaks at 700 cm\(^{-1}\) and 670 cm\(^{-1}\), and a weaker peak at 1260 cm\(^{-1}\), attributable to the \(\text{BCl}_4^-\) ion in K\(\text{BCl}_4\)\(^{141}\). This clearly demonstrates that reaction has occurred with the potassium bromide windows, a phenomenon which probably explains the "\(\text{BCl}_4^-\) envelope" of Gerrard et al.\(^{130,131}\). The 1190 cm\(^{-1}\) assignment of a "\(\text{P}-\text{O}\) stretch" by Waddington et al.\(^{121,122}\) also could not be substantiated. Only a very weak band was found in this area, this being attributable to an overtone of free phosphoryl chloride (2 \(\nu_4\), \(\text{P}-\text{Cl}\) asymmetric stretching mode, 590 cm\(^{-1}\)). \(\text{P}-\text{Cl}\) symmetric stretching frequencies for both complexed and free phosphoryl chloride were present (505 cm\(^{-1}\) and 490 cm\(^{-1}\)), but for the asymmetric stretching modes, only the free band could be detected, (590 cm\(^{-1}\)), the complexed band (ca 640 cm\(^{-1}\)) being hidden. The only prominent feature
in the spectrum which could not be assigned was a \(3\)-type band of moderate intensity at \(330\ \text{cm}^{-1}\). This had not been reported previously, and could not be assigned to any conceivable reaction products, such as free phosphoryl chloride, free boron trichloride, phosphoryl bromide, boron tribromide, tetrachloroborate, tetra bromoborate, phosphorus acids etc.

The nujol mull spectrum confirmed the findings of the solid film spectrum, the main difference lying in the much weaker relative intensities of the adduct bands and of the \(880\ \text{cm}^{-1}\) band. In addition, on standing, the very weak \(1180\ \text{cm}^{-1}\) band increased markedly in intensity, and shifted to \(1190\ \text{cm}^{-1}\), accompanied by the appearance of new bands at \(3200\ \text{cm}^{-1}\) and \(800\ \text{cm}^{-1}\), in the \(\text{O-H}\) stretching and bending regions. These observations together suggest hydrolysis, and the spectrum of boric acid, \(\text{H}_3\text{BO}_3\), indeed contains strong bands at \(3150\ \text{cm}^{-1}\), \(1190\ \text{cm}^{-1}\) and \(800\ \text{cm}^{-1}\). The other main band, at \(1428\ \text{cm}^{-1}\), would be obscured by nujol peaks. This leads to the possibility that some, at least, of the intensity of the \(1190\ \text{cm}^{-1}\) band of Waddington et al. may have been due to a hydrolysis product most of the other hydrolysis product bands being obscured by stronger peaks.

Due to fluorescence, the room-temperature Raman spectrum of the solid adduct could not be obtained above \(ca.\ 500\ \text{cm}^{-1}\). The bands that were observed agreed with the Raman spectrum of Goubeau\(^{127}\), as shown in Table 23.
TABLE 28  
RAMAN SPECTRUM OF $\text{POCl}_3$, $\text{SCl}_3$

<table>
<thead>
<tr>
<th>Present Work</th>
<th>Combesau</th>
<th>POCl$_3$(1)$^{127,139}$</th>
<th>SCl$_3$(1)$^{127}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>161s</td>
<td>170a</td>
<td>193a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>173w</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>223a</td>
<td>225a</td>
<td>255a</td>
<td>3-Cl in-plane</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>deform.</td>
<td></td>
</tr>
<tr>
<td>265a</td>
<td>265w</td>
<td>267a</td>
<td>3-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>deform.</td>
<td></td>
</tr>
<tr>
<td>306m</td>
<td>306w</td>
<td>337a</td>
<td>3-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>deform.</td>
<td></td>
</tr>
<tr>
<td>376a</td>
<td>332a</td>
<td></td>
<td>3-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>deform.</td>
<td></td>
</tr>
<tr>
<td>443a</td>
<td>445a</td>
<td>472a</td>
<td>3-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>sym. str.</td>
<td></td>
</tr>
<tr>
<td>505a</td>
<td>505a</td>
<td>436a</td>
<td>3-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>sym. str.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3-Cl asym. str.</td>
<td></td>
</tr>
<tr>
<td>642a</td>
<td>531w</td>
<td></td>
<td>3-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>asym. str.</td>
<td></td>
</tr>
<tr>
<td>713a</td>
<td></td>
<td></td>
<td>3-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>asy. str.</td>
<td></td>
</tr>
<tr>
<td>727sh</td>
<td></td>
<td>955w</td>
<td>11-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>asy. str.</td>
<td></td>
</tr>
<tr>
<td>750sh</td>
<td></td>
<td></td>
<td>11-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>asy. str.</td>
<td></td>
</tr>
<tr>
<td>765sh</td>
<td></td>
<td>995w</td>
<td>10-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>asy. str.</td>
<td></td>
</tr>
<tr>
<td>795sh</td>
<td></td>
<td></td>
<td>10-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>asy. str.</td>
<td></td>
</tr>
<tr>
<td>1167w</td>
<td>1300m</td>
<td></td>
<td>P-Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>asy. str.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>P-O str.</td>
<td></td>
</tr>
</tbody>
</table>

It appears that there is far less dissociation under the conditions required for the room-temperature Raman spectrum than for the corresponding infra-red spectra.

In conclusion, it may be stated that these results are only compatible with an adduct involving coordination through oxygen, but which is readily dissociated at ambient temperatures.
Values for the enthalpy of dissociation

\[ \text{PCCl}_3 \cdot \text{BCl}_3(s) = \text{PCCl}_3(g) + \text{BCl}_3(g) \] (AH diss) can be derived from three different sources:

(1) Burg and Roas determined the vapour pressure-temperature curve for the complex in the region 10-35°C from which, assuming complete dissociation in the gas, they obtained

\[ \log_{10} K_p = 15.803 - \frac{5714}{T} \]

Since

\[ \frac{\Delta H^0}{RT^2} = \frac{d \ln K_p}{dT} \]

this gives

\[ \Delta H \text{ diss} = 26.1 \text{ kcal mol}^{-1} (109.2 \text{ kJ mol}^{-1}) \]

From vapour density measurements, it was calculated that the vapour was at least 90% dissociated at a temperature (not quoted) higher than for the pressure measurements.

(2) Gutmann et al. measured the enthalpies of solution in phosphoryl chloride, of boron trichloride and of the adduct \( \text{PCCl}_3 \cdot \text{BCl}_3 \), whence

\[ \text{BCl}_3(1) + \text{PCCl}_3(1) \rightarrow \text{PCCl}_3 \cdot \text{BCl}_3(s) \]

\[ \Delta H = -7.9 \text{ kcal mol}^{-1} [-33.1 \text{ kJ mol}^{-1}] \]

Using values from references 71 and 81 for the latent heats of vaporization of boron trichloride and phosphoryl chloride (5.6 and 9.2 kcal mol\(^{-1}\) respectively),
\[ \Delta H_{\text{diss}} = 22.7 \text{ kcal mol}^{-1} \] 

(111) Finch, Gardner and Sen Gupta measured the enthalpy of hydrolysis of the adduct in water:

\[ \text{HCl}_2\cdot\text{BCl}_3(s) + (n + 6)\text{H}_2\text{O}(1) = \text{H}_3\text{PO}_4 + \text{H}_3\text{BO}_3 + 6\text{HCl} + n\text{H}_2\text{O}(1) \]

\[ \Delta H_{\text{hyd}} = -123.2 \text{ kcal mol}^{-1} \] 

This leads to:

\[ \Delta H^0_{\text{f}, \text{HCl}_2\cdot\text{BCl}_3(s)} = -271.2 \text{ kcal mol}^{-1} \] 

and, using values of

\[ \Delta H^0_{\text{f}, \text{HCl}_2(g)} = -134.3 \text{ kcal mol}^{-1} \]

\[ \Delta H^0_{\text{f}, \text{BCl}_3(g)} = -96.7 \text{ kcal mol}^{-1} \]

this gives:

\[ \Delta H_{\text{diss}} = 40.2 \text{ kcal mol}^{-1} \]

Finch et al. confirmed this value by repeating their measurements with a fresh sample of adduct. Burg and Ross' values for the dissociation pressures were also confirmed, suggesting that the different values for the enthalpy of dissociation could not be attributed to differences between the samples of adduct used. It was postulated that one explanation for the discrepancies might be association in the gas phase at 298K, contrary to Burg's assumption i.e.

\[ \text{HCl}_2\cdot\text{BCl}_3(s) \leftrightarrow \text{HCl}_2\cdot\text{BCl}_3(g) \leftrightarrow \text{HCl}_2(g) + \text{BCl}_3(g) \]

It was the object of the present work to test this postulate by measuring the association in mixtures of the two gases.
Experimental

Chemicals

The same sample of POCl₃·BCl₃ was used as for the spectroscopy (p. 151).

The water used for calibrating the pressure gauge was distilled from acid permanganate, and degassed by four trap-to-trap vacuum distillations.

The cyclohexane for testing the pressure gauge was a high purity sample (Phillips Petroleum Co. Ltd; stated minimum purity 99.99%), used directly after drying (grade 4A molecular sieves) and degassing.

Pure, distilled propionic anhydride (minimum purity 98%) was already available in the Department.

Apparatus and Procedure

Pressures were measured using a strain gauge (Bell and Howell Ltd; type 4-366). Pressures experienced by a thin, stainless steel, diaphragm were converted to a controlled strain in a Wheatstone bridge whose four arms consisted of strain gauge windings. A rod welded to the centre of the diaphragm transmitted its displacement to a spring element, the movement of which tilted two of the windings so as to increase their strain, and hence resistance, and the other two windings so as to decrease their strain and resistance. The system was arranged such that the output voltage of the out-of-balance Wheatstone bridge was a linear function of the applied
pressure. The nominal 40mV full range output (0–ca 500 torr) was amplified to ca 10V, giving 0.015 volts per torr. The voltage was registered on a digital voltmeter (Marconi Ltd; TF 2660) reading correct to ±1mV.

The pressure transducer was incorporated in the apparatus shown in diagram 36. The metal take-off from the transducer was sealed into glass tubing of slightly wider diameter using Torrseal resin (Varian Ltd.). The apparatus was fitted with a greaseless tap and joint for connection to the vacuum line. The volume of the apparatus up to the seating of the tap was determined as 561.2 and ±0.1 ml by filling with water from a burette and pipette.

In use, the apparatus was immersed, to the level of the top of the transducer, in a water jacket which could be thermostatted to ±0.1°C. Readings could be taken in the range 0–60°C. When taking a series of measurements over a wide range of temperatures, care had to be exercised that the tap maintained a good seal at its lower seating. Since the coefficient of thermal expansion is much greater for Teflon than glass, on cooling there was a tendency for leaking, while at higher temperatures there was a danger that undue force might crack the tap.

The thermal characteristics of the apparatus were determined in the form of a voltage-temperature graph, after evacuating the vessel to 10⁻⁴ torr (i.e. effectively zero
DIAGRAM 36  PRESSURE-MEASURING APPARATUS

Transducer

Greaseless Tap

To Vacuum Line

Level Of Immersion
DIAGRAM 37  CALIBRATION OF TRANSDUCER
       AT ZERO PRESSURE
pressure). Diagram 37 shows this to approximate to a straight line in the range 25-55°C, with a slope of 0.00307 per degree. A mishap to the apparatus at a later stage necessitated repeating this determination, when readings taken over a wider temperature range (0-60°C) showed the graph to be an extremely gentle curve, approximating to a straight line for smaller temperature ranges. These graphs were used to compensate all measurements for thermal dependence of the voltage by arbitrarily selecting the 25.0°C value as a standard, and correcting voltage readings at other temperatures to 25°C.

The corrected voltage output from the transducer was calibrated in terms of pressure by using water as a standard. The corrected voltage-pressure calibration graph is shown in diagram 38 for the region 0-100 torr. This line can be fitted to the equation

\[ P = 170.373V + 21.733 - 0.07 \]

where \( P \) = Pressure in torr + 0.07 torr.

\( V \) = Corrected voltage in volts.

To test the accuracy of the system, the vapour pressure-temperature curve for cyclohexane was determined in the range 25-40°C (100-200 torr). Cyclohexane has often been suggested as a standard for pressure measurements, and its vapour pressure has been carefully studied. The experimental points are plotted on the same graph as the literature curve in diagram 39.
CORRECTED VOLTAGE (VOLTS)
DIAGRAM 39  VAPOUR PRESSURE OF CYCLOHEXANE

VAPOUR PRESSURE (TORR)

TEMPERATURE °C

Literature Curve
• Experimental Values
However, many of the $\text{POCl}_2/\text{BCl}_3$ pressures to be studied lay in a much lower range (0-20 torr) than the vapour pressures of cyclohexane. So, as a further check on the sensitivity of the apparatus at low pressures (1-6 torr), the vapour pressure-temperature curve was determined for a sample of pure propionic anhydride, already available in the laboratory. The results are plotted against the literature curve in diagram 40. The literature values are from very old papers, so it is possible that their accuracy may be questioned to account for the discrepancy from the present values.

Two experiments were performed for phosphoryl chloride-boron trichloride gaseous mixtures, one in the range 25-55°C, the second from 10-40°C. Below 10°C, maximum permissible pressures (ca 3 torr) were so small that changes in pressure (ca 0.01 torr per degree or lower) could not be registered accurately. The vapour from the solid adduct was again used as the source of a 1:1 gaseous mixture of boron trichloride and phosphoryl chloride. The pressure-measuring apparatus was attached to the grease-free vacuum line (p. 53 diagram 10). The mixing vessel was filled with $\text{POCl}_3/\text{BCl}_3$, evacuated, weighed, and re-attached to the vacuum line. With the line evacuated and isolated from the pump, the adduct was opened to the pressure apparatus while being thermostatted slightly below the lowest temperature at which readings were to be taken (i.e. ca 20°C for the first experiment, ca 8°C for the
VAPOUR PRESSURE OF PROPIONIC ANHYDRIDE

DIAGRAM 40

VAPOUR PRESSURE (TORR)

TEMPERATURE °C

CURVE

LITERATURE
second). This was necessary to achieve as high a gas pressure as possible while avoiding the problem of possible condensation during the experiment. After allowing a few minutes for equilibration, the tap on the pressure apparatus was shut, and the remaining vapour condensed back into the mixing vessel, which could then be removed from the vacuum line and reweighed to determine the weight of vapour in the pressure vessel.

As the result of an accidental pressure shock between experiments one and two, the characteristics of the transducer were altered, necessitating recalibration. The sensitivity remained almost unchanged, but all voltage readings were decreased by a near-constant amount. Hence the calibration graphs in diagrams 37 and 38 apply only to the first experiment. The calibrations for the second experiment gave lines nearly parallel to the originals, but displaced by ca -0.149V.

RESULTS AND DISCUSSION

The results of the two experiments are given in table 29.
### Table 29

**Pressure vs Temperature for Gaseous \( \text{POCl}_3 - \text{BCl}_3 \) Mixtures**

**Experiment One:** 0.0890 g \( \text{POCl}_3 - \text{BCl}_3 \) used.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Compensated Voltage (V)</th>
<th>Pressure (torr)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.005</td>
<td>-0.005</td>
<td>21.43</td>
<td>24.6</td>
</tr>
<tr>
<td>0.020</td>
<td>0.003</td>
<td>21.99</td>
<td>30.6</td>
</tr>
<tr>
<td>0.038</td>
<td>0.009</td>
<td>22.41</td>
<td>34.8</td>
</tr>
<tr>
<td>0.060</td>
<td>0.015</td>
<td>22.84</td>
<td>40.0</td>
</tr>
<tr>
<td>0.080</td>
<td>0.021</td>
<td>23.26</td>
<td>44.7</td>
</tr>
<tr>
<td>0.102</td>
<td>0.027</td>
<td>23.68</td>
<td>50.2</td>
</tr>
<tr>
<td>0.119</td>
<td>0.031</td>
<td>23.96</td>
<td>54.4</td>
</tr>
<tr>
<td>0.102</td>
<td>0.027</td>
<td>23.68</td>
<td>50.0</td>
</tr>
<tr>
<td>0.080</td>
<td>0.022</td>
<td>23.33</td>
<td>46.0</td>
</tr>
<tr>
<td>0.060</td>
<td>0.015</td>
<td>22.84</td>
<td>39.8</td>
</tr>
<tr>
<td>0.044</td>
<td>0.011</td>
<td>22.54</td>
<td>35.0</td>
</tr>
<tr>
<td>-0.003</td>
<td>-0.003</td>
<td>21.57</td>
<td>25.1</td>
</tr>
</tbody>
</table>

**Experiment Two:** 0.03550 g \( \text{POCl}_3 - \text{BCl}_3 \) used.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Compensated Voltage (V)</th>
<th>Pressure (torr)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.384</td>
<td>-0.342</td>
<td>3.13</td>
<td>10.1</td>
</tr>
<tr>
<td>-0.375</td>
<td>-0.343</td>
<td>8.06</td>
<td>13.3</td>
</tr>
<tr>
<td>-0.364</td>
<td>-0.341</td>
<td>8.20</td>
<td>16.7</td>
</tr>
<tr>
<td>-0.353</td>
<td>-0.339</td>
<td>8.34</td>
<td>20.2</td>
</tr>
<tr>
<td>-0.335</td>
<td>-0.337</td>
<td>8.48</td>
<td>25.6</td>
</tr>
<tr>
<td>-0.317</td>
<td>-0.334</td>
<td>8.65</td>
<td>30.7</td>
</tr>
<tr>
<td>-0.302</td>
<td>-0.333</td>
<td>8.76</td>
<td>35.4</td>
</tr>
<tr>
<td>-0.285</td>
<td>-0.331</td>
<td>8.90</td>
<td>40.4</td>
</tr>
</tbody>
</table>

Assuming an equilibrium

\[
A(g) = B(g) + C(g)
\]

then

\[
p_{\text{observed}} = p_A + p_B + p_C
\]
and

\[ \rho \text{ calculated} = \rho A + \frac{1}{3} (\rho 3 + \rho C) \]

where \( \rho \text{ observed} = \text{measured pressure} \)

\[ \rho \text{ calculated} = \text{pressure calculated from the simple gas equation assuming total association} \]

\[ \rho A,3,C = \text{partial pressure A,3,C.} \]

This leads to

Degree of dissociation, \( \alpha = \frac{\rho \text{obs} - \rho \text{calc}}{\rho \text{calc}} \)

Equilibrium, \( K_r = \frac{(\rho \text{obs} - \rho \text{calc})^2}{2 \rho \text{calc} - \rho \text{obs}} \)

The values for the degree of dissociation, \( \alpha \), thus calculated are given in table 30.

These values for the degree of dissociation neglect any deviations from Raoult's law due to Van der Waals' repulsive forces. However, Brown has shown that such interactions can be neglected at pressures less than ca 20 torr.

Calculated values for the equilibrium constant, \( K_r \), are not given because, as \((2 \rho \text{calc} - \rho \text{obs})\) is so small in every case (often less than the limits of error attached to \( \rho \text{obs} \)), the wide limits of error which must be assigned to \( K_r \) render it almost meaningless. These limits range from \( \pm 40\% \) upwards, corresponding to limits of \( \pm 25\% \) or more on \( \ln K_r \); hence a graph of \( \ln K_r \) against the reciprocal of the temperature to determine \( \Delta H \) is not sensible.
<table>
<thead>
<tr>
<th>p obs (torr)</th>
<th>p calc (torr)</th>
<th>a</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>± 0.07</td>
<td>± 0.007</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**EXPERIMENT ONE**

| 21.43 | 10.89 | 0.968 | 297.8 |
| 21.57 | 10.91 | 0.977 | 298.3 |
| 21.99 | 11.11 | 0.979 | 303.8 |
| 22.41 | 11.26 | 0.990 | 303.0 |
| 22.54 | 11.31 | 0.993 | 309.2 |
| 22.84 | 11.45 | 0.995 | 313.0 |
| 22.84 | 11.48 | 0.990 | 313.2 |
| 23.26 | 11.63 | 1.000 | 317.9 |
| 23.33 | 11.67 | 0.999 | 319.2 |
| 23.63 | 11.82 | 1.003 | 323.2 |
| 23.63 | 11.83 | 1.001 | 323.4 |
| 23.96 | 11.93 | 1.000 | 327.6 |

**EXPERIMENT TWO**

| 8.13 | 4.07 | 0.99 | 283.3 |
| 8.06 | 4.11 | 0.95 | 286.5 |
| 8.20 | 4.16 | 0.97 | 239.9 |
| 8.34 | 4.21 | 0.98 | 293.4 |
| 8.48 | 4.23 | 0.98 | 298.8 |
| 8.65 | 4.36 | 0.93 | 303.9 |
| 8.76 | 4.43 | 0.93 | 308.6 |
| 8.90 | 4.50 | 0.98 | 313.6 |
The results show that there is no association between phosphoryl chloride and boron trichloride in the gas phase above ca. 45°C. Below this temperature, association is possible, but sufficiently slight to have only a marginal effect on the value of $\Delta H$ derived by Burg and Ross.

Further, in view of the relative agreement between the values obtained by tensimetry and solution calorimetry in phosphoryl chloride (Gutmann), it would seem that the solution hydrolysis method (Finch, Gardner and Sen Gupta) ought to be reinvestigated.
APPENDIX ONE

JUSTIFICATION OF THE PROPORTIONALITY OF THE DISPLACEMENT FROM ZERO ON CHART RECORDER AGAINST CHANGE IN RESISTANCE OF THERMISTOR

\[ V \text{ volts} \]

\[ \begin{array}{c}
X \\
b \\
\text{CR} \\
a \\
T \\
R_V \\
0 \text{ volts}
\end{array} \]

\[ \text{BATTERY (VOLTAGE V)} \]

\[ \text{CR = Chart recorder} \]
\[ X = \text{Matched pair of resistances } (\pm 1\%) 4.3 \, \text{k} \Omega \]
\[ R_V = \text{Variable resistance } (\equiv R_o) \]
\[ T = \text{Thermistor resistance} \]

Displacement from zero & Applied voltage (Maker's specifications)

Applied voltage = \( V_a - V_b \)

\[ = \left( \frac{T}{T + X} \right) V - \left( \frac{R}{R + X} \right) V \]
As $T$ changes, let $T = R_0 + \Delta R$ ($R_0 = T$ at balance)

**: Applied voltage**

$$V = V - \frac{R_0}{R_0 + \Delta R + x} \frac{V}{R_0 + x}$$

$$\frac{d\text{(applied voltage)}}{d\Delta R} = V \left[ \frac{-R_0}{(R_0 + \Delta R + x)^2} + \frac{1}{(R_0 + \Delta R + x)} \right]$$

$$= \frac{Vx}{(R_0 + \Delta R + x)^2}$$

$$= \frac{Vx}{(R_0 + x)^2 + 2\Delta R(R_0 + x) + (\Delta R)^2}$$

Since $\Delta R = \text{ca} \ 5 \Omega$

$R_0 = \text{ca} \ 4900 \Omega$

$x = 4.3 \ k\Omega$

$$\frac{d\text{(applied voltage)}}{d\Delta R} = \text{constant to a very good approximation.}$$

($< 0.1\%$)
APENDIX TWO

JUSTIFICATION OF LINEAR EXTRAPOLATION OF

RESISTANCE-TIME FORE- AND AFTER-PERIODS

\[ \frac{dT}{dt} = K(T-T_j) + \omega \]  \hspace{1cm} \text{Newton's law of cooling}

where \( T \) = Temperature (K)

\( t \) = Time (minutes)

\( T_j \) = Jacket temperature (K)

\( K, \omega \) = constants.

\[ \frac{1}{K} \ln \begin{bmatrix} K(T-T_j) + \omega \end{bmatrix} = t + c \] \hspace{1cm} \text{by integration}

where \( c \) = integration constant.

\[ T = \frac{1}{K} e^{K(t+c)} - \frac{\omega}{K} + T_j \]

But \( T = \frac{3}{\ln \frac{R}{R'}} \) \hspace{1cm} \text{Thermistor relationship}

\( A, B \) = Thermistor constants

\( R \) = Thermistor resistance

\[ \frac{1}{A} = \ln \frac{R}{R'} \]

Differentiating,

\[ \frac{dR}{dt} = (\pm) \frac{R}{B} (\ln \frac{R}{A})^2 e^{K(t+c)} \]

(Because of the modulus in \( \ln | \cdot | \), the sign of \( \frac{dR}{dt} \) must be determined separately).
Differentiating again,

\[ \frac{d^2 R}{dt^2} = \frac{R}{3^2} \left[ (\ln \frac{R_o}{R})^4 + 2 (\ln \frac{R}{R_j})^3 \right] e^{2K(t+c)} \]

For a straight fore- and after-period,

\[ \frac{dR}{dt} = \text{constant} \]

and \( \frac{d^2 R}{dt^2} = 0 \)

Clearly, this is not rigorously true. However, typical values are 73, 113, 115

\[ B = 3 \times 10^3 K \]
\[ A = 0.05 \Omega \]
\[ K = -0.01 \text{ min}^{-1} \]
\[ \omega = 0.003 K \text{ min}^{-1} \]
\[ R_j = 5000 \Omega \]
\[ R = 4950 \Omega \]

Now, consider the after-period,

\[ c = \frac{1}{K} \ln \left[ \left( \frac{R}{R_o} \right)^3 - \frac{R_j}{R_j} \right] + \omega \]

where \( R_o \) = Resistance at start of after-period

\( R_j \) = Thermistor resistance corresponding to jacket temperature

\[ \therefore c \approx + 580 \text{ min for after period} \]
\[
\begin{align*}
\frac{dR}{dt} \text{ (at } t = 0) &= \frac{-5 \times 10^3 (11.5)^2}{3 \times 10^3} (-0.003) \\
&= 0.7 \Omega \text{ min}^{-1} \\
\frac{d^2R}{dt^2} \text{ (at } t = 0) &= \frac{5 \times 10^3}{9 \times 10^6} \left[17300 + 3040 \right] (5 \times 10^{-6}) \\
&\quad - \frac{10^{-2} \times 5 \times 10^3 (11.5)^2 (3 \times 10^{-3})}{3 \times 10^3} \\
&= -0.006 \Omega \text{ min}^{-2}
\end{align*}
\]

Normally, extrapolation is from \( t = 0 \) min to \( t \approx -2 \) min for the after-period, during which time the slope of the resistance-time plot would change from, say, 0.700 \( \Omega \text{ min}^{-1} \) to 0.712 \( \Omega \text{ min}^{-1} \) giving a maximum error in the extrapolated resistance of \( \pm 0.024 \Omega \). Since resistances can only be read accurately to \( \pm 0.1 \Omega \), the possible error will be insignificant. Although the after-period only has been considered, similar results (with a smaller \( \frac{d^2R}{dt^2} \) in fact) can be obtained for the fore-period.

In conclusion, it can be stated that the extrapolation of fore- and after-periods as straight lines is justified provided

1. The lines are drawn using as short a section of the fore- and after-periods as practicable (ignoring the "overshoot" which occurs at the start of the after-period)
2. The extrapolation periods are less than five minutes
3. The apparatus design should be such as to minimise the values for \( \frac{dR}{dt} \) (i.e. \( k \) and \( \omega \) both very small).
For the heating period \((t_A \rightarrow t_B)\)

\[
\frac{dT}{dt} = K (T - T_j) + \omega \\
= K \int_{t_A}^{t_B} (T - T_j) \, dt + \omega \\
\frac{t_B - t_A}{t_B - t_A}
\]

Newton's law

\(\frac{dT}{dt}\) is rate of change of temperature due only to heat loss to jacket, radiation, and heat of stirring.
where \[
\int_{t_A}^{t_B} (T - T_j) \, dt \quad = \quad \text{Mean temperature difference,} \\
(T - T_j) \, \text{over the heating period.}
\]

Now, total "corrected" temperature change on heating, \( \Delta T \) is given by

\[
\Delta T = T_B - T_A - \left( \frac{dT}{dt} \right) (t_B - t_A)
\]

where \( \left( \frac{dT}{dt} \right)' \quad = \quad \text{Mean rate of temperature change during this period.} \)

\[
= T_B - T_A + K \int_{t_A}^{t_B} (T - T_j) \, dt + \omega(t_B - t_A)
\]

\[
= T_B - T_A + K (T_B - T_A)(t_B - t_A)
\]

\[
= T_B - T_A \rightarrow k(\beta + \gamma + \delta + \epsilon) + \omega(t_B - t_A)
\]

If \( t_x \) is a time such that \( A = C \), then

\[
\Delta T = T_B - T_A \rightarrow k(\beta + \gamma + \delta + \epsilon) + k(\omega + \omega + \omega)
\]

\[
= T_B - T_A \rightarrow k(T_B - T_j)(t_B - t_A)
\]

\[
= [k(T_B - T_j)(t_B - t_A) + \omega(t_B - t_A)] + [k(T_A - T_j)(t_A - t_j) + \omega(t_A - t_A)]
\]

\[
\Delta T = T_B - T_A + (T_B - T_j) + (T_A - T_j)
\]
assuming the slope of the after-period is constant and equal to \( K (T_3 - T_j) + \omega \), and similarly for the fore-period

\[
\frac{dT}{dt} = K (T_A - T_j) + \omega
\]

\[
\therefore \Delta T = T_4 - T_3
\]

The resistances \( R_4 \) and \( R_3 \) corresponding to \( T_4 \) and \( T_3 \) are obtained by extrapolating the fore- and after-periods of the resistance-time graph to the time \( t \), i.e., to the mid-point of the heating period.

A recent paper by Gunn\textsuperscript{145} draws similar conclusions to Appendices Two and Three on the use of thermistors, but from a different approach. The present techniques correspond to Gunn's "hybrid extrapolation method" (reference 145, p. 32, line 10). A typical reaction and calibration, where nearly equal temperature rises occur in each, would correspond to Gunn's set 5 and set 7 respectively (reference 145, p. 26, table 1).
REFERENCES


25. R.S. Mulliken. JACS (1950) 72 600
ibid (1952) 74 811
J. Phys. Chem. (1952) 56 801


    ibid (1907) 56 49
    [See also J.W. Mellor "Inorganic and Theoretical Chemistry" (1923) V 326 Longmans].
46. J.D. Corbett and N.W. Gregory. JACS (1953) 75 5233.
47. J.D. Corbett and N.W. Gregory. JACS (1953) 80 1526.
50. C.T. Mortimer "Reaction Heats and Bond Strengths" (1952) 112. Pergamon Press.


68. M. Trautz. Z. Elektrochem. (1933) 21 323.


84. J. D. Cox. Tetrahedron (1952) 13 1337.
121. T.C. Waddington and P. Klanberg. JCS (1960) 2339.
123. H. Greenwood and K. Wade. JCS (1957) 1516.
<table>
<thead>
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140. R.E. Scruby, J.R. Lacher and J.D. Park. JACS (1951) 19 388.


144. H.C. Brown and M. Gerstein. JACS (1950) 72 2323.

The enthalpy of hydrolysis and thermodynamic properties of carbonyl bromide

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By use of an adiabatic solution-reaction calorimeter, the standard enthalpy of formation of carbonyl bromide, $\Delta H_f(COBr_2, 1, 298 \text{ K})$, was determined as $-(34.7 \pm 0.2) \text{ kcal mol}^{-1}$.

1. Introduction
Evidence for the existence and nature of weak interactions between carbonyl halides and Lewis acids, e.g. aluminium halides, is difficult to interpret. Thus COCl$_2$ and Al$_2$Cl$_6$ are known$^{(1)}$ to form a solid complex, with no halogen exchange, as shown by radio-chlorine measurements.$^{(2)}$ Vibrational spectroscopic work in this laboratory$^{(3)}$, however, indicates that halogen exchange between COCl$_2$ and Al$_2$Br$_6$ occurs, and further that there is (apparently catalytic) decomposition of COBr$_2$ by aluminium tribromide, following very weak complex formation. Clearly there are considerable differences between COBr$_2$ and COCl$_2$, and this has prompted the present determination of the standard enthalpy of formation of carbonyl bromide. Despite its easy synthesis and thorough spectroscopic characterization$^{(5)}$ thermodynamic data are limited to the results of an early$^{(5)}$ investigation of the equilibrium constant of the reaction:

$$\text{COBr}_2(g) = \text{CO}(g) + \text{Br}_2(g),$$

at 346.4 and 454.8 K, whence $\Delta H_f(COBr_2, g) = -23 \text{ kcal mol}^{-1}$.† Vapour pressure studies$^{(6)}$ corrected to 298 K, give $\Delta H_v = 7.4 \text{ kcal mol}^{-1}$, and hence$^{(7)}$ $\Delta H_f(COBr_2, l) = -30.4 \text{ kcal mol}^{-1}$. Limits of error are impossible to assign from the literature data. In the present work, a solution calorimetric method at 25 °C was employed for the measurement of the standard enthalpy of hydrolysis.

2. Experimental
MATERIALS
COBr$_2$ was prepared from carbon tetrabromide and concentrated sulphuric acid according to established procedures$^{(6)}$, distilled, allowed to stand over mercury, re-distilled (normal boiling temperature 64.5 °C; literature$^{(6)}$ 64 to 65 °C), and

† Throughout this paper cal = 4.184 J, M = mol dm$^{-3}$, and Torr = (101.325/760) kN m$^{-2}$.
stored in a grease-free vacuum line at liquid nitrogen temperature. For sampling, fractionation through \(-30\) to \(-96^\circ\text{C}\) was employed, the product being slightly discoloured. Samples were periodically checked by use of standard silver nitrate titrimetry on aqueous hydrolysates. It was found necessary to shake the liquid vigorously in stoppered flasks for not less than 40 min to ensure complete reaction. A typical result, using a 0.3339 g sample, was: Br(found), 84.6 per cent by mass; Br(calc.), 85.1 per cent by mass. Starch-iodide tests on the aqueous hydrolysate showed the free bromine content of COBr\(_2\) to be less than 0.5 per cent by mass.

**CALORIMETER AND PROCEDURE**

The calorimeter was an all-glass Dewar type, containing 200 cm\(^3\) of liquid, and similar to that previously reported\(^{8}\) but modified to operate adiabatically. The design of the automatic adiabatic control is the same (with minor modifications) as that employed in the Gallenkamp Adiabatic Bomb Calorimeter; full details are available elsewhere\(^{9}\) and will be forwarded on application. Before (i) and after (ii) runs using carbonyl bromide, the system was checked using the enthalpy of neutralization of tris(hydroxy-methyl)aminomethane (THAM) in excess aqueous 0.1 M hydrochloric acid. Results were: (i), \(-7.11\) and (ii), \(-7.11\) kcal mol\(^{-1}\); literature\(^{10}\) \(-7.109 \pm 0.001\) kcal mol\(^{-1}\). For this calorimetric system the standard deviation of the mean for this reaction has been shown\(^{10}\) to be \(+0.02\) kcal mol\(^{-1}\).

The reaction studied was:

\[
\text{COBr}_2(l) + n\text{H}_2\text{O}(l) = \text{CO}_2(g) + (2\text{HBr} + (n-1)\text{H}_2\text{O})(l)
\]

for which we denote the enthalpy change by \(\Delta H_{\text{brd}}\). Thus

\[
\Delta H^\circ_{\text{f}}(\text{COBr}_2, l) = \Delta H^\circ_{\text{f}}(\text{CO}_2, g) + 2\Delta H^\circ_{\text{f}}(\text{HBr in } \frac{3}{4}(n-1)\text{H}_2\text{O}) - \Delta H^\circ_{\text{f}}(\text{H}_2\text{O}, l) - \Delta H_{\text{hyd}}.
\]

The water in the calorimeter was pre-saturated with carbon dioxide to ensure that the evolved gas would be in its standard state. Thermal effects arising from the decreased solubility of carbon dioxide with the small temperature increase during reaction and also from the mixing of \(\text{CO}_2(\text{aq})\) and \(\text{HBr}(\text{aq})\) were ignored. The rate of hydrolysis of samples of about 0.3 g in 200 cm\(^3\) of water was relatively slow \((t_k \approx 10\) min\) and initial results, using a constant-temperature-environment calorimeter, were abandoned in favour of adiabatic measurements. Reproducible calorimetric results were obtained only after all contact between carbonyl bromide and grease was eliminated. Hence all-glass ampoules, sealed directly from a grease-free high-vacuum line (about \(10^{-6}\) Torr) were employed to contain the carbonyl bromide, and no grease was used in the calorimetric head. Blank runs showed that the effect of heating the ampoule during sealing, and the enthalpy of ampoule breaking, were negligible. The amount of carbonyl bromide used in each run was measured by post-hydrolysis analysis. Corrections \(\Delta H_{\text{cert}}\) for the carbonyl bromide present in the gas phase in the ampoule were applied.

### 3. Results

The results are given in table 1 from which we obtain \(\Delta H_{\text{hyd}} = -(49.06 \pm 0.16)\) kcal mol\(^{-1}\), the uncertainty interval being calculated as \(\pm \left(\sum \delta_i^2/n(n-1)\right)^{1/2}\). Using
THERMODYNAMIC PROPERTIES OF CARBONYL BROMIDE

TABLE 1. Enthalpies of reaction, \( \Delta H_{\text{obs}} \), and enthalpies of hydrolysis, \( \Delta H_{\text{hyd}} \), of COBr\(_2\) at (25.0 ± 0.1) °C

<table>
<thead>
<tr>
<th>Run</th>
<th>( m(\text{COBr}_2) ) g</th>
<th>(-\Delta H_{\text{obs}}) kcal mol(^{-1})</th>
<th>(\Delta H_{\text{hyd}}) kcal mol(^{-1})</th>
<th>( n )</th>
<th>(-\Delta H_{\text{hyd}}) kcal mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3723</td>
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<td>5587</td>
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</tr>
<tr>
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<tr>
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<tr>
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<td>0.30</td>
<td>24615</td>
<td>49.31</td>
</tr>
</tbody>
</table>

accepted values,\(^{(7)}\) \( \Delta H_{f}^{\circ}(\text{CO}_2, g) = -(94.05 ± 0.01) \) kcal mol\(^{-1}\), \( \Delta H_{f}^{\circ}(\text{H}_2\text{O}, l) = -(68.315 ± 0.001) \) kcal mol\(^{-1}\), and \( \Delta H_{f}^{\circ}(\text{HBr in} \ \frac{1}{2}(n-1)\text{H}_2\text{O}) = -(29.01 ± 0.01) \) kcal mol\(^{-1}\) (mean value between \( n = 5000 \) and \( n = 25000 \)), we obtain \( \Delta H_{f}^{\circ}(\text{COBr}_2, l) = -(34.70 ± 0.21) \) kcal mol\(^{-1}\).

4. Discussion
Statistical thermodynamic functions, based on the usual harmonic oscillator rigid rotor approximation, have been evaluated\(^{(4)}\) for COBr\(_2\)(g). Using these results in conjunction with the enthalpies presented above, the standard Gibbs energy and entropy of formation of COBr\(_2\) (assumed ideal gas) have been calculated, and are compared with the corresponding functions for the analogous halides in table 2.

TABLE 2. Thermodynamic functions for COX\(_2\)(g), (X = F, Cl, Br), at 298.15 K

<table>
<thead>
<tr>
<th></th>
<th>COF(_2)</th>
<th>COCl(_2)</th>
<th>COBr(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\Delta H_{f}^{\circ}) kcal mol(^{-1})</td>
<td>151.7(^{a})</td>
<td>52.3(^{a})</td>
<td>27.3(^{a})</td>
</tr>
<tr>
<td>(-\Delta G_{f}^{\circ}) kcal mol(^{-1})</td>
<td>148.0(^{a})</td>
<td>48.9(^{a})</td>
<td>30.7(^{a})</td>
</tr>
<tr>
<td>(-\Delta S_{f}^{\circ}) cal K(^{-1}) mol(^{-1})</td>
<td>12.4</td>
<td>11.4</td>
<td>-11.5(^{a})(10.7(^{b}))</td>
</tr>
</tbody>
</table>

\(^{a}\) From reference 7.
\(^{b}\) Using data from references 4 and 7.
\(^{c}\) Calculated taking the standard state of bromine as gas.

The apparently anomalous value of the standard entropy of formation of COBr\(_2\) is due to the condensed standard state of bromine; as shown, this disappears if calculation using the appropriate value for bromine gas is adopted.

It is a pleasure to thank Mr. S. Ashdown for technical assistance with the preparation of COBr\(_2\); financial assistance from the Science Research Council (M.E.A.) and from the Central Research Fund of the University of London is also gratefully acknowledged.
REFERENCES