GRAPHITE LAMELLAR COMPOUNDS WITH THALLIUM(III) CHLORIDE AND THE BROMIDES OF THALLIUM(III), CADMIUM, MERCURY, IRON(II) AND URANIUM(V)

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Introduction

In contrast to the extensive studies of the intercalation of metal chlorides the reaction of graphite with metal bromides has received scant attention.

At present more than thirty metal chlorides are known to intercalate into the graphite lattice but only few graphite/metal bromide compounds have been reported until now.

CROFT claimed to have prepared AlBr3-graphite [1]. Recently SASA et al. [2] have investigated the reactivity of graphite with AlBr3 in detail. The formation of ternary compounds was observed with a maximum composition of C9AlBr3·Br2 and a lamellar structure of the 1st stage. Independently BALESTRENI [3] has obtained similar results. She investigated also the system graphite GaBr3·Br2 and succeeded in obtaining ternary compounds analogous to the graphite/AlBr3 compounds. AuBr3 is reported to give a 1st stage compound in which planar Au2Br6 molecules are located in the center between the carbon layers [4]. HÉROLD et al. have tried unsuccessfully to intercalate graphite with other metal bromides [4]. In commenting on their results they expressed the opinion that it may be possible to prepare other graphite/metal bromide compounds under proper conditions.

In fact we have revealed that TlBr3, CdBr2, HgBr2, FeBr2 and UBr5 do form intercalation compounds. The present paper gives some experimental and structural details of the new compounds. In order to draw a comparison with graphite/metal chloride compounds we have done a detailed study of the system graphite-TlCl3-Cl2. Results obtained from these investigations are given first. Apart from CROFT's report [1] of the occurrence of a graphite/TlCl3 compound there is no information concerning its composition or structure.

Graphite/TlCl3, Experimental

Purified natural graphite (flakes) from Passau, Germany, was used. Anhydrous TlCl3 was prepared by dehydrating TlCl3·4H2O using SOCl2. Several methods were explored to synthesize TlCl3-graphite:

1. Heating graphite and TlCl3 or TlCl in sealed tubes filled with chlorine vapour (table 1, samples 1-5); II before sealing liquid chlorine (2 ml) had been condensed onto the reaction mixture (sample 6);
III refluxing a solution of TlCl3 in SOCl2 with graphite with or without bubbling chlorine through the solution (sample 7); IV heating TlCl3 and graphite with SOCl2 in sealed tubes (sample 8). The samples were washed with a solution of chlorine in methanol in which TlCl3 and TlCl are soluble. With sample 6 TlCl3 and graphite were separated by flotation in liquid chlorine. Sample 6a is the same as 6 but washed with chlorine/methanol solution. 6b has been obtained from 6a by keeping several weeks in an evacuated vessel.

Results

It is shown from table 1 that the amount of intercalated TlCl3 and the chlorine to thallium ratio is dependent on the procedure employed. The intercalated TlCl3 is considerably more stable than the free TlCl3 which decomposes above 100 °C. For the 1st stage Lc was determined to be 977 pm and for the 2nd stage 1311 pm.

Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction temp. °C time (h)</th>
<th>Composition</th>
<th>Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>C18.7TlCl3.4</td>
<td>1+2</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>C12.1TlCl4.1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>C11.8TlCl4.4</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>C15.1TlCl3.8</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>C8.7TlCl4.1</td>
<td>1</td>
</tr>
<tr>
<td>6a</td>
<td>140</td>
<td>C11.6TlCl4.4</td>
<td>1</td>
</tr>
<tr>
<td>6b</td>
<td>140</td>
<td>C11.7TlCl3.4</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>75</td>
<td>C10.9TlCl3.2</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>140</td>
<td>C8.2TlCl3.1</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>60</td>
<td>C25.3TlBr5.2</td>
<td></td>
</tr>
<tr>
<td>9a</td>
<td>60</td>
<td>C25.3TlBr5.4</td>
<td></td>
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<tr>
<td>10</td>
<td>60</td>
<td>C21.8TlBr5.3</td>
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<tr>
<td>11</td>
<td>120</td>
<td>C19.5TlBr5.3</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>150</td>
<td>C18.6TlBr3.4</td>
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</tr>
</tbody>
</table>

Graphite/TlBr3, Experimental

TlBr and graphite were given into bromine. This mixture was heated in sealed tubes. The samples were washed with a solution of bromine in methanol.

Results and Discussion

The compositions of some samples are given in table 1. TlBr3-graphite resembles AlBr3- and GaBr3-graphite in forming ternary compounds. The composition of sample 9 may be formulated as C25.3TlBr3.2Br2. When kept in a vacuum it released bromine and a substance with the composition C25.3TlBr3.4 remained.

All listed compounds are of the 2nd stage type but with slightly different Lc values: 1358 pm (sample 9), 1358 (10), 1343 (11), 1340 (12). For compound 9 the
carbon layer spacing containing TlBr$_3$ is 1358 - 335 = 1023 pm. This is exactly the same value reported by SASA [2] for CdAlBr$_3$-Br$_2$. It was found to be 1000 pm for C$_{26}$AlBr$_3$-3 and our X-ray studies give a value of 1005 pm for sample 12. These similarities indicate that the structures of the two intercalated metal bromides closely resemble one another. It is likely that AlBr$_3$ and TlBr$_3$ are isomorphous. The structure of TlBr$_3$ is unknown.

TlBr$_3$-graphite has an unexpected high thermal stability. Free TlBr$_3$ decomposes at room temperature to intermediate compounds and finely to TlBr. As opposed to this TlBr$_3$-graphite can be heated to 120 °C without decomposition. Obviously TlBr$_3$ is stabilized by intercalation.

Graphite/TlCl$_2$/TlBr$_3$

By treating a 2nd stage graphite/TlBr$_3$ compound with TlCl$_2$ in refluxing SOCl$_2$ a 1st stage compound with the composition C$_{12.5}$TlCl$_{1.6}$Br$_{1.6}$ was obtained. As X-ray studies confirmed there is a regular sequence of TlCl$_3$-carbon-TlBr$_3$-carbon layers. Similar compounds with two different metal chlorides have been prepared previously [5].

Graphite/CdBr$_2$ and Graphite/HgBr$_2$

Intercalation compounds with CdCl$_2$ and HgCl$_2$ have been prepared by RÜDORFF et al. [1]. Since CdBr$_2$ and HgBr$_2$ have layer lattice structures resembling the CdCl$_2$ structure it was to be expected that this bromides can form graphite lamellar compounds. Indeed, we succeeded in obtaining graphite/CdBr$_2$ and graphite/HgBr$_2$ compounds by heating the anhydrous metal bromides with graphite in the presence of bromine. Attempts to intercalate these metal bromides in the absence of bromine were unsuccessful. The products were washed with dilute HNO$_3$ to remove excess CdBr$_2$ and with acetone to remove HgBr$_2$.

Only a representative compound is mentioned: C$_{15.5}$CdBr$_2$.06, prepared at 500 °C, I$_c$ = 1330 pm, 2nd stage. C$_{23}$HgBr$_2$, prepared at 100 °C, I$_c$ = 1684 pm, 3rd stage. CdBr$_2$ and HgBr$_2$ can also be intercalated in refluxing nitromethan. Products with the compositions C$_{28.6}$CdBr$_2$.2 and C$_{25}$HgBr$_2$.1 were obtained. They have both a 3rd stage structure I$_c$ = 1662 pm and I$_c$ = 1688 pm.

Graphite/FeBr$_2$

Heating of FeBr$_3$ or FeBr$_2$ with graphite in the presence of bromine results in various compounds depending on the experimental conditions. Mixed compounds with FeBr$_3$ and FeBr$_2$ can be prepared. A product with the composition C$_{16}$FeBr$_2$.0 was obtained by heating anhydrous FeBr$_2$ with graphite in a sealed tube filled with bromine vapour up to 350 °C. It was identified to be a 2nd stage with I$_c$ = 1328 pm.

It is generally said that a metal halide can only react with graphite in its highest oxidation state. This example demonstrates that this is not a necessary condition.

Graphite/UBr$_5$

Like other bromides with the metal in a high formal oxidation state UBr$_5$ has a low stability.

Although UBr$_5$ is soluble in liquid bromine we did not succeed in intercalating UBr$_5$ in refluxing bromine. Positive results were obtained by heating UBr$_5$ with graphite under a high bromine pressure at 300 °C. The compound with the highest UBr$_5$ amount had the composition C$_{36}$UBr$_5$.1. This compound was a mixture of a 2nd and 3rd stage (I$_c$ = 1328 and 1645 pm).

Conclusion

The present investigations have shown that there is a great similarity between graphite/metal chloride and graphite/metal bromide compounds. It is likely that many other metal bromides can react with graphite. However, the total number of the members of this class of graphite lamellar compounds will be always smaller than the number of graphite/metal chloride compounds. This would be expected because the electronegativities of chlorine and bromine are different and because the metal bromides are thermal less stable than the chlorides. More metal chlorides are known than metal bromides.

For intercalation of metal halides the presence of halogen is a necessary condition. The intercalation reaction can be interpreted in terms of an electron transfer process, the graphite acting as an electron donor the halogen and in certain cases the metal halide as an electron acceptor. For intercalation of metal chlorides, chlorine or bromine may be used, for bromides, of course, only bromine is applicable.

We have investigated the intercalation of many metal chlorides in the presence of bromine. Always only the 2nd stage has been obtained with such metal chlorides which form the 1st stage if the intercalation occurs in a chlorine atmosphere at the same temperature. Therefore, we suppose that genuine graphite/metal bromide compounds can form at the 2nd stage structure. There is a close relationship between the intercalates of acids and metal chlorides [6,7]. If sulphuric acid is intercalated using chlorine as oxidising agent the 2nd stage in obtained, with bromine only the 3rd stage is formed [8]. SASA et al. concluded that the 1st stage graphite/AlBr$_3$ compound may be bromine graphite stabilized by AlBr$_3$.

References

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3. C.BALESTRERI, Thése, Nancy 1973
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