Beitrag zur Chemie des Galliums
The Synthesis and some Properties of Gallium Ethoxide

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Experimental

Preparation of materials. Preliminary tests showed that it is most essential to work only with carefully dried solvents, and with ethanol, absolutely free from benzene (see also later).

Gallium trichloride was prepared by reacting the metal with dry HCl-gas, as widely described in the literature. Purification was made by double distillation in HCl-gas, and in N₂.

Sodium was the "pro Analysi" quality of Merck, Darmstadt, Germany.

Ethanol. Benzen free ethanol was refluxed with Mg chips during 8 hours, according to Lund and Bjerrem. and then distilled. The remaining water content was 0.003% (Karl Fischer titration).

Benzene was refluxed with Na during 3 hours, and then distilled. Remaining water 0.01 per cent.

Isopropanol was dried with K₂CO₃ for 24 hours, and distilled over Ca. Remaining water 0.18 per cent.

Apparatus and Procedure. Gallium triethoxide is prepared in the following way:


Sodium metal is carefully freed from its superficial crust in a glove box under dry nitrogen, weighed, and dissolved in ethanol under reflux. The stoichiometric amount of gallium trichloride, dissolved in cooled ethanol, is added dropwise to the sodium ethoxide solution. The mixture is finally heated to ebullition for about 30 minutes. After cooling, when the NaCl and the major part of the Gallium ethoxide are precipitated, benzene is added to about 30–40% of the final mixture. The latter is heated to ebullition, until the ethoxide is dissolved again. For the hot filtration from the NaCl at reduced pressure, a closed apparatus which protects the compound from moisture, is used.

The filtrate is distilled at normal pressure until the solid ethoxide appears, which is then dried in a vacuum. Finally, the raw product is cautiously distilled from a "Krangenkolben" in the vacuum of an oil pump.

Purification. The distilled gallium ethoxide always contains some chloride, which cannot be removed by further distillation or by crystallisation from ethanol/benzene mixtures.

This chloride can be eliminated by addition of an alcoholic AgNO₃ solution to the dissolved ethoxide, which is then filtered from the precipitated AgCl.

Analysis. Since the ethoxide is very sensitive to moist air, samples for C, H (5–10 mg each), and for ethoxy (40–50 mg each) determinations are directly distilled in weighed, small tubes, which can be sealed off.

Found

<table>
<thead>
<tr>
<th>Found (not purified)</th>
<th>Found (purified)</th>
<th>Calcd. samples %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>34.75; 35.01</td>
<td>34.83; 34.61</td>
</tr>
<tr>
<td>H</td>
<td>6.81; 7.23; 6.95</td>
<td>7.07; 7.12</td>
</tr>
<tr>
<td>O₁₂₃₄₅₆</td>
<td>68.3; 67.8</td>
<td>66.8; 67.3</td>
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<tr>
<td>Cl</td>
<td>&lt;0.1</td>
<td></td>
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</tbody>
</table>

* samples hydrolysed and ethanol oxidised with KMnO₄.

3 H. Lund and J. Bjerrem, Ber. dtsch. chem. Ges. 64, 210 [1931].
Properties of gallium triethoxide.
Colourless needles, volatile at elevated temperature. Thermal decomposition from about 200 °C. Melting point: 144.5 °C. Density (solid): 1.23 g/cm³. Very soluble in benzene and in boiling ethanol; slightly soluble in cold ethanol and in hydrocarbons.

Gallium triisopropoxide. The isopropoxide is easily obtained from the ethoxide by alcohol interchange reaction.

\[
\text{Ga(OC}_2\text{H}_5\text{)}_3 + 3 \text{C}_3\text{H}_7\text{OH} \rightarrow \text{Ga(OC}_3\text{H}_7\text{)}_3 + 3 \text{C}_2\text{H}_5\text{OH.}
\]

The ethoxide is refluxed with excess isopropanol for 2 hours. The alcohol is then distilled off at normal pressure, and the residue distilled in vacuum. The isopropoxide crystallises very slowly in colourless needles. The melting point could therefore only be determined very approximately to be at about 60 °C.

The vapor pressure is: 0.15 mm Hg at 109.5 °C, and 0.52 mm Hg at 123.0 °C.

This corresponds well with the indication of Mehrotra.

Analyses of gallium triisopropoxide

<table>
<thead>
<tr>
<th></th>
<th>Found %</th>
<th>Calcd. %</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>43.18; 43.72</td>
<td>43.76</td>
</tr>
<tr>
<td>H</td>
<td>8.10; 8.47</td>
<td>8.58</td>
</tr>
<tr>
<td>O(C₃H₇)</td>
<td>71.24; 71.53</td>
<td>71.76</td>
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</table>

Discussion

In preliminary tests we tried various methods for the preparation of the ethoxide, but without success. The direct reaction of the metal with ethanol, very practical in the synthesis of the aluminium compound, the reaction of gallium trialkyl with ethanol and others gave no positive results. Only the reaction of sodium ethoxide with gallium trichloride, both in ethanol, according to an old principle of Grimaux, gave us the ethoxide with a good yield.

\[
3 \text{NaOC}_2\text{H}_5 + \text{GaCl}_3 \rightarrow \text{Ga(OC}_2\text{H}_5\text{)}_3 + 3 \text{NaCl.}
\]

On the other hand, excess GaCl₃ is difficult to remove, because of its “organic” behaviour.

It is most essential to use benzene-free ethanol for the primary reaction, benzene and ethanol being subject to Friedel Crafts reaction in the presence of GaCl₃.

Excess AgNO₃ must be strictly avoided in purification, for its catalytic effect on the decomposition of the compound when distilling. For the same reason the bath temperature should not be raised above 190 °C.

The described reaction has been made with amounts up to 60 grams of GaCl₃, corresponding to approx. 50 g of the purified gallium triethoxide, the yield being about 70 per cent. Losses are mainly due to hydrolysis.

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5 E. Grimaux, C. R. hebd. Séances Acad. Sci. 98, 105 [1884].