TRIMETHYL GALLIUM, TRIMETHYL GALLIUM ETHERATE
AND TRIMETHYL GALLIUM AMMINE

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In the course of a comparative investigation of the elements of the third group in the Brown laboratories, we have had occasion to prepare trimethyl gallium. In our initial attempt, we employed the familiar Grignard reagent, but obtained a compound which proved to be an etherate, from which trimethyl gallium could not be prepared in the pure state. We were, however, able to substitute ammonia for ether and thus obtain an ammoniate. In the meantime, Dennis and Patnode prepared ethyl gallium by the action of diethyl mercury on metallic gallium at elevated temperatures (160°). By means of the Grignard reagent they obtained only an etherate. Very recently Renwanz describes the preparation of trimethyl gallium etherate by means of the Grignard reagent. Below, we communicate our results on the preparation and properties of trimethyl gallium as well as those of trimethyl gallium etherate and trimethyl gallium ammoniate. In a second paper, we will communicate our results on chlorine derivatives of trimethyl gallium.

Trimethyl Gallium.—(1) Preparation. We prepared trimethyl gallium by the action of dimethyl zinc on gallium trichloride. Approximately 20 g. of gallium trichloride were treated with dimethyl zinc in an apparatus of the form outlined in figure 1. The dimethyl zinc was prepared by the action of methyl iodide upon the familiar zinc copper couple; the reaction mixture was heated to boiling for 40 hours, when the methyl iodide had disappeared and the contents of the reaction vessel were completely solidified. On heating the reaction mixture, dimethyl zinc began to be formed at a temperature of 80° and the reaction was completed at 150°. The dimethyl zinc was condensed and collected under an atmosphere of nitrogen in an ampule cooled in liquid ammonia. The product was almost completely free from methyl iodide, a trace of the latter being removed by the addition of a very small quantity of sodium to the dimethyl zinc at a temperature of 40°. The product was redistilled and condensed into ampules of known capacity for use as required. These ampules, of the form shown at A in figure 1, were provided with a small capillary B. When it was desired to withdraw dimethyl zinc, the ampule was attached to the apparatus as shown in figure 1 by means of deKhotinsky cement, the capillary projecting through the stopcock C. The apparatus being exhausted, on turning the stopcock the capillary was broken and dimethyl zinc vapor could be introduced into the apparatus as required.
Gallium trichloride, prepared by the action of chlorine on metallic gallium, was sublimed several times and introduced directly into the reaction tube \( D \) through tube \( E \), which was then sealed off. A second tube \( F \) was joined to \( D \) and this tube was in turn joined to the ampule \( A \), containing dimethyl zinc as already described. The apparatus was attached to a manometer at \( G \) and to a pump and a source of dry nitrogen through a trap \( H \), which was cooled in a bath of liquid ammonia.

Dimethyl zinc vapor reacts vigorously, and even violently, with gallium trichloride at room temperatures. The reaction is controlled by means of the stopcock \( C \) which limits the rate of flow of vapor. As the reaction proceeds, it becomes less vigorous and, when a third or more of

![Diagram of the apparatus](image)

FIGURE 1

the dimethyl zinc has been introduced into the reaction tube, it is necessary to heat the reaction mixture to temperatures ranging from 80° to 120°. When approximately one half of the dimethyl zinc has been introduced, trimethyl gallium begins to be formed. As the tube \( D \) is heated, tube \( F \) is cooled in liquid ammonia and the gallane, together with unreacted dimethyl zinc, is condensed. The reaction tube is cooled in ice water. Dimethyl zinc is again introduced through stopcock \( C \) and the liquid in \( F \) is recondensed in the reaction tube. The reaction mixture is then heated to approximately 120°. The course of the reaction can be followed by means of the manometer. The volatile products in the reaction tube are again condensed in \( F \), dimethyl zinc is condensed on the material in \( D \) as before and this process is repeated until the dimethyl zinc has been
used up. The volatile materials are heated and recondensed in $D$ several times to insure complete disappearance of the dimethyl zinc.

The total reaction takes place according to the equation:

$$2\text{GaCl}_3 + 3(\text{CH}_3)_2\text{Zn} = 2\text{Ga(CH}_3)_3 + 3\text{ZnCl}_2$$

and is practically quantitative. In the initial stages of the reaction, the gallium is only partially methylated. Dimethyl zinc, however, reacts completely with the formation of zinc chloride. As the trimethyl gallium is formed in the course of the reaction, its presence is evidenced on condensing the product in $F$ at liquid ammonia temperatures. Dimethyl zinc freezes at $-40^\circ$ while trimethyl gallium freezes at $-19^\circ$. At liquid ammonia temperatures, the gallane separates out in crystalline form in the presence of considerable quantities of dimethyl zinc.

When the reaction is completed, the product is condensed in $F$ and the tube is sealed off from the remainder of the apparatus. The product may be transferred from the tube through the attached capillary as already described. The crude product was distilled several times and samples were condensed into weighed, fragile, glass bulbs for analysis. The remainder of the product was filled into a small ampule provided with a capillary for use as needed.

(2) Analysis.—For analysis, trimethyl gallium was oxidized to $\text{Ga}_2\text{O}_3$ in weighed Pyrex test tubes. The compound, sealed in a weighed, fragile, glass bulb, is introduced into a test tube which is then cooled to a temperature of $-76^\circ$ in freezing ammonia and the fragile bulb is broken. The compound is so reactive toward air that it ignites and oxidizes with evolution of light in a bath of freezing ammonia. No product is lost in this process and, when the initial process of oxidation is over, sulphuric and nitric acids are added to complete oxidation. The acids are fumed off and the tube is weighed in the usual way.

Analysis: substance, 0.2554, 0.1858; $\text{Ga}_2\text{O}_3$, 0.2090, 0.1519; per cent Ga found, 60.87, 60.81, mean 60.84; Ga required for $(\text{CH}_3)_2\text{Ga}$, 60.72.

The molecular weight of trimethyl gallium vapor was determined by introducing the vapor into a bulb of 347.4-cc. capacity at known pressures (approximately 15 cm.). The result of several determinations gave a mean value of 115.1 against the theoretical value of 114.8.

(3) Properties.—Trimethyl gallium is a volatile liquid boiling at 55.7 ± 0.2° under a pressure of 762 mm. and freezing at −19°. Its vapor pressure is given by the equation $\log_{10}P_{\text{mm}} = -1705/T + 8.07$. At −33.5°, 0° and 25°, the vapor pressure is 8.9, 66.6 and 221.8 mm., respectively. The molal heat of vaporization according to the vapor pressure equation is 7800 calories and the specific heat of vaporization is 68 calories. Trimethyl gallium is extremely reactive toward oxygen. The solid reacts pyrophorically with air at −76°; a trace of the vapor combines explosively with air at ordinary temperatures.
Trimethyl gallium combines with ether to form an etherate which boils at 98.3°. It forms an ammoniate melting at 31°, which is fairly volatile at room temperatures. It reacts with hydrogen chloride in the pure state or in solution in ether, one or more methyl groups being substituted by chlorine.

**Trimethyl Gallium Monoetherate.—** (1) *Preparation.* Approximately 30 g. of gallium trichloride were dissolved in 150 cc. of ether and added slowly to twice the equivalent amount of methyl magnesium iodide in ether solution under an atmosphere of nitrogen. The reaction was not vigorous, although there was a noticeable evolution of heat. The apparatus employed is shown in figure 2. The gallium trichloride, after preparation, was sublimed into the tube A, which was then detached and connected to a tube containing ether (not shown in the figure), and 150 cc. of ether were condensed on the trichloride. The siphon tube B was then introduced through the top of the condensation column at C and the solution of gallium trichloride was blown into the Grignard reagent contained in the flask D. The siphon tube was then removed and replaced by a thermometer. The apparatus was connected with a source of nitrogen at E, a pump at F and a manometer at G. The reaction mixture was refluxed for 40 hours, when about two-thirds of the ether was distilled off. At this point, a white solid began to appear. After again refluxing the mixture for 12 hours, most of the remaining ether was distilled on a bath at 170°. The residue in the reaction flask was then heated to the boiling point for an additional 4 hours. The ether which had collected in H was
distilled into \( J \) under reduced pressure and flask \( J \) was detached and replaced. The system was then evacuated to 3 cm. and, with an ice bath surrounding \( H \) and a liquid ammonia bath surrounding \( K \), the reaction flask \( D \) was gradually heated to 260\(^\circ\). The liquid distilled into the receivers \( H \) and \( K \). The crude product in \( H \) was distilled under a pressure of 5 cm. into receiver \( K \), cooled in liquid ammonia. The product was finally purified by distillation through a fractionating column. The liquid was collected in ampules which were provided with capillaries as already described. From these ampules, the liquid was transferred by distillation as needed. Based on the gallium trichloride used, a yield of 90\% was obtained.

(2) Analysis.—The compound was analyzed for gallium by oxidizing known samples with fuming sulphuric and nitric acids in a Pyrex test tube and weighing as \( \text{Ga}_2\text{O}_3 \). The samples were weighed in sealed fragile bulbs similar to those described in the preceding section. The bulb was broken in a test tube cooled in liquid ammonia and 2 cc. of fuming sulphuric and 5 cc. of nitric acid were added dropwise. When the reaction at liquid ammonia temperature had subsided, the tube was cautiously warmed to room temperatures, being re-cooled if necessary. After fuming off the acids, the tube was weighed. The results are tabulated below.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>( \text{Ga}_2\text{O}_3 )</th>
<th>% Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4345</td>
<td>0.2153</td>
<td>36.86</td>
</tr>
<tr>
<td>0.2994</td>
<td>0.1502</td>
<td>37.32</td>
</tr>
<tr>
<td>0.2931</td>
<td>0.1500</td>
<td>38.07</td>
</tr>
<tr>
<td>0.2972</td>
<td>0.1499</td>
<td>37.52</td>
</tr>
<tr>
<td>0.4180</td>
<td>0.2085</td>
<td>37.10</td>
</tr>
</tbody>
</table>

The gallium content of the various samples varied from 36.86 to 38.07; the gallium content of the monoetherate, \( (\text{CH}_3)_3\text{Ga} \cdot (\text{C}_2\text{H}_5)_2\text{O} \), is 36.91\%. The variation in the gallium content of the samples analyzed is due to the fact that the etherate is largely dissociated in the vapor phase and measurable separation of the two components occurs during distillation.

(3) Properties.—Trimethyl gallium monoetherate is a colorless liquid which fails to freeze at \(-76^\circ\) and boils at 98.3\(^\circ\). It is readily soluble in liquid ammonia. The vapor pressure is given approximately by the equation: \( \log_{10} P_{\text{mm.}} = -2440/T + 9.45 \). The vapor pressure is 0.18, 3.2 and 18.3 mm. at \(-33.5^\circ\), 0\(^\circ\) and 25\(^\circ\), respectively. From the vapor pressure curve, the molal heat of vaporization is calculated to be 11,200 calories.

The vapor density of trimethyl gallium monoetherate at room temperatures was determined by weighing a known volume (of vapor) at a pressure somewhat below the saturation pressure. The density varied some-
what with the sample employed, the molecular weight ranging from 107 to 115. The calculated molecular weight for the monoetherate is 180, whence it follows that the vapor is dissociated to the extent of about 70% at 25°.

Trimethyl gallium etherate is oxidized slowly by atmospheric oxygen if the exposed surface is not too large. It is hydrolyzed by an aqueous solution of potassium hydroxide. At room temperatures only one methyl group is substituted while, at 100°, two methyl groups are replaced by hydroxyl. In two experiments, at 35°, the methane was collected and the gallium residue was analyzed for gallium. In two other experiments at 100°, the methane was collected but the gallium was not determined. In this case, however, the gallium content was known fairly closely from the amount of etherate used. The results are as follows:

(4) Determination of Methane, 35°, m. mols. compound, 1.145, 1.224; m. mols. CH₄, 1.16, 1.31: 100°, m. mols. compound, 1.745, 1.28; m. mols. CH₄, 3.35, 2.55: ratio CH₄/Ga; (35°) 1.01, 1.07; (100°) 1.92, 1.99.

The salts formed upon hydrolysis are soluble in water but have not been studied further.

Trimethyl Gallium Monoammine.—When liquid ammonia is condensed on trimethyl gallium monoetherate, it dissolves readily and, upon evaporation of the ammonia, there is left behind a white solid containing one molecule of ammonia. The compound is sufficiently volatile at ordinary temperatures to permit of its transfer as a vapor. It is convenient as a starting material for the preparation of other compounds.

(1) Preparation.—A sample of trimethyl gallium monoetherate, sealed in a suitable fragile bulb, is introduced into a reaction tube, and cooled in a bath of liquid ammonia. After breaking the fragile bulb, liquid ammonia is condensed in the reaction tube to dissolve the etherate. The ammonia is allowed to evaporate and the tube is pumped for some time through a liquid ammonia trap to remove all traces of ether. The ammine tends to form a supersaturated solution at room temperatures and it is usually necessary to induce crystallization by chilling. The product can be transferred to a suitable weighed tube by carrying the vapors at very low pressures through a tube cooled in liquid ammonia.

(2) Physical Properties.—Trimethyl gallium monoammine, (CH₄)₃Ga-NH₃, is a white, crystalline solid which melts at 31°. It sublimes in a vacuum at room temperatures. It is readily soluble in ether and liquefies in ammonia vapor at atmospheric pressure and room temperature. It is fairly stable toward oxidation but is quite sensitive to water vapor.

(3) Hydrolysis and Analysis.—Trimethyl gallium monoammine dissolves readily in an aqueous solution of potassium hydroxide, under which condition it is hydrolyzed with evolution of one molecule, each, of methane and ammonia. Samples of the ammine, sealed in weighed, fragile bulbs,
were treated with $7.5 \text{ N}$ potassium hydroxide. The gases produced in the reaction were carried through standard sulphuric acid to absorb the ammonia and the remaining gas was collected over mercury by means of a Toepler pump. The residue remaining in the reaction tube was analyzed for gallium.

(4) Analysis for Nitrogen: substance, 0.1619, 0.2141; cc. 0.09367 $\text{N}_2\text{SO}_4$, 13.15, 17.38; \% N found, 10.66, 10.65, mean 10.65; \% N required for $(\text{CH}_3)_2\text{Ga-NH}_3$, 10.63.

(5) Analysis for Gallium: substance, 0.1619, 0.2141; $\text{Ga}_2\text{O}_3$, 0.1152, 0.1525; \% Ga found: 52.93, 52.98, mean 52.95; \% Ga required for $(\text{CH}_3)_3\text{Ga-NH}_3$, 52.89.

(6) Methane Determination: m. mols $(\text{CH}_3)_3\text{Ga-NH}_3$, 1.23, 1.63; cc. of gas, 27.4, 56.9; mol. wt., 16.3, 16.3; m. mols. CH$_4$, 1.22, 1.64.

Hydrolysis evidently occurs according to the equation:

$$(\text{CH}_3)_3\text{Ga-NH}_3 + \text{KOH} \rightarrow (\text{CH}_3)_2\text{GaOK} + \text{CH}_4 + \text{NH}_3.$$