[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GALLIUM TRIETHYL MONOETHERATE, GALLIUM TRIETHYL, GALLIUM TRIETHYL AMMINE[1]

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RECEIVED SEPTEMBER 21, 1931 PUBLISHED JANUARY 7, 1932

Introduction

Of the elements of the third group in the Periodic Table, boron, aluminum and thallium are known to form normal alkyls, but those of gallium and indium have not hitherto been isolated.

The study of the possible preparation of gallium triethyl was begun several years ago in the Cornell Laboratory by H. A. Lovenberg. He added to a solution of ethylmagnesium bromide in ether, 45 g. of gallium bromide dissolved in 100 cc. of ether. The glass apparatus was of sealed joints throughout, and was kept filled with pure nitrogen during the experiment. The reaction was strongly exothermic, and the rate of addition of the gallium bromide was so adjusted that the ether refluxed quietly. After the addition of the gallium bromide, the mixture was further refluxed for thirty minutes. The condenser and dropping funnel were then sealed off from the flask and the stopcock on the inlet tube was closed. Mr. Lovenberg died shortly after this stage of the investigation was reached and the flask remained sealed until Mr. Patnode took up the examination of its contents in January of this year.

Experimental

Gallium Triethyl Monoetherate.—The flask containing the reaction mixture just described was opened at the inlet tube for nitrogen, and the ether was drawn off by a pump until a sample of it, liquefied by solid carbon dioxide, became turbid upon the addition of very dilute ammonium hydroxide. All of the residual solution in the flask was then distilled in a current of carbon dioxide under a pressure of 30–40 mm. at 60–80°. The receiver was next attached by a normal slip-joint to a vacuum fractionation apparatus similar to that described by Laubengayer and Corey[2] except that the mercury valves were replaced by wide-bore stopcocks. The liquid was cooled to $-50°$, and the gas above it was pumped out. It was then gradually raised in temperature and was distilled into other bulbs of the chain by cooling them in liquid air. There were thus obtained two fractions, one volatile below $-25°$ and the other above that temperature. The first fraction was chiefly ether and was discarded. The other portion was subjected to prolonged fractionation. There was finally obtained a liquid that had a vapor tension of somewhat less than 0.4 mm. Samples of this product were distilled into small (0.5 cc.) bulbs which were then sealed off from the chain and were used in the following experiments.

Analysis.—When one of the small sample bulbs was broken under ice-cold water,

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[1] This article is based upon the thesis presented to the Graduate School of Cornell University by Winton Patnode in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1943 (1926).

drops of an oil-like substance were formed. On spectroscopic examination, these drops were found to be high in gallium and to contain no other metal. The water contained a trace of gallium but no other metal.[3]

In the analysis, one of the small sample bulbs was weighed, was then broken under cold water and the oily drops were dissolved by the addition of 6 *N* hydrochloric acid. The glass was collected on a filter and weighed. The acid solution was made strongly ammoniacal and 30% hydrogen peroxide was added. After standing for some hours, the solution was boiled until nearly all of the ammonia had been expelled, and the white, granular precipitate of gallium hydroxide was collected on an ashless filter, dried, ignited, treated with a few drops of concentrated nitric acid, again ignited and then weighed as gallium oxide in a stoppered weighing bottle.

Carbon and hydrogen were determined by combustion over copper oxide, one of the small weighed sample bulbs being broken in the combustion tube after the apparatus had been filled with nitrogen.

Anal. Calcd. for $Ga(C_2H_5)_3 \cdot (C_2H_5)_2O$: Ga, 30.19; H, 10.91; C, 51.97. Found: Ga, 30.64, 30.40; H, 10.60, 10.67; C, 50.34, 51.53.

These results, although not in close agreement with the calculated percentages, indicate that the substance is a monoetherate of gallium triethyl, and this conclusion is supported by a determination of the molecular weight of the compound by measuring the depression of the freezing point of benzene. This gave mol. wt., 232.8; calculated mol. wt., 230.9.

Chemical Properties.—Gallium triethyl monoetherate is a colorless liquid that is rapidly decomposed by moisture as already noted. In contact with air, dense white fumes are formed, and when dry oxygen was admitted to one of the small bulbs, the formation of the fumes was accompanied by a sharp report, a purple-colored flame and the deposition of a dark brown gum on the walls of the bulb. On breaking a bulb containing about 0.3 g. of the compound under 6 *N* nitric acid, the reaction was so violent as to break the Pyrex beaker and spray the acid to a distance of several feet.

Until quite recently, normal alkyls of trivalent thallium had eluded synthesis, one of the valences apparently differing from the other two, with the result that compounds of the type $Tl(alkyl)_2X$, salts of the strong base $Tl(alkyl)_2OH$, are formed.

Gallium also exhibits a tendency to form compounds of the type $Ga(alkyl)_2X$, as was evidenced by the fact that when a sample of the etherate was broken under a measured volume of standard hydrochloric acid, and the evolved ethane was measured and the excess of the acid was titrated with sodium hydroxide, the results were approximately

$$Ga(C_2H_5)_3 \cdot (C_2H_5)_2O + HCl = Ga(C_2H_5)_2Cl + C_2H_6 + (C_2H_5)_2O.$$

The volume of the evolved ethane was somewhat greater than that called for in the equation, which indicates that $Ga(C_2H_5)_2OH$ is a much weaker base than the corresponding thallium compound.

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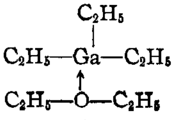
[3] These spectroscopic analyses were made in this Laboratory by Professor Papish and his staff, to whom we wish to express our sincere appreciation of their invaluable assistance.

Gallium has a theoretical maximum covalency of six. In the monoetherate (A) the covalency would be four, the stability of the compound being due to the completely shared octet.



$$\begin{array}{c} C_2H_5 \\ | \\ C_2H_5-Ga-C_2H_5 \\ \uparrow \\ C_2H_5-O-C_2H_5 \end{array}$$

A

Gallium Triethyl.—Inasmuch as the reaction between gallium bromide and an ethereal solution of ethylmagnesium bromide yielded an etherate of the gallium alkyl, the possibility of the preparation of the simple alkyl by the action of mercury diethyl upon metallic gallium was next investigated.

Three small distilling bulbs, each of about 25 cc. capacity, were fused together in series, and the last bulb was attached to a fourth by a normal slip-joint carrying a glass stopcock, which permitted this fourth bulb to be closed and detached. and then connected with the vacuum fractionation apparatus.[2] Ten grams of metallic gallium was placed in the first bulb, and 2 g. in each of the next two. Fifty-two grams of mercury diethyl was run into the first bulb, the little chain was filled with nitrogen, and the necks of the three flasks, hitherto open, were sealed before the lamp. The first bulb was surrounded by a small air-bath and was very gradually raised in temperature up to 165° during a period of 200 hours. The bulb was then cooled, the nitrogen in the chain was pumped out, and the liquid in the first bulb was distilled. under diminished pressure, into the second bulb upon the 2 g. of gallium that it contained. The first bulb was then sealed off from the chain. Examination of the residual metal in the first bulb showed that it was nearly pure mercury, and its amount indicated that the reaction had proceeded practically to completion.

$$3Hg(C_2H_5)_2 + 2Ga = 3Hg + 2Ga(C_2H_5)_3$$

To make sure that all of the mercury diethyl had reacted with the gallium, the contents of the second bulb was heated for twenty-four hours at 120–125° and then for eighteen hours longer at about 150°. No change in the appearance of the colorless distillate or the bright metallic gallium resulted. The procedure was repeated by distillation into the third bulb, the second bulb was sealed off and the third bulb was heated for twenty-four hours longer. Again the absence of change in the appearance of the liquid or metallic gallium furnished quite conclusive evidence that the distillate contained no mercury diethyl.

The liquid was now distilled into the fourth bulb, the stopcock of this bulb was closed, and it was connected to the vacuum fractionation apparatus by the slip-joint. Its contents was held at 0°, and was separated into three fractions by distillation in the usual manner.[4] The middle fraction was used in the experiments described below.

Analysis.—A weighed sample of the liquid, contained in an evacuated bulb that was attached to the vacuum fractionation apparatus, was cooled with solid carbon dioxide. and an excess of 6 *N* sulfuric acid was added. The bulb was then allowed to warm up very slowly and was finally heated[5] to 90° for an hour. It was again cooled with

ANALYSES

Sample, g.	Corr. vol. ethane, cc. Calcd.	Corr. vol. ethane, cc. Found	Ga, % Calcd.	Ga, % Found
0.2666	113.0	112.5	...	...
.1775	75.2	75.2	44.45	44.13
.3299	139.8	141.0	44.45	44.24

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[4] Dennis, Corey and Moore, THIS JOURNAL, **46**, 657 (1924).

[5] This procedure is patterned after that employed by Laubengayer and Fleckenstein in the analysis of zinc ethyl, *Z. anorg. allgem. Chem.*, **191**, 283 (1930).

carbon dioxide, and the liberated gas was drawn off and measured. Combustion analysis showed it to be pure ethane. The gallium in the acid solution was determined by the method used by Dennis and Bridgman.[6]

Spectroscopic examination of the liquid showed it to be free from all metals but gallium.

Molecular Weight.—This was determined by the measurement of the depression of the freezing point of benzene.

Sample, g.	Benzene, g.	Depression, °C.	Mol. wt.
0.3382	43.8	0.15	263.5
.2541	43.8	.11	270.0
.2778	43.8	.12	270.0

The molecular weight of $Ga(C_2H_5)_3$ is 156.84. Consequently the above results show that the compound is associated in solution in benzene, which was to be expected since Roux and Louise[7] obtained similar results for aluminum ethyl in ethylene bromide.

Density as Liquid.—A sample of the alkyl was distilled into a bulb with a calibrated stem that made possible the measurement of volume with an accuracy of 0.005 cc. The bulb was held in a thermostat at 30° until the volume was constant, and was then weighed: density at 30°, 1.0576, 1.0583 g./cc.

Melting Point.—This was determined by the dropping ring method.[4] The average of two quite closely agreeing measurements was $-82.3°$.

Vapor Tension.—This was measured by the method of Dennis, Corey and Moore[4] from 0 to 144°. The vapor tension below 0° is too small to permit of accurate determination. The results of two experiments were in close agreement, and when plotted as the logarithm of the pressure against the reciprocal of the absolute temperature, gave a straight line. The equation of this line is

$$\log P = -2162 \times 1/T + 8.083$$

Boiling Point.—The boiling point as taken from the vapor tension curve is 142.6°.

Chemical Properties.—Gallium triethyl is a colorless, somewhat viscous liquid of unpleasant odor. It is spontaneously inflammable in the air, burning with a purple flame and producing a brown smoke. When a small, sealed bulb containing about 0.2 g. of the liquid was broken under cold water, there was a violent reaction which broke the Pyrex beaker and threw the water over a considerable area. With 95% alcohol instead of water, the reaction was somewhat less energetic. The alcoholic solution was slightly alkaline to litmus and to methyl orange, which indicated the formation of diethyl gallium hydroxide, a weak base.

[6] Dennis and Bridgman, THIS JOURNAL, **40**, 1531 (1918).

[7] Roux and Louise, *Bull. soc. chim.*, **50**, 511 (1888).

Quantitative Reaction with Water.—A weighed sample of the gallium alkyl was decomposed with water at room temperature in the same manner as described under Analysis, and the evolved ethane was measured. The liquid remaining in the bulb was added to an excess of standard hydrochloric acid, and the excess of acid was titrated with sodium hydroxide.

Sample, g.	0.1034 *N* HCl, cc. Calcd.	Found	Corr. vol. ethane Calcd.	Found
0.1655	10.20	10.22	23.35	23.1

These data indicate that the reactions proceed as follows

$$Ga(C_2H_5)_3 + H_2O = Ga(C_2H_5)_2OH + C_2H_6\cdot$$
$$Ga(C_2H_5)_2OH + HCl = Ga(C_2H_5)_2Cl + H_2O$$

Gallium Triethyl Ammine.—Theoretically, gallium triethyl should be capable of uniting with three molecules of ammonia, since gallium has a maximum covalency of six. Because of the stability of the completely shared octet, it was to be expected that one molecule of ammonia would be firmly held and form a quite stable compound. The results given below support this supposition. No experiments were made to ascertain whether more ammonia would enter into combination, but the evidence indicates that if the triammine were formed, it would readily lose two molecules of ammonia when subjected to diminished pressure.

To prepare the ammine, a weighed sample of the alkyl was brought into a bulb that was attached to the vacuum fractionation apparatus, the bulb was immersed in an ice-bath, and measured volumes of ammonia were admitted. The equilibrium vapor tension at 0° was measured after each addition. The pressure remained constant until one mole of ammonia for each mole of gallium triethyl had been added, and then rose rapidly, which indicated the formation of $Ga(C_2H_5)_3 \cdot NH_3$.

The product is a colorless liquid that is attacked only very slowly by the air. A few drops, exposed to the air overnight, changed to a white solid.

A drop of the liquid, held in a stream of oxygen, underwent no apparent change.

Small portions of the ammine, about 0.1 cc. each, were added to the following reagents in test-tubes.

(a) **Distilled Water.**—The sample sank to the bottom of the tube without visible reaction, but on standing for a few minutes, minute bubbles of gas which had the odor of ammonia were evolved. When the contents of the tube was heated, a white precipitate formed and an inflammable gas smelling strongly of ammonia was set free. The precipitate was soluble in dilute hydrochloric acid, and also in alcohol, to which it imparted an alkaline reaction. When this alcoholic solution was evaporated to dryness and the residue was dissolved in alcohol, the solution was still alkaline to litmus. These results indicate that the ammine is attacked by water with the evolution of ammonia and ethane, and the formation of diethyl gallium hydroxide.

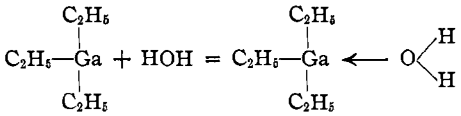
$$Ga(C_2H_5)_3{\cdot}NH_3 + H_2O = Ge(C_2H_5)_2OH + NH_3 + C_2H_6$$

(b) **Sulfuric Acid, 6N.**—*Dropped into this reagent, the ammine was* immediately decomposed, with the evolution of white fumes and an inflammable gas. A white precipitate that appeared at first dissolved when the acid was gently warmed, probably with the formation of diethyl gallium sulfate, $[Ga(C_2H_5)_2]_2SO_4$.

(c) **Potassium Hydroxide, Dilute Solution.**—The liquid ammine reacted slowly in the cold, and quite rapidly when warmed. Ammonia and an inflammable gas were given off. No precipitate appeared. This indicates that diethyl gallium hydroxide is amphoteric, and that it here formed $Ga(C_2H_5)_2OK$.

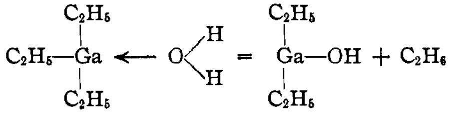
(d) The ammine was instantly dissolved by 95% alcohol, ether and benzene without apparent change in any case.

It is interesting to note that the simple gallium alkyl reacts violently with cold water, the etherate vigorously, and the ammine only very slowly. The reasons for these differences become obvious if the hydrolysis proceeds as follows. The first step may be assumed to be the coördination of a molecule of water



$$C_2H_5-\overset{C_2H_5}{\underset{C_2H_5}{Ga}} + HOH = C_2H_5-\overset{C_2H_5}{\underset{C_2H_5}{Ga}} \longleftarrow O\begin{matrix}H\\H\end{matrix}$$

A molecule of ethane is then set free with the formation of diethyl gallium hydroxide.



$$C_2H_5-\overset{C_2H_5}{\underset{C_2H_5}{Ga}} \longleftarrow O\begin{matrix}H\\H\end{matrix} = \overset{C_2H_5}{\underset{C_2H_5}{Ga}}-OH + C_2H_6$$

The hydrolysis does not proceed further, and this is probably due to the insolubility of the product in water and to the fact that the gallium alkyls, resembling those of trivalent thallium as is to be expected, tend to form compounds in which one of the alkyl groups is replaced by hydroxyl or by an acid radical. But the position of gallium in the Third Group warrants the assumption that the univalent di-alkyl radical should be less stable than that of thallium, and this is confirmed by the fact that the thallium compounds are distinctly more stable in the presence of acids than is the gallium triethyl.

That hydrolysis of gallium triethyl etherate and gallium triethyl ammine proceeds more slowly than that of the normal alkyl, may be due to the fact that the fourth covalency is already occupied, in the one case by ether, and in the other by ammonia, and that hydrolysis cannot result until either the ether or ammonia has been displaced by the water. That the ammine reacts more slowly than the etherate is explainable by the fact that in the ammine both the gallium and nitrogen have completely shared octets, while in the etherate only the gallium has a completely shared octet, that of oxygen still having an unshared lone pair.

Summary

This article deals with the preparation and the properties of gallium triethyl monoetherate, gallium triethyl and gallium triethyl ammine. The behavior of the compounds upon hydrolysis is discussed in some detail, and evidence as to the existence of gallium diethyl hydroxide, a base, is presented. The latter substance is now being further investigated in the Cornell Laboratory.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF REED COLLEGE]

STUDIES IN THE MEASUREMENT OF ELECTROMOTIVE FORCE IN DILUTE AQUEOUS SOLUTIONS. II. THE SILVER CHLORIDE ELECTRODE

BY WALTER R. CARMODY

RECEIVED SEPTEMBER 21, 1931 PUBLISHED JANUARY 7, 1932

In a former paper[1] the writer discussed the importance of and difficulties involved in the measurement of electromotive force in dilute aqueous solutions and introduced a type of cell and a method designed to eliminate the relatively large variations in electromotive force encountered in such measurements. In the following paper this method has been applied to the measurement of the potential of the silver chloride electrode by means of the cell

$$\text{Pt}, H_2\,(g), \text{HCl}, \text{AgCl}\,(s), \text{Ag}\,(s)$$

with such modifications of cell design and method as the problem necessitated.

Three investigators[2] have made measurements on this cell which permit extrapolation to be made to infinite dilution. Their results, although checking very well in concentrated solutions, diverge as the dilution is increased until at zero concentration they differ by as much as 1.0 mv. In each case glass has been used as material for cell and containers. Kraus and Parker[3] have shown that for strong acids, concentrations below 0.005 molar cannot be kept in glass containers without change, the relative effect of which increases with the dilution of the acid. Randall and

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[1] Carmody, THIS JOURNAL, **51**, 2905 (1929).

[2] Noyes and Ellis, *ibid.*, **39**, 2532 (1917); Linhart, *ibid.*, **41**, 1175 (1919); Nonhebel, *Phil. Mag.*, [7] **2**, 1085 (1926).

[3] Kraus and Parker, THIS JOURNAL, **44**, 2429 (1922).