Values of Λ_0 and of K have been computed and the influence of constitution upon dissociation is discussed.

PROVIDENCE, RHODE ISLAND RECEIVED APRIL 21, 1933
PUBLISHED SEPTEMBER 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Action of Sodium upon Trimethylgallium and Dimethylgallium Chloride in Liquid Ammonia

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I. Introduction

The present paper is concerned with the action of metallic sodium upon trimethylgallium and dimethylgallium chloride. In the light of our knowledge of reactions of similar derivatives of the elements of the fourth group, it might be expected that dimethylgallium chloride would be reduced to the free group $(CH_3)_2Ga$ and that this, in turn, might be further reduced to the negative ion, $(CH_3)_2Ga^-$. On the other hand, no reaction is to be expected in the case of trimethylgallium or, otherwise, a reaction in which one methyl group is substituted by the reducing metal as in the case of tetramethyltin.[2]

Excepting that free dimethylgallium $(CH_3)_2Ga$ is obtained by reduction of the corresponding chloride, there is little resemblance between reactions of organic derivatives of the elements of the third and those of the fourth group of the periodic system. Perhaps the most characteristic reaction of third group elements is that of addition of neutral molecules or negative ions, with formation of coördination compounds. Thus, in the case of boron, we have such coördinate linkage in the BF_4^- ion. Similarly, boron trifluoride combines with neutral molecules, such as ammonia or the amines, to form compounds of the type $BF_3 \cdot NH_3$.[3] There are similar compounds of the organic boron derivatives. Thus, we have $(C_6H_5)_3B \cdot NH_3$,[4] $(C_6H_5)_3B \cdot NH_2^-$,[5] and $(C_6H_5)_3B \cdot OH^-$.[6] The coördinate linkage in these compounds has a striking influence on their stability. For example, triphenylboron oxidizes in air with extreme ease, while potassium amide, under similar conditions, oxidizes explosively; yet the coördinated compound of the two is relatively stable in air.

Gallium shows much the same properties as boron in respect to the formation of coördinate linkages. Thus, trimethylgallium forms an

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[1] Du Pont Fellow in Chemistry at Brown University.

[2] Kraus and Sessions, THIS JOURNAL, **47**, 2361 (1925).

[3] Kraus and E. Brown, *ibid.*, **51**, 2690 (1929).

[4] Krause, *Ber.*, **57**, 813 (1924).

[5] Hawes, Thesis, Brown University, 1927.

[6] Frankland, *Ann.*, **124**, 130 (1862); Fowler, unpublished observations, Brown University (1933).

etherate and an ammoniate[7] and gallium trichloride forms a tetrachlorogallate ion.[8] Dimethylgallium chloride and methylgallium dichloride both form rather stable ammoniates or ammines.[8]

Trimethylgallium, when treated with sodium in liquid ammonia, undergoes a reaction in which the coördinated ammonia molecule is probably involved. Dimethylgallium chloride is reduced to the free group $(CH_3)_2$-Ga which is probably combined with ammonia. The free group reacts with additional sodium in a rather complex manner.

The methylgallium compounds are exceedingly reactive toward oxygen and many of the products of reduction are not only reactive toward oxygen and other substances but are intrinsically unstable. Accordingly, in order to arrive at some notion of the nature of the reactions involved, it has been necessary to depend largely upon indirect means. Only in exceptional cases has it been possible to separate out the products of reaction in pure form for analysis.

II. Action of Sodium upon Trimethylgallium

Weighed samples of trimethylgallium were treated with metallic sodium in liquid ammonia and the evolved gases were collected and measured. Ammonium bromide was added to the resulting solution and the gases evolved in the several stages of this reaction were collected and measured separately.

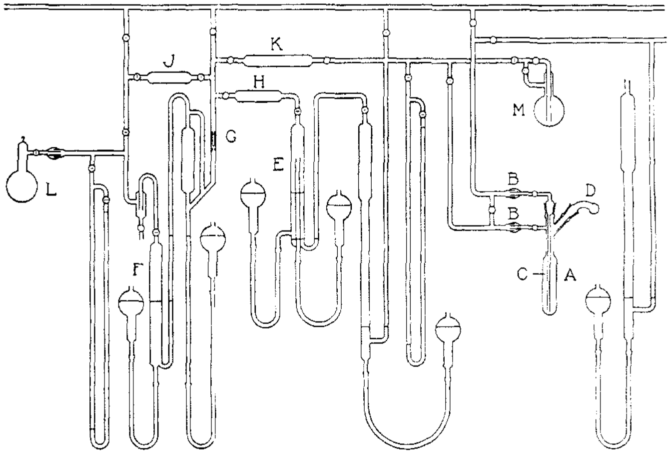

Fig. 1.—Apparatus used in reduction of trimethylgallium.

Apparatus and Procedure.—The apparatus used in this and other reactions described below is illustrated in Fig. 1. A weighed reaction tube A is attached to the system by means of de Khotinsky cement at BB. The tube is provided with a stirring tube C and an addition tube D for adding weighed quantities of substances, such as ammonium bromide, which can be formed into pellets. Gases evolved during the reaction are collected over water in E. These gases are transferred by means of a

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(7) Kraus and Toonder, *Proc. Nat. Acad.*, **19**, 292 (1933).

(8) Ref. 7, p. 298.

Toepler pump and collected over mercury in F. Water vapor and ammonia are removed by means of drying tubes H, J, K, and the density of the residual gas is determined by weighing in the calibrated density bulb L.

A weighed sample of trimethylgallium monoammine in a fragile glass bulb[7] is introduced into the reaction tube A and, after exhausting and cooling, the bulb is broken. The reaction tube is attached to the system and ammonia is condensed on the gallane, which is readily soluble. Sodium is introduced into the addition tube D previous to exhausting the reaction tube.

The Mechanism of the Reduction Process.—In several experiments known samples of trimethylgallium ammine were treated with one atomic equivalent of metallic sodium in the apparatus described above. Reaction took place immediately with evolution of hydrogen; about 0.4 atom of hydrogen per atom of gallium was evolved in the course of two hours, when reaction ceased. There was no indication of further reaction over a period of fifty hours. Ammonium bromide was then added until the characteristic blue color due to sodium was just discharged. Approximately 0.4 atom of hydrogen per atom of gallium was evolved in this stage of the reaction. On further addition of ammonium bromide to the now colorless solution, approximately 0.2 atom of hydrogen was evolved per molecule of trimethylgallium.

It is evident that several reactions are involved when trimethylgallium is treated with sodium in liquid ammonia. One of these reactions is accompanied by evolution of hydrogen while the second reaction involves some sort of a reduction process, the product of which reacts with ammonium bromide with evolution of hydrogen. Since, on completion of the reaction, approximately 40% of the sodium remains in the free state, it follows that, in one of the reactions, at least two molecules of trimethylgallium per atom of sodium are concerned. The results may be accounted for if we assume the reactions

$$Na + 2(CH_3)_3Ga\cdot NH_3 \longrightarrow (CH_3)_3Ga\cdot NH_2\cdot Ga(CH_3)_3^- + Na^+ + {}^1/_2H_2 + NH_3 \quad (1)$$

$$2Na + 2(CH_3)_3Ga\cdot NH_3 \longrightarrow (CH_3)_3Ga:Ga(CH_3)_3^= + 2Na^+ + 2NH_3 \quad (2)$$

In the first reaction one atom of sodium is converted to sodium amide with the evolution of hydrogen, and the amide ion forms a coördinated compound with two molecules of trimethylgallium. Reactions of this type are well known in the case of boron, although, in all known cases, only one molecule of borane combines with one amide ion.[9] The second reaction involves the direct reduction of trimethylgallium to a negative trimethylgallium ion. A compound of this type is formed when triphenylboron is treated with metallic sodium in ether solution.[10] The resulting compound, however, is highly colored. In view of the fact that the solutions, in the case of trimethylgallium, are colorless, it is probable that two trimethylgallium ions link together to form a coördinated compound.

On adding ammonium bromide to the reaction mixture, we have, first, the reaction of the ammonium ion with the metallic sodium, in which hydrogen is evolved; then, a reaction of the ammonium ion with the reduced trimethylgallium, in which hydrogen is formed and trimethylgallium is regenerated. Finally, the balance of the ammonium bromide reacts with the sodium amide complex, containing two molecules of trimethylgallium, trimethylgallium being regenerated.

Experimental Data.—A number of reactions were carried out with a view to determining the precise nature of the products of the reaction. The reaction, in general, proceeded much as described above, although the relative amounts of the substances formed in the two reactions varied measurably, depending upon conditions. In one case, where the solution was quite concentrated, one-half of an atomic equivalent of

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(9) Hawes, Thesis, Brown University, 1927. J. E. Smith, Thesis, Brown University, 1930.

(10) Krause and Polack, *Ber.*, **59**, 777 (1926).

sodium reacted according to reaction (1), and reaction (2) was entirely absent. There was introduced into the reaction tube 0.6475 g. (5.64 m. moles) of trimethylgallium and there was added 0.0844 g. (3.67 m. at.) of sodium. At the end of three hours, 31.6 cc. (2.82 m. at.) of hydrogen was evolved which corresponds precisely to one-half atom of sodium per mole of trimethylgallium. On allowing the reaction tube to stand for twenty-two hours, there was evolved an additional 4.9 cc. (0.44 m. at.) of hydrogen. This evolution of hydrogen was due to slow reaction with the solvent, sodium amide being formed. The initial reaction took place quantitatively according to equation (1). The ammonia was evaporated and the tube allowed to warm to room temperature. On exhausting the reaction tube through a liquid ammonia trap, no material collected in the trap, indicating a complete absence of trimethylgallium ammine, which sublimes readily under these conditions. Ammonia was recondensed in the reaction tube and ammonium bromide was added until the blue color due to sodium just disappeared. On further addition of ammonium bromide to the now colorless solution, no hydrogen was evolved. This indicates the absence of reaction (2).

The attempt was made to vary the proportion of reactions (1) and (2) by carrying out the reduction at lower temperatures. At −76° no reaction whatever occurred. There was a very slow reaction at −48°, accompanied by the evolution of hydrogen. At lower temperatures, both reactions proceeded so slowly that it was not practicable to carry them out. Accordingly, a reaction was carried out at −33°, using a large volume of ammonia and adding the sodium in small pieces (of about 4 milligrams each), one at a time. Of twenty pieces of sodium, seventeen had reacted at the end of six and one-half hours while the eighteenth piece required more than twelve hours for complete reaction. After collecting and determining the gases due to the initial reaction of metallic sodium, ammonium bromide was added to the now colorless solution, the hydrogen was collected and its volume and density were determined. The results were: $(CH_3)_3Ga{\cdot}NH_3$, 0.7330 (5.56 m. moles); H evolved, 19.0 cc. (1.70 m. at.); Na reacted (by wt.), 0.0775 (3.37 m. at.); NH_4Br added, 0.509; H evolved on adding NH_4Br, 18.4 cc. (1.64 m. at.); total H, 37.4 cc. (3.34 m. at.). According to the above data, of 3.37 m. atoms of sodium that reacted, 1.70 m. atoms reacted according to equation (1), yielding 1.70 m. atoms of hydrogen. The remaining 1.67 m. atoms of sodium reacted for the most part according to equation (2). On addition of ammonium bromide, the sodium which was combined with trimethylgallium yielded 1.64 m. atoms of hydrogen according to the equation

$$Na_2[(CH_3)_3Ga]_2 + 2NH_4Br = 2(CH_3)_3Ga{\cdot}NH_3 + 2NaBr + H_2$$

After completion of the last described reaction, 93% of the trimethylgallium ammine was recovered by sublimation from the reaction tube into a weighed, fragile bulb cooled in liquid ammonia.

Reaction in Ethylamine.—In the hope that reaction (1) might be absent if reduction were carried out in ethylamine solution, the reduction of trimethylgallium ammine with lithium in ethylamine solution was investigated. The reactions in ethylamine were similar to, but not identical with, those in liquid ammonia. They took place as follows

$$Li + (CH_3)_3Ga{\cdot}C_2H_5NH_2 \longrightarrow (CH_3)_3Ga{\cdot}C_2H_5NHLi + {}^1/_2H_2 \qquad (3)$$

$$2Li + 2(CH_3)_3Ga{\cdot}C_2H_5NH_2 \longrightarrow [(CH_3)_3Ga]_2^{-} + 2Li^{+} + 2C_2H_5NH_2 \qquad (4)$$

The lithium, cut into small pieces, was added to a solution of trimethylgallium in ethylamine at liquid ammonia temperatures. Prior to adding the lithium, the trimethylgallium ammine was dissolved in ethylamine which was then evaporated in order to carry off the ammonia initially present. Reaction between lithium and trimethylgallium took place somewhat slowly, but, at the end of twelve hours, one atomic equivalent of lithium had reacted. The hydrogen evolved during this stage of the reaction was collected and its molecular weight and volume were determined. On distilling the ethylamine from the colorless solution, hydrogen was evolved. This hydrogen was collected and its molecular weight and density were determined. Since no ammonium bromide had been added, the hydrogen evolved during distillation of the amine must have resulted through a process of oxidation and reduction, presumably according to the reaction

$$Li_2[Ga(CH_3)_3]_2 + 2C_2H_5NH_2 \longrightarrow 2LiC_2H_5NH{\cdot}Ga(CH_3)_3 + H_2 \qquad (5)$$

The data relating to this reaction are as follows: $(CH_3)_3Ga{\cdot}NH_3$, 0.2709 (2.06 m. moles); Li, 0.0144 (2.06 m. at.); H evolved during reaction, 9.2 cc. (0.82 m. at.); H evolved during evaporation, 14.2 cc. (1.26 m. at.); total hydrogen evolved, 23.4 cc. (2.08 m. at.).

According to the above results, 39.8% of the gallium reacted according to equation (3) with evolution of hydrogen, while 61.2% reacted according to equation (4), without evolution of hydrogen. The equivalent quantity of hydrogen was, however, given off during evaporation of the solution, reaction (5) taking place. The total hydrogen, 101.0% of the theoretical, is within the limit of experimental error. While the product of reduction according to equation (3) is stable in the dry state as well as in ethylamine solution, the simultaneously formed product of reduction according to equation (4) is measurably stable only in solution at −33° and breaks down on evaporating the solvent.

On finally dissolving the product in liquid ammonia and treating with ammonium bromide, no hydrogen was evolved. This was to be expected in view of equation (5). After evaporating the liquid ammonia, the reaction tube was exhausted through a weighed trap cooled to liquid ammonia temperatures. The recovered material was obviously not the original trimethylgallium ammine, since it was liquid at ordinary temperatures and was markedly less volatile than the original ammine. One should naturally expect trimethylgallium ethylammine to be formed in this case. The weight of recovered material, which was too high for trimethylgallium ammine, would correspond to a recovery of 86% of trimethylgallium ethylammine.

Sodium bis-Trimethylgallium Ammide.—If reactions (1) and (2) express correctly what takes place when trimethylgallium is treated with sodium in liquid ammonia, then we should expect that one molecule of sodium amide would react with two molecules of trimethylgallium in liquid ammonia. Accordingly, a known quantity of sodium in a weighed, fragile bulb was introduced into the reaction tube, where the bulb was broken and the metal converted to sodium amide in the usual way. The ammonia was then evaporated and the bulb of trimethylgallium ammine, previously introduced, was broken and liquid ammonia was condensed in the reaction tube. That reaction took place was indicated by the disappearance of sodium amide, which is very slightly soluble in liquid ammonia. The solvent was now evaporated, the tube was exhausted and the product of the reaction weighed. The results were as follows: Na, 0.0497 (2.16 m. at.); $NaNH_2$, 0.0842 (2.16 m. moles); $(CH_3)_3Ga{\cdot}NH_3$, 0.5668 (4.30 m. moles); wt. product found, 0.5783 (2.15 m. moles); wt. $[(CH_3)_3Ga]_2{\cdot}NH_2Na$, calcd., 0.5775 (2.15 m. moles).

On completion of the reaction, the tube was heated to 50° and exhausted through a trap cooled in boiling ammonia. The quantity of material collected amounted to 0.0017 g., showing that the reaction between one molecule of sodium amide and two molecules of trimethylgallium was practically quantitative. On heating the product to 140° *in vacuo*, the material in the reaction tube failed to melt, although some crystals sublimed to the cooler portions of the tube. Trimethylgallium ammine melts at 30°. On cooling the tube and treating the product with ammonium bromide in liquid ammonia and thereafter exhausting the reaction tube through a trap, 48% of the original trimethylgallium ammine was recovered. Evidently some decomposition or rearrangement occurred on heating to 140°, since ordinarily the recovery amounts to 90% or more.

III. Reduction of Dimethylgallium Chloride

A. With One Atomic Equivalent of Sodium.—When dimethylgallium chloride is treated with one atomic equivalent of sodium in liquid ammonia, reduction occurs according to the equation

$$(CH_3)_2GaCl + Na = (CH_3)_2Ga + NaCl \tag{6}$$

The free dimethylgallium combines with one or more molecules of ammonia, probably to form an ammine. When the solvent ammonia is evaporated, a brownish colored solid is precipitated, which decomposes on warming to room temperature with evolution of hydrogen according to the equation

$$(CH_3)_2Ga{\cdot}NH_3 = (CH_3)_2GaNH_2 + {}^1/_2H_2 \tag{7}$$

Dimethylgallium.—Dimethylgallium chloride monoammine was prepared in a reaction tube of the type illustrated in Fig. 2a. It was attached to the system in place of the reaction tube (A) shown in Fig. 1. One atomic equivalent of sodium was introduced into the arm A, which was cut open for the purpose and then sealed. After condensing ammonia in the reaction tube, the sodium was added. Reaction took place immediately without evolution of gas and without formation of a precipitate, except that toward the end of the reaction sodium chloride appeared. The color of the solution changed gradually from yellow to orange; this color, seemingly, was due to dimethylgallium. As the liquid ammonia evaporated, a brown solid appeared and, when nearly all the liquid was gone, gas was evolved and the color of the solid changed from brown to gray. The volume and density of the gas were determined and found to correspond to one atom of hydrogen per molecule of dimethylgallium. At a temperature of 60° or above, a crystalline solid sublimed from the residue. This was later shown to be dimethylgallium amide. Equations (6) and (7) account for the products of reaction.

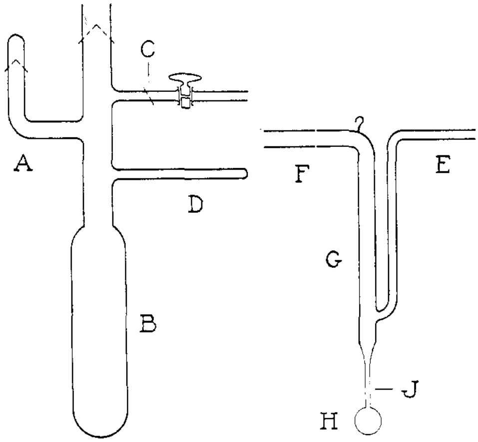

Fig. 2a. Fig. 2b.

Fig. 2.—Apparatus used in preparation of dimethylgallium amide.

In order to determine the stability of dimethylgallium, a second reaction was carried out, identical with the first, except that the ammonia was evaporated at −33°. The ammonia from the reaction tube was absorbed in sodium iodide, contained in a flask M cooled to ice temperature. In this way any evolved gases were not contaminated by air or water, nor were gases lost by absorption in water. On completion of the reaction and evaporation of the solvent, a brownish colored solid remained and no permanent gases were collected. However, on standing overnight, an appreciable quantity of hydrogen was evolved. About half the hydrogen required according to equation (7) was obtained at the end of twenty-four hours. On now warming the residue to room temperature, hydrogen was given off rapidly and the color of the solid in the reaction tube changed from brown to gray. The quantitative data were: m. moles $(CH_3)_2$-

$GaCl\cdot 2NH_3$, 5.47, 5.63; m. atoms Na added, 5.61, 5.66; m. atoms H evolved, 5.40, 5.62; ratio H/Ga, 0.987, 0.998. The dimethylgallium amide resulting from the above reactions was separated and identified.

Dimethylgallium Amide.—Since dimethylgallium amide sublimes readily in a vacuum at 100°, this compound was separated from the residue by sublimation. The material was prepared in tube B of Fig. 2a. On completion of the reaction, the tube was exhausted, filled with nitrogen, and the stopcock was sealed off at C. A Y-tube of the form shown in Fig. 2b, provided with a fragile bulb at the bottom, was weighed and arm E was attached to the pump system by means of de Khotinsky cement. Tube D of the reaction tube was cut and quickly attached to tube F (Fig. 2b) by means of a rubber slip-joint. The tube was at once evacuated and a liquid ammonia bath was placed around the Y-tube and an air-bath, heated to 100°, around the reaction tube. Dimethylgallium amide collected in arm G of the Y-tube. When a sufficient quantity had collected, the tube was heated with a small flame to melt the amide which ran into a bulb H, which was then sealed off at J. The bulb and the Y-tube were then weighed. A number of bulbs were filled in this way for analysis.

Two samples were analyzed for nitrogen and gallium. The sample bulbs were broken in an evacuated tube containing potassium hydroxide. Dimethylgallium amide dissolves slowly in water, and it was necessary to heat to 60° to effect complete solution. The ammonia formed on hydrolysis was absorbed in standard acid and titrated back with standard alkali. The gallium in the residual solution was oxidized with hydrogen peroxide and precipitated with tannin in the presence of acetic acid. A third sample was oxidized completely with sulfuric and nitric acids.

Anal. Subs., 0.2070, 0.3510: cc. of 0.09367 *N* H_2SO_4, 19.14, 32.24. Found: N, 12.13, 12.13. Ga_2O_3, 0.1672, 0.2647. Found: Ga, 60.09, 60.34. Subs., 0.1435: Ga_2O_3, 0.1163. Found: Ga, 60.26; mean: N, 12.13, Ga, 60.23. Calcd. for $(CH_3)_2GaNH_2$: N, 12.10, Ga, 60.21.

B. With Two Equivalents of Sodium.—A single experiment was carried out in which dimethylgallium chloride was treated with two equivalents of sodium. The first equivalent of metal reacted immediately with the formation of dimethylgallium, which formed an orange colored solution. The second equivalent yielded the familiar blue solution. In the course of twenty hours, 0.37 of an equivalent of hydrogen was evolved. On adding an equivalent of ammonium bromide, 0.54 equivalent of hydrogen was evolved, and a deep brownish-red solution resulted. When the solvent was evaporated, a brown solid was deposited, which yielded one equivalent of hydrogen on warming to room temperature. The color of the solid changed from brown to gray. The data are: m. moles $(CH_3)_2GaCl\cdot NH_3$, 3.74; m. atoms H before adding NH_4Br, 1.38; after adding NH_4Br, 1.95; after evaporation of solvent and warming, 3.74; total H, 7.08.

The total hydrogen collected was a little less than two atoms per mole of compound, which may perhaps be accounted for by loss in transferring. The first stage of the reaction proceeds according to equation (6). The excess sodium then reacts slowly with ammonia, perhaps catalyzed by the gallium compound, to form sodium amide and hydrogen. The resulting sodium amide probably combines with gallium to form a coördinated compound. On adding ammonium bromide, the excess sodium reacts to yield hydrogen, while the sodium amide is neutralized, regenerating dimethylgallium. At room temperature, this compound decomposes with evolution of hydrogen according to equation (7).

IV. Summary

The reaction of trimethylgallium ammine with sodium in liquid ammonia is in accord with the equations

$$2(CH_3)_3Ga\cdot NH_3 + Na = [(CH_3)_3Ga]_2NH_2Na + {}^1/_2H_2 + NH_3$$
$$2(CH_3)_3Ga\cdot NH_3 + 2Na = [(CH_3)_3Ga]_2Na_2 + 2NH_3$$

Depending on conditions, reaction takes place according to the first equation to the extent of from 60 to 100% of the total gallium and according to the second, from 30 to 0%. A similar reaction takes place when trimethylgallium is treated with lithium in ethylamine, except that the first reaction is replaced by the following

$$(CH_3)_3Ga\cdot C_2H_5NH_2 + Li = (CH_3)_3Ga\cdot C_2H_5NHLi + {}^1/_2H_2$$

The compound $Na_2[(CH_3)_3Ga]_2$ reacts with ammonium bromide with evolution of one atom of hydrogen per atom of sodium and the regeneration of trimethylgallium. The corresponding salt of lithium decomposes with evolution of hydrogen as the ethylamine is evaporated, lithium trimethylgallium ethyl ammide being formed.

Dimethylgallium chloride is reduced to dimethylgallium when treated with one atomic equivalent of sodium in liquid ammonia. The free dimethylgallium combines with ammonia and may be obtained as a solid at −33°, where an internal oxidation–reduction takes place slowly according to the equation $(CH_3)_2Ga\cdot NH_3 = (CH_3)_2GaNH_2 + H_2$. At room temperature the reaction is rapid. The trimethylgallium amide resulting from this reaction has been identified.

When trimethylgallium chloride is treated with two atomic equivalents of sodium, dimethylgallium is first formed, which reacts slowly with sodium presumably according to the equation $(CH_3)_2Ga\cdot NH_3 + Na = (CH_3)_2Ga\cdot NaNH_2 + {}^1/_2H_2$. In this compound the amide ion is linked to gallium by a coördinate linkage. On neutralizing with ammonium bromide, dimethylgallium ammine is regenerated and this compound undergoes internal oxidation–reduction with evolution of hydrogen on evaporation of the solvent.

PROVIDENCE, RHODE ISLAND

RECEIVED APRIL 21, 1933
PUBLISHED SEPTEMBER 5, 1933