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Quaternary Ammonium Salts with Anions Containing Triphenylboron

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Introduction

In solvents other than liquid ammonia, it is difficult to obtain negative ions with more than one organic group attached to the central atom. Nevertheless, salts of such ions are highly desirable for study in determining the influence of constitutional factors on the properties of electrolytes. Hawes found that sodium and potassium amides react with triphenylboronammine in liquid ammonia to form salts in which the NH_2^- ion is joined to boron by a coördinated linkage.[1] He measured the conductance of these salts in liquid ammonia[2] and found that the ammidotriphenylboron ion has a very low mobility and that its salts are exceptionally highly dissociated, the sodium salt having a dissociation constant of 150×10^{-4}. In solvents other than ammonia, it is necessary that the electrolytes have a high degree of stability, which is not the case with the ammidotriphenylboron salts. It seemed probable, however, that other small ions, particularly the fluoride and the hydroxyl ions, would coördinate with triphenylboron and that the resulting salts would be stable. It is well known that the lower alkyl boranes are absorbed by sodium or potassium hydroxide.

The general procedure in preparing the desired salts was to treat the quaternary ammonium fluoride or hydroxide with triphenylboronammine in alcohol solution. The ammonia is replaced by the fluoride or the hydroxyl ion and the salts are recovered from the solvent by crystallization.

Experimental

Tetramethylammonium Triphenylborofluoride, $(CH_3)_4NF \cdot B(C_6H_5)_3$.—The triphenylboronammine used was a stock sample which had been prepared in this Laboratory. Its preparation has been described by Hawes.[1] Tetramethylammonium hydroxide was prepared from the bromide by means of freshly precipitated silver oxide and the resulting base was titrated with hydrogen fluoride after separating from the solid material. The fluoride is very soluble in water but it may be obtained in anhydrous form by concentrating the aqueous solution and thereafter gradually heating to 115° while exhausting the system with a pump. The solid which is formed under these conditions reaches constant weight and is evidently anhydrous since a small sample of the salt was found to decompose at 180° in accordance with the earlier observations of Lawson and Collie.[3]

Equivalent quantities of tetramethylammonium fluoride and triphenylboronammine are introduced into alcohol, in which both are soluble, and the solution is refluxed for several hours during which time ammonia is evolved and crystals are formed. After cooling, the crystals are separated from the supernatant liquid and recrystallized from alcohol; melting point 175–177°.

The compound was analyzed for boron by the method of Booth.[4] The sample was warmed with a few cubic centimeters of concentrated sulfuric acid in a distilling flask. Thereafter, approximately 50 cc. of carefully dried methyl alcohol was added and the mixture was warmed for a few minutes to permit the reaction between the alcohol and the boric acid to complete itself. Thereafter, successive fractions of about 10 cc. of the methyl alcohol were distilled through a fractionating column into a suitable receiver until no further boron was carried over. Two or three fractions were generally sufficient. The boron was determined after hydrolysis of the methyl borate by titration with sodium hydroxide in the presence of mannitol. Sample, 0.2192, 0.1870; cc. 0.04413 N sodium hydroxide, 14.86, 12.62; % B found, 3.237, 3.222; calcd. for $C_{22}H_{27}BNF$, 3.229. The fluorine content of the compound was determined by the method of Allen and Furman[5] in which triphenyltin chloride is used as the precipitant. In order to break the fluorine–boron linkage, the compound was first hydrolyzed with sodium hydroxide solution, in which process it dissolved completely. However, when the solution was neutralized with hydrochloric acid, a precipitate appeared which was removed by filtration. The neutralized solution was then treated with triphenyltin chloride according to the directions of Allen and Furman. Sample, 0.3144, 0.3037; triphenyltin fluoride, 0.3445, 0.3398; % F found, 5.645, 5.764; calcd. for $C_{22}H_{27}BNF$, 5.671.

Tetrabutylammonium Triphenylborofluoride, $(C_4H_9)_4NF \cdot B(C_6H_5)_3$.—Tetrabutylammonium fluoride was prepared from tetrabutylammonium iodide in the same manner as was tetramethylammonium fluoride from the corresponding bromide. The anhydrous salt, together with triphenylboronammine, was dissolved in alcohol where reaction took place readily with the formation of crystals of the desired compound. After separating, these were recrystallized from ethyl alcohol and were found to melt at 161–162°. The compound was found to be stable in air.

Analyses were carried out as in the case of the tetramethylammonium compound. B: sample, 0.1932, 0.2101; cc. 0.04413 N sodium hydroxide, 8.68, 9.76; % B found,

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(1) W. W. Hawes, Master's Thesis, Brown University, 1928.

(2) W. W. Hawes, THIS JOURNAL, **55**, 2776 (1933).

(3) Lawson and Collie, *J. Chem. Soc.*, **53**, 627 (1888).

(4) R. B. Booth, Thesis, Brown University, 1934.

(5) Allen and Furman, THIS JOURNAL, **54**, 4425 (1932).

2.145, 2.218; calcd. for $C_{34}H_{51}BNF$, 2.150. F: sample, 0.3133, 0.3171; triphenyltin fluoride, 0.2275, 0.2285; % F found, 3.741, 3.712; calcd. for $C_{34}H_{51}BNF$, 3.776.

Tetramethylammonium Triphenylborohydroxide Monoalcoholate, $(CH_3)_4NOH \cdot B(C_6H_5)_3 \cdot C_2H_5OH$.—Tetramethylammonium hydroxide was prepared by treating an aqueous solution of tetramethylammonium bromide with moist silver oxide. After separating from the silver bromide and excess silver oxide, the solution was concentrated. The residual water was removed by pumping through a phosphorus pentoxide tube while at the same time placing the tube containing the base in a bath whose temperature was gradually raised to 100°. A small sample of the final product was found to decompose at 125–130°, which corresponds to the range given by Walker and Johnston[6] for the monohydrate. All attempts to remove the last molecule of water were unsuccessful. It should be stated that all operations described above were carried out under strict exclusion of carbon dioxide. The reaction between the monohydrate of tetramethylammonium hydroxide and triphenylboronammine was carried out in ethyl alcohol, as in the case of the fluoride. The product formed immediately on warming the solution. After separating from the alcohol, it was recrystallized from the same solvent. When heated to 230°, it puffed up slightly but did not melt until the temperature reached 359–360°, where it decomposed upon melting. This compound was not analyzed directly but was quantitatively converted to the corresponding monohydrate which was analyzed as will be described in the following section.

Tetramethylammonium Triphenylborohydroxide Monohydrate, $(CH_3)_4NOH \cdot B(C_6H_5)_3 \cdot H_2O$.—When the alcoholate described in the preceding paragraph was treated with water for a few minutes and immediately pumped dry, a substance resulted which melted at 185–187°. When this, in turn, was dissolved in absolute alcohol and dried, the compound again melted at 360°. Evidently the alcoholate and the hydrate may be converted one to the other by treatment with the appropriate solvent. That the conversion is quantitative is shown by the following figures: wt. original alcoholate, 0.0937, 0.0910; wt. hydrate, 0.0870, 0.0845; observed loss in wt., 0.0067, 0.0065; calcd. loss, 0.0069, 0.0067. Wt. original hydrate, 0.2504; wt. alcoholate, 0.2705; observed gain in wt., 0.0201; calcd. gain, 0.0200.

Samples of the hydrated compound were analyzed for boron as described above. The results were: sample, 0.1915, 0.2182; cc. sodium hydroxide (0.04413 *N*), 12.30, (0.0657 *N*), 9.32; % B found, 3.067, 3.036; calcd. for $C_{22}H_{30}BNO_2$, 3.082.

In order to determine the amount of the base present in the compound, a known quantity of dilute hydrochloric acid, slightly in excess of that required to neutralize the base, was added to the salt and the resulting solution was refluxed for a couple of hours. At the end of this process, the salt had broken down and dissolved completely in the hot acid solution. Upon cooling, some solid precipitated, which was filtered off, after which the solution was titrated with standard alkali. Sample, 0.2501, 0.3279; cc. hydrochloric acid (0.0577 *N*), 12.38, (0.1084 *N*), 8.84; % OH found, 4.858, 4.970; calcd. for $C_{22}H_{30}BNO_2$, 4.845.

Tetrabutylammonium Triphenylborohydroxide, $(C_4H_9)_4NOH \cdot B(C_6H_5)_3$.—This compound was prepared by two methods; the first was similar to that used in the case of the tetramethylammonium salts. This method, however, is disadvantageous because of the difficulty experienced in dehydrating tetrabutylammonium hydroxide. Accordingly, the base was prepared in absolute alcohol solution by allowing equivalent quantities of tetra-*n*-butylammonium chloride and potassium hydroxide to react. After the potassium chloride had been separated by filtration, an equivalent amount of the triphenylboronammine was added. The product, after recrystallization from alcohol, was found to melt at 143.5–145.5°. This compound, like those previously described, was perfectly stable in the atmosphere.

Analyses were carried out as in the case of the tetramethylammonium salt. B: sample, 0.1980, 0.1476; cc. 0.04413 *N* sodium hydroxide, 9.01, 6.88; % B found, 2.173, 2.226; calcd. for $C_{24}H_{52}BNO$, 2.159. Base: sample, 0.2205, 0.2916; cc. 0.0577 *N* hydrochloric acid, 7.49, 10.05; % OH found, 3.333, 3.382; calcd. for $C_{34}H_{52}BNO$, 3.393.

Some Other Salts.—In general, it is only the small ions, such as NH_2^-, OH^- and F^-, which form stable complexes with triphenylboron. Neither tetramethylammonium chloride nor tetramethylammonium bromide forms complexes with triphenylboron. Alcohol solutions of these salts brought together with amminotriphenylboron show no reaction and the original materials are recovered from solution unchanged.

Potassium cyanide reacts with amminotriphenylboron in alcohol solution. On addition of petroleum ether, hair-like crystals are precipitated which decompose in the neighborhood of 300°. They react vigorously with water. Sodium phenolate shows little reaction with amminotriphenylboron in liquid ammonia solution. Most of the reactants are recoverable. Sodium benzhydrolate reacts with amminotriphenylboron in liquid ammonia. The white solid which results upon evaporation of the solvent oxidizes slowly in air and is unstable in organic solvents at higher temperatures. Sodium triphenylcarbinolate reacts with amminotriphenylboron in liquid ammonia. The product may be recrystallized from benzene and it seems to be stable in air and in organic solvents at ordinary temperatures. The potassium salt exhibits similar properties. Sodium phenylacetylate reacts with amminotriphenylboron in liquid ammonia with the formation of a white solid which shows low stability when dissolved in organic solvents under ordinary conditions; the solutions develop color.

Summary

On treating amminotriphenylboron with quaternary ammonium hydroxides or fluorides, complex ions are formed in which the hydroxyl or the fluoride ion is coördinated with triphenylboron. The salts are stable in air. The following salts have been prepared: $(CH_3)_4NF \cdot B(C_6H_5)_3$, $(n\text{-}C_4H_9)_4NF \cdot B(C_6H_5)_3$, $(CH_3)_4NOH \cdot B(C_6H_5)_3 \cdot C_2H_5OH$, $(CH_3)_4NOH \cdot B(C_6H_5)_3 \cdot H_2O$, $(n\text{-}C_4H_9)_4NOH \cdot B(C_6H_5)_3$.

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(6) Walker and Johnston, *J. Chem. Soc.*, **87**, 958 (1905).