$$(SO_3)_2NO^{\underset{\cdot}{=}} + HO\cdot \xrightarrow{k_2} \text{intermediate} \longrightarrow \left\{ \begin{array}{l} N_2O \\ HNO_2 \\ SO_4^{=} \\ H_3O^+ \end{array} \right. \quad (9)$$

The differential rate equation should be equation (10), and with the logical supposition that $k_2 \cdot [HO\cdot] \ll k_1[H_3O^+]$ the observed reaction should be first order in respect to each of the reacting species, nitrosyl disulfonate ion and hydronium ion as was found to be the case.

$$-d[(SO_3)_2NO^{\underset{\cdot}{=}}]/dt = [(SO_3)_2NO^{\underset{\cdot}{=}}]\{k_1[H_3O^+] + k_2[HO\cdot]\} \quad (10)$$

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SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Studies Relating to Boron. V. Chemistry of the Dibutylboron Group[1]

BY ROBERT W. AUTEN[2] AND CHARLES A. KRAUS

RECEIVED DECEMBER 15, 1951

The reduction of dibutylboron chloride by means of sodium–potassium alloy in ether solution takes place in two steps. One equivalent of chloride reacts with one equivalent of metal to produce dibutylboron which is soluble in ether. On evaporation of solvent, the compound disproportionates to form tributylboron and a solid, presumably monobutylboron. With excess metal, the chloride is reduced to the boride, $MB(C_4H_9)_2$; the yield is 65%. This boride reacts with methyl iodide to yield methyldibutylboron. On treating the boride with dibutylboron chloride, there was obtained, in addition to tributylboron and monobutylboron, a small quantity of a difficulty volatile substance whose boron content corresponds to that of dibutylboron. When the metal boride reacts with one equivalent of hydrogen chloride (at −70°), there are obtained hydrogen, tributylboron and monobutylboron. With two equivalents of hydrogen chloride, the products are hydrogen and dibutylboron chloride. Similar reactions take place with triethylammonium chloride.

I. Introduction

Alkylboron halides of the type R_2BX, heretofore, have not been reduced to the free group R_2B or to the negative ion R_2B^-. However, Booth[3] has obtained evidence which indicates that such reduction may be effected by means of sodium–potassium alloy in diethyl ether. Using dibutylboron chloride, we have confirmed Booth's observation.

The reduction of dibutylboron chloride by means of sodium–potassium alloy takes place in two stages. In the first stage, the chlorine is split off quantitatively according to the equation

$$(C_4H_9)_2BCl + M = (C_4H_9)_2B + MCl \quad (1)$$

The free group, $(C_4H_9)_2B$, is soluble in ether; it doubtless exists as a polymer of unknown complexity. For the sake of brevity we shall omit any symbol indicating polymer complexity; the formulas indicate composition only. In the second stage, reaction occurs according to the equation

$$(C_4H_9)_2BCl + 2M = MB(C_4H_9)_2 + MCl \quad (2)$$

If an attempt is made to separate the product of reaction (1) by evaporation of the solvent, the product undergoes disproportionation according to equation

$$2(C_4H_9)_2B = (C_4H_9)_3B + C_4H_9 \cdot B \quad (3)$$

Reaction (2) is not quantitative; somewhat more than 60% of the dibutylboron is converted to metal boride. The existence of the metal boride, which is soluble in ether, is established by its reaction with methyl iodide, methyldibutylboron being formed according to the equation

$$MB(C_4H_9)_2 + CH_3I = CH_3B(C_4H_9)_2 + MI \quad (4)$$

On treating the metal boride with dibutylboron chloride, the final, over-all reaction is in accord with the equation

$$(C_4H_9)_2BM + ClB(C_4H_9)_2 = (C_4H_9)_3B + C_4H_9B + MCl \quad (5)$$

Doubtless, the dibutylboron initially formed disproportionates according to equation (3). In this reaction, a small quantity of a difficultly volatile substance was obtained whose composition, on analysis, corresponded to that of $(C_4H_9)_2B$.

On treating the metal boride with excess hydrogen chloride, reaction occurs according to the equation

$$MB(C_4H_9)_2 + 2HCl = (C_4H_9)_2BCl + H_2 + MCl \quad (6)$$

On treating the boride with one equivalent, the final products conform to the over-all reaction

$$2MB(C_4H_9)_2 + 2HCl = (C_4H_9)_3B + C_4H_9B + H_2 + 2MCl \quad (7)$$

Dibutylboron chloride is initially formed and this in turn reacts with metal boride according to equation (5). The reaction of the boride with triethylammonium chloride is similar to that which hydrogen chloride. The products may be accounted for by the equation

$$2MB(C_4H_9)_2 + 2(C_2H_5)_3NHCl = (C_4H_9)_3B + C_4H_9B + 2(C_2H_5)_3N + H_2 + 2MCl \quad (8)$$

No evidence was found which indicated the formation of the hydride $(C_4H_9)_2BH$. The metal boride appears to be stable in liquid ammonia solution but reacts slowly with ammonia vapor at room temperature.

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(1) This paper is based on a portion of a thesis presented by Robert W. Auten in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1937.

(2) Anthony Fellow in Brown University, 1933–1934; University Fellow, 1935–1937.

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

II. Apparatus, Procedure and Materials

1. **Reaction Tube.**—Since the boron compounds employed in this investigation are extremely sensitive to water and oxygen, all manipulations were designed to rigidly exclude moisture and air. For the most part, reactions in ether were carried out in sealed, two-legged reaction tubes somewhat similar in form to those described by Franklin.[4] Ether-insoluble substances (*e.g.*, K–Na alloy) were confined to the leg in which the reactions were carried out and ether-soluble products were collected in the second leg. The two legs were connected by an upper tube through which solvent could be distilled and a lower tube, carrying a plug of fine glass cotton, through which solutions could be filtered. After separating the reaction products, the two tubes were usually separated by sealing off at constrictions in the connecting tubes.

2. **Isolation of Products.**—The tube containing the ether solution of reaction products was provided with a side arm which was drawn down to a fine capillary tube. This capillary tube was attached with de Khotinsky cement to a tube opener[5] which communicated with a series of traps leading to a Toepler pump and ending in a gasometer tube and a gas density bulb; the latter could be detached from the system and weighed. After removing permanent gases and solvent, the products were vacuum distilled into weighed, fragile-bulb traps of the type described by Kraus and Toonder.[6] If sufficient purity was not obtained by this procedure, the material was subjected to repeated vacuum distillations in an auxiliary apparatus before filling into fragile bulbs.

3. **Materials.**—Tri-*n*-butylboron, prepared by Dr. R.B. Booth, was on hand in the laboratory. Di-*n*-butylboron chloride was prepared by treating tri-*n*-butylboron with dry hydrogen chloride at 110° according to the procedure developed by Booth.[7] In making up the sodium–potassium alloy, the constituents (atom ratio $K/Na = 2$) were weighed under Nujol and melted together *in vacuo*. The molten alloy, under nitrogen, was forced through a fine capillary into weighed, fragile bulbs. Commercial ether, after preliminary purification, was dried with sodium benzophenone as recommended by Smith.[8] Nitrogen was purified by passing over copper heated to redness in a silica tube.

4. **Analyses.**—Booth's procedure[7] was followed in analysis for boron. Volatile samples were contained in fragile bulbs, which were broken under a basic solution of hydrogen peroxide. The boric acid was then determined in the usual fashion.

III. Reduction of Di-*n*-butylboron Chloride with Sodium–Potassium Alloy in Ether Solution

1. **With One Equivalent of Alkali Metal.**—The general experimental procedure of Section II was followed. Reaction was allowed to proceed until a faint yellow color was noted. Ether-soluble material was separated from excess alloy and alkali metal chlorides as described above. After evaporation of solvent, a distillate commenced to collect when the pressure fell to approximately 0.1 mm. The volatile product was collected in fragile bulbs for analysis: wt. subs. g., 0.0598, 0.0860; cc. 0.1043 *N* NaOH, 3.10, 4.51; % B found, 5.85, 5.92; calcd. for $(C_4H_9)_3B$, 5.94. Analysis identified the product as tributylboron.

The clear, glassy residue in the tube was treated with water. Solution was accompanied by the evolution of hydrogen; the resulting solution was practically neutral. The total boron content was determined.

Data for two experiments follow: mmoles $(C_4H_9)_2BCl$, 1.938, 1.520; mmoles $(C_4H_9)_3B$, 0.378, 0.521; m. at. B in residue, 1.307, 0.776. In experiment (1), approximately 20% of the boron was recovered as tributylboron while 67.5% was found in the residue; in experiment (2), 34.3% was recovered as borine and 51% in residue. Indications are that removal of borine was not complete.

Since the hydrolyzed solution of the residue was essentially free from acid or base it follows that the reaction was complete in the sense of equation (1). Apparently, dibutylboron was formed as an unstable intermediate which disproportionated under the conditions imposed in its attempted isolation.

2. **Complete Reduction to Alkali Metal Di-*n*-butylboride.**—Complete reduction of the chloride led, in the main, to the formation of the alkali metal boride in accordance with equation (2). The reduction was carried out according to the procedure described above. After standing for approximately 10 days, to ensure as complete a conversion as possible, the ether-soluble fraction was isolated in one leg of the reaction tube, which was then attached to the vacuum system. No volatile products were collected on exhausting the reaction tube to 0.01 mm. Water was added to hydrolyze the product; hydrogen was evolved and the brown color of the boride disappeared. After breaking open the reaction tube, the solution was titrated with standard acid to determine the amount of alkali metal and an analysis was made for boron. The leg containing unreacted alloy and alkali halides was likewise opened, and the chlorine was determined gravimetrically as silver chloride. Following are the results of two experiments: mmoles $(C_4H_9)_2BCl$, 2.614, 1.953; m.at. metal in product, 1.536, 1.163; m.at. B in product, 2.544, 1.884; atoms M/atom B, 0.604, 0.617; m.at. Cl as MCl, 2.556, 1.868.

The recovery of chlorine was somewhat low; this may be accounted for, since small amounts of alkali metal chlorides were invariably washed over with the ether solution (the refinement of a filter plug was not introduced until later.) The low ratio of alkali metal to boron in the ether-soluble product indicates that conversion to metal boride was not quantitative. Assuming the alkali metal to have been present as $MB(C_4H_9)_2$, the conversion of the chloride to alkali metal salt was approximately 60% of theory. Similar values for the conversion were obtained indirectly as is pointed out below.

3. **Methyl Di-*n*-butylboron.**—The nature of the alkali metal boride was further established by its reaction with methyl iodide. Methyldi-*n*-butylboron was formed, furnishing convincing proof that the alkali metal salt actually present was $MB(C_4H_9)_2$, and that it reacted according to equation (4).

The alkali metal di-*n*-butylboride was prepared as described above. The reaction tube and an ampule containing a slight excess of purified methyl iodide were attached through tube openers to a system provided with vacuum and with fragile, glass-bulb traps in which to collect and fractionate volatile products. After opening the connection between the reaction tube and the ampule containing the methyl iodide, the reaction tube was cooled with liquid ammonia and the methyl iodide was distilled into the solution of alkali metal boride. The color of the solution immediately began to fade and alkali metal iodide precipitated. When all the methyl iodide had been added, the ammonia-bath was removed and solvent and excess methyl iodide were distilled into a trap cooled with liquid ammonia. When distillation was completed, the trap and methyl iodide ampule were sealed off. A connection was then made between the reaction tube and a fragile bulb trap and the pressure was reduced by pumping. When the pressure had fallen to 0.15 mm., a clear liquid commenced to collect in the trap; the pressure soon dropped to 0.05–0.07 mm. and remained there as long as material continued to collect.

The product was purified by repeated vacuum distillation and collected in two fractions, while a small amount of less volatile liquid was discarded. Fraction (1) was slightly the more volatile. These fractions were analyzed for boron; fraction (1) wt. subs. g., 0.1073, 0.0982; cc. 0.0155 *N* NaOH, 6.95, 6.93; % B, 7.39, 7.42. (2) 0.0532, 0.0742; 3.60, 5.00; % B, 7.72, 7.69; calcd. for $CH_3(C_4H_9)_2B$, 7.73. Evidently, the more volatile fraction (1) contained a small amount of impurity.

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[4] E. C. Franklin, "Nitrogen System of Compounds," A. C. S. Monograph No. 68, Reinhold Publ. Corp., 1935.

[5] C. A. Kraus and F. E. Toonder, *Proc. Natl. Acad. Sci.*, **19**, 292 (1933); A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[6] C. A. Kraus and F. E. Toonder, THIS JOURNAL, **55**, 3552 (1933).

[7] R. B. Booth and C. A. Kraus, *ibid.*, **74**, 1415 (1952).

[8] J. E. Smith and C. A. Kraus, *ibid.*, **73**, 2751 (1951).

If it is assumed that reaction is quantitative according to equation (4), then it should be possible to estimate the quantity of metal boride present after reduction of the chloride, either by obtaining a quantitative recovery of methyldibutylboron or by determining the amount of alkali metal iodide which was formed. The latter method was adopted.

Following are data relating to two reactions: (1) mmoles $(C_4H_9)_2BCl$, 5.080; mmoles $CH_3B(C_4H_9)_2$, 2.307; m.at. I, 2.989. (2) $(C_4H_9)_2BCl$, 6.097; m.at. I, 3.633. Based on the recovery of iodine, it would appear that 60% of the di-*n*-butylboron chloride was in each case converted to the alkali metal salt. These results are in agreement with those based on the direct analysis for alkali metal as recorded in paragraph 2 above. It may be noted that, in reaction (1), 45% of the boron was recovered as methyldibutylboron, or 75% based on iodine recovered. It would seem that dibutylboron is present in two forms, one of which (60%) is reduced by alkali metal while the remaining dibutylboron is not reduced.

IV. Reaction of Di-*n*-butylboron Chloride with Alkali Metal Di-*n*-butylboride

In the reduction of di-*n*-butylboron chloride with one equivalent of metal, evidence was obtained which indicated that the free di-*n*-butylboron group was formed; but attempted isolation of the free group resulted in disproportionation. As was to be expected, similar results were obtained when the alkali metal salt was treated with di-*n*-butylboron chloride. In accord with equation (5), the principal products isolated were tri-*n*-butylboron and a non-volatile substance. However, in addition, a small amount of material was isolated which was distinctly less volatile than tributylboron. This may have been $(C_4H_9)_2B$ (or its polymer), since its boron content was in close agreement with that calculated for the free group.

The reaction tube resembled that described in Section II, but an additional leg was provided. One leg was charged with 2.09 g. of alloy (a large excess), a second with 0.6277 g. (3.91 mmoles) of di-*n*-butylboron chloride and the third leg, with 0.5886 g. (3.68 mmoles) of dibutylboron chloride. The alkali metal boride was prepared in leg 2, using the materials in legs 1 and 2. The resulting solution was transferred to leg 1 and leg 2 was sealed off at constrictions provided for the purpose.

The bulb of chloride in the third leg was now broken open, the compound was put into solution with ether and added slowly to the solution of metal boride. Alkali metal chloride precipitated and the color of the solution faded gradually to a pale yellow. Not quite all the chloride solution was needed to complete the reaction. Finally, the leg containing a small amount of unused chloride was sealed off.

Ether was removed from the materials in the reaction tube and volatile products were isolated in fragile bulbs as described above. The first fraction distilled at about 0.5 mm. and doubtless consisted chiefly of excess, unreacted dibutylboron chloride; this weighed 0.0906 g. A second fraction was collected at pressures between 0.10–0.02 mm. Distillation was extremely slow toward the end and was continued for 15 hours. The tube was warmed to 70° during the last 5 hours of distillation; 0.5674 g. of product was obtained. In addition to alkali metal halide, a very pale yellow solid remained in the reaction tube. Water was added to this residue; the gas formed on hydrolysis was collected and identified as hydrogen. On analysis, the residue was found to contain 2.57 m.at. of boron.

The volatile product was purified by repeated vacuum distillations as described above. Four fractions were separated: (1) was small and contained the more volatile constituents; (2) was the largest; (3) was too small for analysis and contained all residual liquid which could be distilled at room temperature at pressures between 0.01–0.02 mm.; (4) was somewhat larger than the first and was obtained by heating with a water-bath. Analysis for boron gave the following results: fraction (1) wt. subs. g., 0.0913; cc. 0.1070 *N* NaOH, 5.24; % B, 6.64. (2) 0.2980; 15.43, % B, 5.99. (4) 0.1249; 8.77, % B, 8.13. % B calcd. for $(C_4H_9)_2BCl$, 6.75; $(C_4H_9)_3B$, 5.94; $(C_4H_9)_2B$, 8.66. From these analyses, it appears that fraction (1) was mainly dibutylboron chloride; (2) was practically pure tributylboron, while (4) can be best represented as di-*n*-butylboron admixed with a small quantity of tributylboron.

V. Other Reactions of Alkali Metal Di-*n*-butylboride

1. Reaction with Hydrogen Chloride.

—Reactions were carried out at −70°. Hydrogen was always evolved and, with an equivalent quantity of hydrogen chloride, tri-*n*-butylboron and a non-volatile product were obtained; with an excess of hydrogen chloride, the principal product was di-*n*-butylboron chloride. It seems that a hydride such as di-*n*-butylboron hydride is not stable under these conditions if, indeed, it exists at all.

(a) **One Equivalent of Hydrogen Chloride.**—A calculated equivalent of hydrogen chloride was bubbled through a solution of the boride, cooled with a mixture of Dry Ice and ether. It was noted that only approximately one-half of the solution was decolorized on the complete addition of the hydrogen chloride, namely, that portion in the immediate vicinity of the inlet tube. Hydrogen was given off. On mixing, the color of the solution was discharged completely, but no further hydrogen was evolved. When solvent was evaporated, and the residue was distilled, tri-*n*-butylboron was recovered; % B found, 5.99; calcd. for $(C_4H_9)_3B$, 5.94. A non-volatile substance containing boron (presumably C_4H_9B) was left behind; hydrogen was evolved on treating this material with water. Evidently, before mixing, reaction took place according to equation (6) followed by reaction (5) on mixing.

Following are data for a typical experiment: mmoles $(C_4H_9)_2BCl$, 7.778; mmoles HCl added, 5.274. Since the conversion of chloride to alkali metal boride is not quantitative, it was assumed that the conversion was 67% or that 5.3 mmoles of HCl would be equivalent to the metal boride. M. atoms H evolved, 5.274. One atom of hydrogen was evolved per mole of HCl added, as demanded by equation (7), while 3.69 mmoles of $(C_4H_9)_3B$ were recovered and 2.91 m.at. of boron was found in the residue. Evidently, the over-all result may be represented by equation (7). On hydrolysis, the non-volatile material evolved 3.07 m.at. of hydrogen, or, roughly, one atom per atom of boron; heating was required to effect complete hydrolysis.

(b) **Excess Hydrogen Chloride.**—Reaction was carried out as described above. The volatile product, excluding hydrogen, was identified as di-*n*-butylboron chloride by analysis for boron and chlorine; found, % B, 7.08; % Cl, 20.23; calcd. for $(C_4H_9)_2BCl$, 6.75, 22.10. Apparently, the residue after distillation was inert, since no hydrogen was formed on treatment with water. It contained chlorine, which was assumed to be present as MCl. Following are data for a typical reaction; mmoles $(C_4H_9)_2BCl$, used in forming boride, 8.557; mmoles hydrogen formed in treating boride with HCl, 5.558; mmoles MCl, 5.717; mmoles $(C_4H_9)_2BCl$ recovered, 4.251. From the amount of MCl in the residue, it appears that approximately 67% of the di-*n*-butylboron chloride had originally been converted to the alkali metal salt. This value is in agreement with the conversion figures arrived at in other experiments as described above. Furthermore, these data indicate that each mole of alkali metal boride reacted with two moles of hydrogen chloride to form one mole of hydrogen as required by equation (6). These data support the reaction mechanisms proposed in Section I above.

2. Reaction with Triethylammonium Chloride.

—The reaction was carried out at room temperature with equivalent quantities of alkali metal boride and ammonium salt, calculated on the assumption that approximately a 67% yield of the alkali metal boride would be obtained from the chloride. Hydrogen and tri-*n*-butylboron were isolated from the reaction products. The reaction appears to be similar to that between equivalent quantities of hydrogen chloride and the metal bôride and may be represented by equation (8).

Reaction was carried out in a three-legged tube of the type described in Section IV. When solutions of the metal boride (prepared from 7.441 mmoles of chloride) and triethylammonium chloride (5.016 mmoles; not all was used) were mixed, hydrogen (2.311 mmoles) was evolved and the solution was decolorized. After removing solvent, two fractions of volatile material were collected. The first (0.1113 g.) distilled between 0.5–0.1 mm. and was identified as dibutylboron chloride (% B found, 6.47; calcd. for $(C_4H_9)_2BCl$, 6.75). The second (0.3748 g.) distilled between 0.1–0.02 mm.; this was refractionated and the more volatile fraction (0.2472 g.) was identified as tributylboron (% B found,5.88; calcd. for $(C_4H_9)_3B$, 5.94).

Since not quite all of the triethylammoniun chloride was needed to completely discharge the color of the metal boride solution, it follows that somewhat less than 5 mmoles of alkali metal boride could have been present. The recovery of 2.3 mmoles of hydrogen indicates that one atom of hydrogen was formed per mole of alkali metal boride. The nonvolatile product contained boron, and, when hydrolyzed, it yielded 0.917 mmole of hydrogen, suggesting the presence of C_4H_9B. Evidently, the results may be represented by equation (8).

3. Reaction with Gaseous Ammonia at Room Temperature.—Although the alkali metal boride may be dissolved in liquid ammonia without apparent reaction, it was found to react slowly with gaseous ammonia at room temperature with the formation of hydrogen. In a preliminary experiment, when a paste of the boride in ether was allowed to remain in contact with ammonia gas for several days, a brown, glassy solid was formed. Approximately 6.2 mmoles of di-*n*-butylboron chloride had been used in preparing the alkali metal salt. Judging by the results obtained above, this should have produced roughly 4.0 mmoles of the alkali metal salt. In the reaction with ammonia, 2.4 mmoles of hydrogen was formed. It seems likely, therefore, that one mole of boride had reacted with ammonia to form one-half mole of hydrogen. If so, the products were probably similar to those described in earlier sections of this paper.

PROVIDENCE, R. I.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Heat of Formation of B-Trichloroborazole[1]

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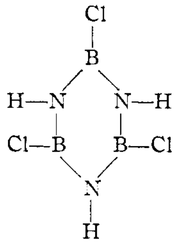
The heat of hydrolysis of B-trichloroborazole to yield dilute aqueous ammonium chloride and boric acid has been measured using a slight modification of a calorimeter described previously. The heat of hydrolysis is 113.8 ± 0.7 kcal./mole. Combining this value with other thermal data it has been calculated that the heat of formation of crystalline B-trichloroborazole is 252.2 kcal./mole. The average boron–nitrogen bond strength in this compound has been estimated from its heat of formation, heat of sublimation and other established thermal data to be 82.5 kcal./mole bond and this value is discussed in connection with other boron–nitrogen bond dissociation energies.

The compound B-trichloroborazole has been known for several years, having been described briefly in the literature by Wiberg and Bolz.[3]



An improved method of preparation and purification has been accomplished by Brown,[4] who has also studied its chemical and certain physical properties. All the chemical evidence Brown obtained indicated that the chlorines were substituted on the boron atoms and this has been substantiated by X-ray and electron diffraction studies by Coursen[5] and Coffin.[6] Borazole and its derivatives are of considerable interest because the borazole ring is isoelectronic with benzene. Although several compounds containing the borazole ring have been described in the literature, heretofore no thermochemical data have been reported for them. In line with our thermochemical studies of boron compounds we plan to determine the heats of formation of borazole and a number of its derivatives, and it appeared that B-trichloroborazole was the easiest compound with which to begin. Brown[4] has shown that B-trichloroborazole reacts vigorously and quantitatively with water to yield boric acid and ammonium chloride according to the equation

$$B_3N_3H_3Cl_3 + 9H_2O = 3H_3BO_3 + 3NH_4Cl$$

The heat of this reaction, which is strongly exothermic, has been measured by us and the heat of formation of $B_3N_3H_3Cl_3$ computed from this and other established thermochemical data.

Experimental

Apparatus.—The heat of hydrolysis was measured at 25° in a calorimeter previously used by Van Artsdalen and Anderson,[7] but modified to obtain more effective stirring. The stirrer well of the original instrument, which carried heater and thermometer, was eliminated and separate tubes for the copper resistance thermometer and manganin heater were substituted in its place. The original stainless steel stirrer was retained. A basket constructed of stainless steel was suspended rigidly in the center of the calorimeter vessel to contain the ampules of chemical agents to react with the water in the calorimeter.

An improved, very rapidly responding, four lead copper resistance thermometer (CUV-7) was designed and built.

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[1] In part from the M.S. thesis of Arthur S. Dworkin, Cornell University, September, 1951.

[2] Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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