drogen 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 boride 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]

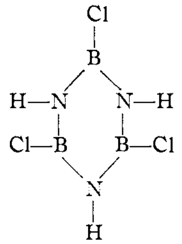
The Heat of Formation of B-Trichloroborazole[1]

BY ERVIN R. VAN ARTSDALEN[2] AND ARTHUR S. DWORKIN[2]

RECEIVED FEBRUARY 20, 1952

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.

[3] E. Wiberg and A. Bolz, *Ber.*, **73**, 209 (1940); E. Wiberg, "Fiat Review of German Science 1939–1946," Inorganic Chemistry, part 1, pp. 138–147; ONR serial No. 12987, June, 1947.

[4] Charles Brown, Thesis, Cornell University, 1948.

[5] D. L. Coursen, Thesis, Cornell University, 1950; D. L. Coursen and J. L. Hoard, THIS JOURNAL, **74**, 1742 (1952).

[6] K. Coffin, Thesis, Cornell University, 1951.

[7] E. R. Van Artsdalen and K. P. Anderson, THIS JOURNAL, **73**, 579 (1951).

It consisted of 26 feet of No. 40 enameled copper magnet wire wound bifilarly on a hollow, thin-walled copper mandrel, closed at one end, over which a very thin copper sleeve was soldered. This assembly was threaded and sealed to a bakelite tube through which the four leads (No. 34 copper) were passed, the bakelite tube serving to minimize heat conduction. The thermometer was filled with wax, and the metal parts carefully gold plated. It had a zero point resistance of 26.0543 ohms.

The manganin heater used was similar to that in the earlier calorimeter[7] and had a resistance of 30.5887 ohms at 25°.

All measuring and control circuits were those employed by Van Artsdalen and Anderson[7] and included the revamped Radar rectifying unit for production of stable d.c. voltage for the precision calorimeter heating circuit and the tape recording timer with interlocking switches. The resistance thermometer circuit included a Leeds and Northrup G-2 Mueller bridge with high sensitivity galvanometer, capable of detecting resistance differences of 0.00001 ohm. All leads were thermally lagged and shielded. Thermostatic control circuits maintained the calorimeter bath temperature constant to ±0.002°.

Calibration of Apparatus.—The copper resistance thermometer was calibrated *in situ* against a Leeds and Northrup precision certified platinum thermohm over the temperature range 20 to 30°. A quadratic equation was developed for the copper thermometer from resistances at three different temperatures and was found to reproduce separate readings to about ±0.00002 ohm corresponding to about ±0.0002°.

The calorimeter was calibrated electrically by determining the temperature rise produced on passing a measured direct current through the standard manganin heater for a specified time interval. In all cases the calorimeter contained 520.0 (±0.1) g. of water and an ampule of the type used to contain the material for the dissolution and hydrolysis measurements. The procedure was described in our previous communication.[7] A series of 13 calibration measurements made during the course of determinations of the heat of hydrolysis of B-trichloroborazole gave for the heat capacity of the filled calorimeter 568.4 ± 1.2 (±0.21%) cal./deg.

Materials.—The B-trichloroborazole was given to us by Professor A. W. Laubengayer from a pure supply prepared by Brown. The most likely contaminants of this material were ammonium chloride and boric acid. Since both of these are relatively non-volatile at 50-60° while B-trichloroborazole can be sublimed easily at such a temperature, we refined the sample further by careful, high vacuum sublimation at about 55°. It was obtained as fluffy, water-white crystals. Approximately 0.1- to 0.15-g. samples of material purified in this way were sealed into uniform, small, thin-walled glass ampules for use in the calorimeter. Great pains were taken to exclude moisture in all these operations.

Results and Discussion

Heat of Hydrolysis.—A series of six measurements of the heat of hydrolysis of B-trichloroborazole was made at 25°, which gave 113.8 ± 0.7 kcal./mole $B_3N_3H_3Cl_3$ for this value when the average concentration of the H_3BO_3, and hence also NH_4Cl, produced in the hydrolysis was 0.0034 *m*. The actual molality varied between 0.0023 and 0.0051, but there was no evidence of any trend in the heat of hydrolysis with changing concentration. Indeed one would not expect a trend within our limits of error at the low concentrations and over the limited range studied. We thus write

$$B_3N_3H_3Cl_3(c) + 9H_2O\ (l) + Aq = 3H_3BO_3\ (0.0034\ m) + 3NH_4Cl\ (0.0034\ m)$$

$$\Delta H_{298} = -113.8 \pm 0.7 \text{ kcal.}$$

Heat of Formation.—Knowing the heats of formation of water, H_3BO_3 and NH_4Cl under the conditions of this equation, one can calculate the heat of formation of B-trichloroborazole. We may write

$$\Delta Hf_{(B_3N_2H_3Cl_3)} = 113.8 + 3\Delta Hf_{(NH_4Cl)} + 3\Delta Hf_{(H_3BO_3)} - 9\Delta Hf_{(H_2O)}$$

where the conditions are those specified in the chemical equation for the hydrolysis reaction at 25°. Substituting values from the Bureau of Standards[8] for the heats of formation on the right, we obtain

$$\Delta Hf^0_{298(B_3N_3H_3Cl_3,c)} = -252.2 \text{ kcal./mole}$$

We see that B-trichloroborazole in its standard state is a strongly exothermic compound. It is impossible, from the information given in ref. 8, to assess with precision the probable error in this quantity, particularly in view of the uncertainty in the heat of formation of boric oxide. However, we feel that our value for the heat of formation of B-trichloroborazole is probably reliable to about 3 or 4 kcal./mole. In any case it can be corrected if a revised value of the heat of formation of boric oxide is obtained.

Bond Strengths.—It is possible to arrive at a reasonable estimate of the average[9] boron–nitrogen bond strength (bond dissociation energy) in the borazole ring by making use of our value of the heat of formation of B-trichloroborazole and other thermal data. Brown[4] determined that the heat of evaporation of crystalline $B_3N_3H_3Cl_3$ is 17.1 kcal./mole. Heats of atomization of nitrogen, hydrogen and chlorine plus the heat of evaporation of boron (to yield monatomic boron) have been tabulated by the Bureau of Standards.[8] We may then use the following set of thermochemical equations to obtain the heat of atomization of $B_3N_3H_3Cl_3$.

$$\begin{array}{lll}
B_3N_3H_3Cl_3(c) = 3B(c) + 3/2N_2 + 3/2H_2 + 3/2Cl_2 & & -\ 252.2 \\
B_3N_3H_3Cl_3(g) = B_3N_3H_3Cl_3(c) & & +\ 17.1 \\
3/2N_2 = 3N & & -\ 256.70 \\
3/2H_2 = 3H & & -\ 156.27 \\
3/2Cl_2 = 3Cl & & -\ 87.03 \\
3B(c) = 3B(g) & & -\ 291.6 \\
\hline
B_3N_3H_3Cl_3(g) = 3B(g) + 3N + 3H + 3Cl & & -1026.7
\end{array}$$

If one makes the assumption that the average B–Cl and average N–H bond strengths are one-third of the heats of atomization of BCl_3 and NH_3, respectively, one obtains 92.9 kcal./mole bond for the former and 84.3 kcal./mole bond for the latter using Bureau of Standards[8] data. X-Ray and electron diffraction studies of Coursen[5] and Coffin[6] show that the B–Cl and N–H bond lengths in $B_3N_3H_3Cl_3$ correspond within experimental error (*ca.* ±0.02 Å.) to the bond lengths in BCl_3 and NH_3, respectively. One may, therefore, feel reasonably justified in carrying over the above average bond strengths to our compound. We then find that the contribution to the heat of atomization of B-trichloroborazole by 3 B–Cl bonds plus 3 N–H bonds is 531.6 kcal./mole. Subtracting this from the total heat of atomization (1026.7) leaves 495.1 kcal./mole for the heat of atomization of the

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(8) Natl. Bur. Standards, "Selected Values of Chemical Thermodynamic Properties," Series I, (1947 et seq.). The values of heats of formation used were: $H_2O(l)$ = 68.32 kcal./mole, NH_4Cl (aq. ∞) = 71.76 kcal./mole, H_3BO_3 (aq. ∞) = 255.2 kcal./mole. This latter value agrees with the heats of solution of H_3BO_3 and B_2O_3 determined by Van Artsdalen and Anderson if one accepts the NBS value for the heat of formation of B_2O_3.

(9) We do not mean to imply that there is more than one type of B–N linkage in the borazole ring, but only that our bond strength estimate is the average value for breaking all six bonds simultaneously.

stripped borazole ring. There are 6 B–N bonds in this ring, hence the average B–N bond strength in B-trichloroborazole is 82.5 kcal./mole bond at 25°.[10]

Gaydon[11] recommends 4.0 ± 0.5 e.v. (92 ± 11.5 kcal.) for the dissociation energy of gaseous diatomic boron nitride (BN) and states that this rather imprecise value has been obtained by a graphical Birge–Sponer extrapolation of spectral data. Certainly it is not surprising to find that the dissociation energy of gaseous BN exceeds the average B–N bond strength of the borazole ring.

It is instructive to compare the strength of the B–N bond in the B-trichloroborazole ring with values which have been estimated for donor–acceptor bonds involving boron and nitrogen. These latter bonds are in general weak and the compounds, while stable in the solid state, frequently undergo extensive dissociation in the vapor phase. Thus Burg and Green[12] have found evidence for boron–nitrogen bond strengths in the series $(CH_3)_3NBF_2CH_3$ to $(CH_3)_3NB(CH_3)_3$ varying from about 23 to 14 kcal./mole, respectively. Likewise Brown, Bartholomay and Taylor[13] have found B–N bond strengths in the range of 14 to 19 kcal./mole in a series of compounds of general formula $R_3NB(CH_3)_3$. Physical evidence is in accord with the much higher dissociation energy for the ring B–N bond in borazole and B-trichloroborazole. Thus it is found that the B–N internuclear distance is in the range of 1.6 Å. for the donor–acceptor compounds[14a] while in borazole[14b] it is 1.44 Å. and in B-trichloroborazole 1.41 Å.[5,6]

We believe that at least as a first estimate the average B–N bond strength in borazole itself can be considered to be of the order of 80 kcal./mole bond since the B–N internuclear distances closely approximate each other in borazole and B-trichloroborazole.

Acknowledgment.—We wish to thank Professor A. W. Laubengayer and Dr. Charles Brown for our supply of B-trichloroborazole. One of us (E.R.V.) wishes to express his sincere appreciation to the Faculty Research Grants Committee and the Office of the Vice President for Research of Cornell University for a grant in purchase of a calibrated, precision, platinum resistance thermometer used in this work.

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[10] One can arrive at the values of 100.6 and 78.6 kcal./mole bond, respectively, for the B–Cl and N–H bond strengths by using Bureau of Standards[8] data for heats of formation of the gaseous monatomic molecules BCl and NH which are known spectroscopically. When these bond strengths are used, one estimates the average B–N bond strength in B-trichloroborazole to be 81.5 kcal./mole bond. We, however, favor the value obtained in the text, 82.5 kcal./mole bond.

[11] A. G. Gaydon, "Dissociation Energies," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 205.

[12] A. B. Burg and A. A. Green, THIS JOURNAL, **65**, 1838 (1943).

[13] H. C. Brown, H. Bartholomay and M. D. Taylor, *ibid.*, **66**, 435 (1944).

[14] (a) S. H. Bauer, *ibid.*, **59**, 1804 (1937); (b) **60**, 524 (1938).

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Iodide-ion Catalysis of the Elimination of Iodine from *trans*-Diiodoethylene and of the Addition of Iodine to Acetylene[1,2]

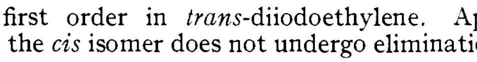
BY SIDNEY I. MILLER AND RICHARD M. NOYES

RECEIVED FEBRUARY 8, 1952

trans-Diiodoethylene in methanol reacts with iodide ion at temperatures below 110° with the formation of triiodide ion and acetylene. From studies of the final equilibrium and of the kinetics of this elimination reaction, we have obtained kinetic information concerning the rate of the reverse (addition) reaction. The rate of elimination of the *cis* isomer under the same conditions is immeasurably slow even at temperatures as high as 140°. Two reaction mechanisms appear plausible. In one mechanism the two carbon-iodine bonds break almost simultaneously in a concerted process. The other mechanism involves a neutral intermediate complex of acetylene and molecular iodine.

Introduction

Although it is well known that iodide ion can cause the elimination of halogen from 1,2-dihaloalkanes, there do not appear to be any reports of similar elimination reactions of 1,2-dihaloalkenes. We have found an example of such an elimination in the equilibrium reaction



$$CHI{=}CHI + I^- \rightleftarrows HC{\equiv}CH + I_3^- \quad (1)$$

This elimination reaction is first order in iodide ion and first order in *trans*-diiodoethylene. Apparently the *cis* isomer does not undergo elimination at a significant rate under the conditions of our experiments.

By combining our kinetic observations with measurements on the equilibrium constant for reaction (1), we have also been able to calculate the rate of the reverse reaction involving the addition of iodine to acetylene. These results are of interest because of the paucity of kinetic data on the iodination of acetylenes.

Experimental

Materials.—The preparation of the anhydrous methanol solvent and of the eutectic and *trans*-diiodoethylene have been described elsewhere.[3] Since pure *cis*-diiodoethylene has not yet been obtained, we used the eutectic material which contained about 20% of the *trans* isomer.[4]

Dried reagent-grade sodium iodide was checked against standard silver nitrate and used directly in the kinetic runs.

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[1] Based on a dissertation submitted by Sidney I. Miller to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry.

[2] Persons desiring to consult the more complete report or to obtain a microfilm thereof may address the Library, Columbia University, New York 27, N. Y.

[3] S. I. Miller and R. M. Noyes, THIS JOURNAL, **74**, 629 (1952).

[4] S. I. Miller and R. M. Noyes, *ibid.*, **73**, 2376 (1951).