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A Study of the Reaction of Boric Acid with Amines: Hydroxyboroxin–Amine Salts

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The reaction of boric acid with amines has been found to yield either N-substituted ammonium triborates or N-substituted ammonium pentaborates. The major factors governing which product is formed are the steric requirements of the amine and the mole ratio of the reactants. Evidence is presented for the proposed structure of these products.

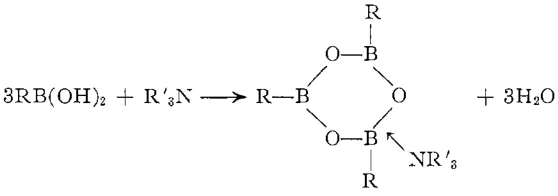
Introduction

Although the interaction of boric acid with aqueous alkali has been extensively investigated, there have been few reports of its reaction with amines. Ferrari[1] obtained materials which he called decaborates [$(R_3NH)_2B_{10}O_{16}\cdot 4H_2O$] from the reaction of alkyl amines with boric acid. Metaboranilide (C_6H_5NHBO) was the indicated product from the reaction of boric acid with aniline[2]; however, reaction of boric acid with various diamines has been reported to give water-soluble resinous products of unknown structure.[3]

Results and Discussion

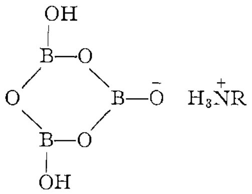
We have found that the reaction of boric acid with an amine, either in homogeneous or heterogeneous media, results in dehydration of the boric acid and formation of a hydroxyboroxin–amine salt. A benzene–water (14 to 1 by volume) mixture is a facile reaction medium. Water is removed conveniently by azeotropic distillation and the benzene-insoluble product isolated by filtration. The reaction is fast, being complete in a few minutes, and the resulting materials are obtained in high yield (90–100%). Steric requirements of the amine and mole ratio of the reactants determine the nature of the product. Base strength of the amine is of minor importance; however, amines less basic than pyridine (*e.g.*, aniline or *p*-toluidine) fail to give discrete products under the conditions employed by us.

Primary and other relatively nonhindered amines (*e.g.*, triethylenediamine) form stable products which have three boron atoms for each molecule of amine if the boric acid to amine mole ratio is three or less. Somewhat related to our findings, other workers[4–6] have reported that boronic acids react with amines to give boronic anhydride–amine complexes (I).

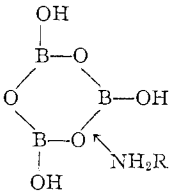


I

R = aryl or alkyl; R′ = alkyl or hydrogen



II



III

The elemental analyses and amine content (acid titration) suggest that the structure of the products isolated by us is either II or III. Also the reactions of *n*-octylamine and *n*-propylamine with 1,3,5-trihydroxyboroxin (metaboric acid)[7] under anhydrous conditions gave products which were identical with the corresponding amine–boric acid reaction products as shown by elemental, infrared, and X-ray powder diffraction analyses.

It has been recognized that there is rapid formation and breakdown of the polyborate structures and that the products are generally thermodynamically controlled.[8,9] For this reason, formation of the same products from metaboric acid does not prove necessarily that the cyclic trimer structure has remained intact.

Boron n.m.r. of an aqueous solution of the *n*-propylammonium triborate shows only one broad peak. The one shift at δ −9.3 p.p.m. is intermediate between that expected for tetrahedral boron bonded to four oxygen atoms (δ 0.0 to −3.0 p.p.m.) and that characteristic for trigonal boron bonded to three oxygen atoms (δ −14.0 to −19.0 p.p.m.).[10]

Since polyborates are generally thought to equilibrate in terms of boric acid and borate ion in aqueous solution, it is impossible to state conclusions concerning the structure of the anhydrous solids from aqueous solution data. The products, as expected, in water give strongly

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[1] A. Ferrari and L. Coghi, *Gazz. chim. ital.*, **71**, 129 (1939).

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[3] W. L. Morgan, U. S. Patent 2,408,332 (March 6, 1945); *Chem. Abstr.*, **41**, 623*e* (1947).

[4] A. B. Burg, *J. Am. Chem. Soc.*, **62**, 2228 (1940).

[5] H. R. Snyder, M. S. Konecky, and W. J. Lennarz, *ibid.*, **80**, 3611 (1958).

[6] R. T. Hawkins, W. J. Lennarz, and H. R. Snyder, *ibid.*, **82**, 3053 (1960).

[7] Metaboric acid was prepared by dehydration of boric acid in refluxing toluene. X-Ray analysis of the product was in agreement with that reported for the cyclic trimer $(HO)_3(BO)_3$: J. L. Parsons, *J. Chem. Phys.*, **33**, 1860 (1960).

[8] N. Ingri, G. Lagerström, M. Frydman, and L. G. Sillén, *Acta Chem. Scand.*, **11**, 1034 (1957).

[9] J. Dale, *J. Chem. Soc.*, 922 (1961).

[10] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

TABLE I

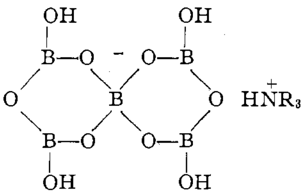
N-SUBSTITUTED AMMONIUM TRIBORATES (II)

Amine	H_3BO_3:amine mole ratio	Method	Formula	Boron, % Calcd.	Boron, % Found	Nitrogen % Calcd.	Nitrogen % Found
n-Butylamine	Excess amine	B	$C_4H_{14}O_6NB_3$	15.9	15.3	6.9	6.23
n-Octylamine[a]	1	A	$C_8H_{22}O_6NB_3$	12.47	12.26	5.38	5.25
n-Propylamine[a]	1	A	$C_3H_{12}O_6NB_3$	17.0	16.8	7.35	7.54
Pyridine	Excess amine	B	$C_5H_9O_6NB_3$	15.4	16.0	6.62	6.27
t-Butylamine	1	B[b]	$C_4H_{16}O_6NB_3$	15.9	16.0	6.86	6.68
Triethylenediamine	2	A	$C_6H_{15}O_6N_2B_3$	13.30	13.02	11.52	11.20
Ammonia	1	C	$H_6O_6NB_3$	21.8	21.8	9.40	9.69

[a] Reaction of the amine with metaboric acid gave the same product. [b] Acetonitrile–water medium (20 to 1 by volume) was employed.

conducting solutions. In addition, dimethyl sulfoxide solutions of the anhydrous solids are ionic. The N-substituted ammonium triborates isolated during this study are shown in Table I.

Attempts to form triborates from the more sterically hindered amines were unsuccessful. Instead, polyborate–amine salts were isolated which contained five boron atoms for each molecule of amine. The most probable structure for these products is IV, an N-substituted ammonium spiro[(3,5-dihydroxyboroxin)-1,1′-(3′,5′-dihydroxyboroxin)] (pentaborate).



IV R = alkyl or hydrogen

These N-substituted ammonium pentaborates are formed from the more hindered amines (*e.g.*, secondary or tertiary) regardless of the boric acid to amine mole ratio. Pure pentaborates can be prepared from the nonhindered amines (*e.g.*, primary) if the boric acid to amine mole ratio is five. Pentaborates are also formed by interaction of the ammonium triborates with boric acid (1 to 2 mole ratio).

The infrared spectra are consistent with structure IV. A typical curve is shown in Fig. 1. Absorption at 700–710 cm.$^{-1}$ is assigned to the boroxin ring.[5,11] The absorption at 1600–1650 cm.$^{-1}$ is common to secondary amine salts.[12] The bands in the 3100–3400 cm.$^{-1}$ area can be attributed to hydroxyl and amino groups.

Boron n.m.r. of an aqueous solution of *n*-propylammonium pentaborate shows shifts at δ 0.0 and -17.5 p.p.m. The area ratio of the peaks could not be accurately determined. These shifts are in agreement with those reported for sodium pentaborate (δ -1.3 and -14.4 p.p.m.).[10]

X-Ray analysis furnished additional evidence for structure IV. The single crystal X-ray data for *n*-propylammonium pentaborate are given in Table II. Strong support for the suggested structure was obtained when the space dimensions of a scale atomic model fitted into the determined volume occupied by each molecule in the crystal lattice. The amine cation fits into the angle formed by the two perpendicular planes of the pentaborate anion.

TABLE II

X-RAY CRYSTAL DATA ON *n*-PROPYLAMMONIUM PENTABORATE

Space lattice	Orthorhombic
Unit cell dimensions	a = 20.377 Å. b = 14.359 Å. c = 14.017 Å.
Volume	4084 Å.^{3}
Cell content	$12[C_3H_7NH_3\cdot B_5O_{10}H_4]$
Density	Calcd. 1.356 Found 1.340

The spiro structure has been indicated for several natural and synthetic pentaborates. These include potassium pentaborate ($KB_5O_8\cdot 4H_2O$),[13] ammonium pentaborate ($NH_4B_5O_8\cdot 4H_2O$, which is probably the mineral Larderellite),[14] and several quaternary ammonium pentaborates.[15]

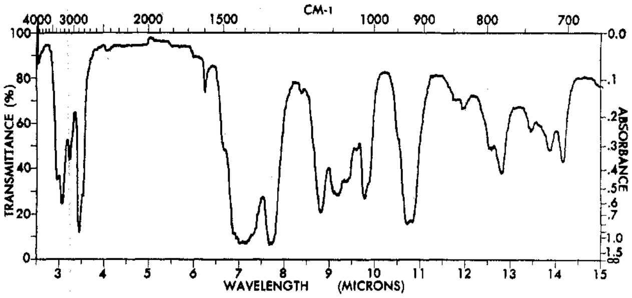


Fig. 1.—Infrared spectrum of diethylammonium pentaborate, Nujol mull, Perkin-Elmer Infracord spectrometer.

The N-substituted ammonium pentaborates prepared during this investigation are given in Table III.

Attempts to form a polyborate–amine salt that contains more than five boron atoms per molecule of amine were unsuccessful. Reactions of boric acid with *n*-octylamine (6 to 1 and 7 to 1 mole ratio) gave mixtures of *n*-octylammonium pentaborate and boric acid.

Reaction of the more hindered amines with metaboric acid gave pentaborates instead of the expected triborates. Apparently, as in the boric acid reactions, the more sterically hindered amines form only pentaborates with metaboric acid.

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(11) D. W. Aubrey, M. F. Lappert, and H. Pyszora, *J. Chem. Soc.*, 1931 (1961).

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(13) W. H. Zachariasen, *Zh. Krist.*, **98**, 266 (1937).

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TABLE III

N-SUBSTITUTED AMMONIUM PENTABORATES (IV)

Amine	H_3BO_3:amine mole ratio	Method	Formula	Boron, %		Nitrogen, %		Equiv. wt.[a]	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Triethylamine	1	A	$C_6H_{20}O_{10}NB_5$	16.9	16.8	4.38	4.59	320	333
Piperidine[b]	1	A	$C_5H_{16}O_{10}NB_5$	17.8	17.8	4.62	4.50	304	313
Dimethylamine	1	A	$C_2H_{12}O_{10}NB_5$	20.5	20.1	5.30	5.30	264	267
Di-*n*-butylamine[b]	Large excess of amine	B	$C_8H_{24}O_{10}NB_5$	15.5	15.2	4.02	3.80	...	...
Diethylamine	Large excess of amine	B	$C_4H_{16}O_{10}NB_5$	18.5	18.5	4.80	4.89	292	304
Trimethylamine	1	C	$C_3H_{14}O_{10}NB_5$	19.5	19.0	5.04	4.93	278	295
Isopropylamine	5	A	$C_3H_{14}O_{10}NB_5$	19.5	20.1	5.04	5.24	278	292
n-Octylamine	5	A	$C_8H_{24}O_{10}NB_5$	15.5	15.3	4.02	4.06	324	337
n-Propylamine[c]	5	A	$C_3H_{14}O_{10}NB_5$	19.5	19.5	5.04	5.28	278	295
N,N′-Dimethylethylenediamine	2	C	$C_4H_{15}O_{10}N_2B_5$	17.6	17.7	9.10	9.00	...	...

[a] Equivalent weights were calculated from the amine content as determined by titration with 0.1 *N* HCl using bromothymol blue as indicator. [b] Reaction of the amine with metaboric acid gave the same product. [c] Single crystal for X-ray analysis was prepared by slow evaporation of an acetonitrile–water (5:1 by volume) solution.

Experimental

Method A (Benzene–Water Medium). N-Substituted Ammonium Triborates.—To a solution of 0.10 mole of nonhindered amine (*e.g.*, primary amines, triethylenediamine, etc.) in 100 ml. of benzene, 0.10–0.30 mole of boric acid and 7 ml. of water were added. After the resulting mixture was stirred at 40–50° for 30 min., the temperature was increased to reflux (70–75°). Water (1 equiv. per equiv. of boric acid, in addition to that charged) was removed by azeotropic distillation with a Dean–Stark trap (1–1.5 hr.). It was desirable to add 50 ml. of acetonitrile when 80–90% of the water had been removed in order to prevent the product from caking to the sides of the flask. The white solid was collected on a filter, washed with diethyl ether, and dried.

N-Substituted Ammonium Pentaborates.—The procedure was the same except with the more sterically hindered amines (secondary and tertiary) the boric acid charge can be between 0.1 and 0.5 mole. For nonhindered amines, the boric acid charge must be 0.5 mole.

Method B (Excess Amine Medium). N-Substituted Ammonium Triborates.—Boric acid (0.2 mole) was added to a nonhindered amine (0.3–0.5 mole) and the mixture stirred at 50–60° for 1.5–3 hr. Acetonitrile (50–70 ml.) was added to the cooled mixture, and the solid product was collected on a filter, washed with diethyl ether, and dried.

N-Substituted Ammonium Pentaborates.—The procedure was the same except a hindered amine was employed.

Method C (Water Solvent). N-Substituted Ammonium Pentaborates.—Boric acid (0.2 mole) was added to a solution of 0.2 mole of a hindered amine in 50 ml. of water. The resulting mixture was held between 40 and 50° for 1–2 hr. Benzene (100 ml.) was then added to the reaction mixture and the water removed by azeotropic distillation. Acetonitrile (50 ml.) was added when approximately 80% of the water had been removed. The solid product was collected on a filter, washed with acetonitrile, and dried.

Rate of Formation of the Triborate from Triethylenediamine and Boric Acid.—Triethylenediamine[16] (16.8 g., 0.15 mole) in 50 ml. of benzene was added to a slurry of 18.6 g. (0.3 mole) of boric acid, 10 ml. of water, and 150 ml. of benzene. The mixture was then stirred for 5 min. at room temperature. A sample of the reaction mixture (1.0 g.) was removed; the solid was removed by filtration, washed with diethyl ether, and dried. The remaining reaction mixture was refluxed (70–80°) until approximately the theoretical amount of water (15–16 ml.) had been removed azeotropically. The benzene-insoluble product was then collected on a filter, washed with diethyl ether, and dried; yield 98%. The infrared spectrum and elemental analysis of this product were identical with the product obtained from the 1.0-g. sample removed after 5 min.

1,3,5-Trihydroxyboroxin (Metaboric Acid).—A slurry of boric acid (18.6 g., 0.3 mole) was dehydrated in refluxing toluene. The theoretical amount of water (5.4 ml.) was removed by azeotropic distillation in 2 hr. The insoluble metaboric acid was then filtered from the reaction mixture and dried.[7,17]

Anal. Calcd. for $H_3B_3O_6$: B, 24.4. Found: B, 24.7.

***n*-Propylammonium Triborate. From Boric Acid.**—This material was prepared by allowing 11.8 g. (0.2 mole) of *n*-propylamine and 12.4 g. (0.2 mole) of boric acid to react according to method A. Boron n.m.r. analysis of the product (aqueous solution) showed only one peak (δ −9.3 p.p.m.).

From Metaboric Acid.—Addition of 14.4 g. (0.238 mole) of *n*-propylamine to 4.0 g. (0.035 mole) of freshly prepared metaboric acid gave a 20° temperature increase. The resulting solution was stirred at 40–50° for 1.5 hr. Diethyl ether (60 ml.) was added to the cooled solution and the precipitated product isolated by filtration. The product was obtained in essentially quantitative yield. Amine content (acid titration), X-ray powder diffraction, and elemental analyses indicated that this material was identical with the above boric acid–*n*-propylamine reaction product.

***n*-Propylammonium Pentaborate. From Boric Acid.**—*n*-Propylamine (4.7 g., 0.08 mole) and 24.8 g. (0.4 mole) of boric acid were allowed to react according to method A. The yield of the product was 97%. The infrared spectrum showed bands at 709 and 1640 cm.$^{-1}$ (boroxin ring and amine salt, respectively). Boron n.m.r. analysis of an aqueous solution showed two types of boron atoms with shifts of δ 0.0 and −17.5 p.p.m.

From *n*-Propylammonium Triborate.—A solution of 1.9 g. (0.01 mole) of *n*-propylammonium triborate and 1.23 g. (0.02 mole) of boric acid in 10 ml. of water was stirred at 40–50° for 1 hr. Benzene (75 ml.) was added and the water removed by azeotropic distillation. When approximately 80% of the water had been removed, acetonitrile (50 ml.) was added and the remaining water distilled. The product was isolated in essentially quantitative yield. Infrared and elemental analyses, X-ray powder diffraction, and amine content (acid titration) indicate that the product was identical with the above boric acid–*n*-propylamine reaction product.

Attempted Thermal Degradation of Trimethylammonium Pentaborate.—The compound (0.2732 g.) was charged to a drying pistol and subjected to refluxing xylene (140°) and a pressure of 90 mm. After 5 hr., the sample weighed 0.2645 g. This represented only 3.2% loss in weight. Amine content (acid titration) of the compound before and after heat treatment: 3.40 and 3.44 mequiv./g. Elemental analyses also indicated that no decomposition had occurred.

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[16] This material is more correctly named 1,4-diazabicyclo[2.2.2]octane and is marketed under the trade name "Dabco" by Houdry Process Corp., Marcus Hook, Pa.: A. Farkos, G. A. Mills, W. E. Erner, and J. B. Mearker, *Ind. Eng. Chem.*, **51**, 1299 (1959).

[17] Metaboric acid must be stored in a dry atmosphere to prevent regeneration of boric acid.

Determination of the Molar Limits of the Reaction of Boric Acid with an Amine: Boric Acid-*n*-Octylamine Reaction (7 to 1 Mole Ratio).—*n*-Octylamine (6.45 g., 0.05 mole) was added to a slurry of 22.3 g. (0.36 mole) of boric acid in a mixture of 10 ml. of water and 100 ml. of benzene. The mixture was stirred at 50° for 30 min. and then heated to reflux (70°). Refluxing was continued until 12–13 ml. of water had been removed by azeotropic distillation. Acetonitrile (100 ml.) was added and the solid product (23.4 g.) collected on a filter. Infrared analysis and X-ray powder diffraction indicated that the product was a mixture of *n*-octylammonium pentaborate and boric acid. This result shows that the reaction stops at the spiropentaborate even in the presence of excess boric acid.

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Thermodynamic Properties of Dichloroborane

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The disproportionation reaction for $HBCl_2$, $6HBCl_2 \rightleftharpoons 4BCl_3 + B_2H_6$, was followed spectrophotometrically in the infrared region and an equilibrium constant (K_p (298°K.) = 532 ± 15 atm.$^{-1}$) was obtained. Statistical thermodynamic functions in the range 298–1200°K. were computed from fundamental frequencies and molecular constants of $HBCl_2$. Experimental results and statistical calculations were combined and the change of zero-point energy, ΔE°_0, was calculated to be −18.62 ± 0.02 kcal./mole. The molar free energy and heat of formation at 298°K. for $HBCl_2$ were calculated to be −56.68 ± 0.05 and −60.37 ± 0.05 kcal., respectively.

Introduction

A vibrational analysis of the dihaloboranes made possible the observation and assignment of fundamental frequencies for the isotopic species $HB^{11}Cl_2$, $HB^{10}Cl_2$, $DB^{11}Cl_2$, and $DB^{10}Cl_2$. The frequencies were computed by utilizing the Green's function and matrix partitioning techniques applied to molecular systems[1] without invoking a force constant model.[2] The vibrational spectrum of these molecules consists of six fundamentals, which are all infrared and Raman active for both a planar (C_{2v}) and nonplanar (C_s) model. Although there is no evidence to eliminate the latter, we shall make the reasonable assumption that the molecules are planar.[3] This form allows the maximum opportunity for π-orbital interactions, which act to stabilize the planar structure of BX_3 molecules, when X contains lone-pair electrons. Coupled with the recent determination of the rotational constants and molecular geometry of $HBCl_2$ and $DBCl_2$,[3] it was possible to obtain the thermodynamic functions for $HB^{11}Cl_2$ from statistical calculations. The disproportionation reaction for dichloroborane

$$6HBCl_2 \rightleftharpoons 4BCl_3 + B_2H_6 \qquad (1)$$

was followed spectrophotometrically utilizing well-characterized and noninterfering infrared bands of the reaction partners. From the experimentally derived equilibrium constant and statistical computations, some additional thermodynamic properties of dichloroborane and equilibrium constants at various temperatures for reaction 1 were calculated.

Experimental

Dichloroborane was prepared by reducing BCl_3 with hydrogen in the presence of magnesium maintained at 350° in a stainless-steel tube.[3,4] The stainless-steel reactor was sealed into a vacuum system having a facility for low temperature separations. Dichloroborane was separated from reactants (H_2, BCl_3) and other products (HCl) by repeated distillations through series of traps maintained at −125, −135, and −196°. After numerous passes, the fraction retained in the −135° trap was introduced into a 10-cm. infrared cell fitted with NaCl windows. The cell was monitored continuously during the first hour of disproportionation and periodically for 336 hr. Since the cell temperature (25°) and volume remained constant during the disproportionation, optical densities of certain preselected bands were directly related to the partial pressures of the reaction constituents. From Beer's law and total pressure measurements the partial pressures of each constituent could be calculated. Details of this technique have been reported previously.[5] Total cell pressures in the range 20–25 mm. were convenient to work with in this case and avoided complications from pressure broadening and nonideal behavior.

Results

At room temperature, dichloroborane disproportionated to form BCl_3 and B_2H_6 according to the stiochiometry given in eq. 1. After 30 min. at 25°, the reaction appeared to be approximately 50% complete; after 168 hr. further changes were not observed and equilibrium appeared to be attained. Monochlorodiborane and other possible products were not observed. Final measurements were made on systems which had been

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