on attempted distillation at 0.7 mm. with a pot temperature of 227°.

Ferric Chloride and Isoöctane in Chlorobenzene.—The reaction mixture from the corresponding experiment in Table II was worked up in the following manner. The organic distillate from steam distillation was fractionated through a 15 × 1 cm. column packed with glass helices to yield isoöctane (2.52 moles), chlorobenzene (1.14 moles) and *tert*-butylchlorobenzene (12.7 g.) with 4.3 g. of residue.

The organic residue from steam distillation consisted of 34 g. of black, semi-solid material.

Ferric Chloride (moles) and Alkanes (95% minimum purity) (moles, temp., % HCl) in Chlorobenzene (0.049 mole) (time: 20–25 min.): $FeCl_3$ (0.061), isoöctane (0.121, 91–100°, 69); $FeCl_3$ (0.055), 2,2,5-trimethylhexane (0.109, 94–111°, 72).

Aluminum Chloride and Alkanes.—(a) A mixture of 20 ml. (0.12 mole) of isoöctane (Eastman, 99.5%) and 3 g. (0.022 mole) of anhydrous aluminum chloride was heated with stirring. At about 50° water-insoluble gas began to evolve at a slow rate. At 65–70° the rate was appreciably faster and increased progressively with increase in temperature. The reaction mixture, which was heated from 40 to 98.5° during 25 minutes, yielded no hydrogen chloride.

(b) No water-insoluble gas or hydrogen chloride was evolved in the following experiments (alkane, 95% minimum purity); methylcyclohexane (0.156 mole), $AlCl_3$ (0.029 mole), 15 min. at 90–99°; *n*-octane (0.123 mole), $AlCl_3$ (0.057 mole), 40 min. at 110–118°.

CLEVELAND 6, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Quaternary Ammonium Polyborates[1]

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Several quaternary ammonium polyborates have been prepared. Quaternary ammonium halides were prepared by standard methods and the halides were converted to hydroxides by reaction with silver oxide or by means of an ion exchange resin. The hydroxides were converted to polyborates by reaction with boric acid or ammonium pentaborate. The compositions of the products obtained indicate that the pentaborate is a favored form and that the fundamental unit of the pentaborate ion is $H_4B_5O_{10}^-$ Some of the pentaborates have been obtained with water of crystallization, usually easily removable, while others contain one additional boric acid molecule. It is suggested that this boric acid molecule is not added to the pentaborate ion, thereby producing a true hexaborate, but rather crystallizes with certain pentaborates by virtue of a favorable size relationship between it and spaces in the crystal lattice, perhaps forming hydrogen bonds to the pentaborate ions.

The existence of polyborates is a subject which has received considerable attention. The existence of such polyborate salts as sodium tetraborate, $Na_2B_4O_7$, potassium pentaborate, $KH_4B_5O_{10}·2H_2O$, and ammonium pentaborate, $NH_4H_4B_5O_{10}·2H_2O$, is well established. The crystal structure of potassium pentaborate has been determined by Zachariasen.[2,3]

Polyborate ions have been detected in solution by many workers, including Ingri, *et al.*,[4] while Edwards[5] has detected their presence by *p*H measurements on aqueous solutions of boric acid.

In aqueous solutions of salts, such as potassium pentaborate, fairly large concentrations of polyborate ions are obtainable, but quantitative measurements of activity (of hydrogen ion, for example) lack significance with respect to concentrations or equilibrium constants since activity coefficients of boric acid and the various ionic species are unknown. In solutions of boric acid alone, the concentrations of polyborate ions in equilibrium with monoborate ions and boric acid are quite small, hence not easily detectable, since most of the boric acid is present in the undissociated form. However, in this case, the activity coefficients are all nearly unity and activity measurements retain some value in an attempt to determine equilibrium constants and concentrations of the various species.

Edwards concludes that the most important polyborate ions in aqueous boric acid solutions are singly charged triborate and hexaborate ions. Unfortunately, his data can be fitted as well by other combinations of polyborates, such as the combination of dimer, trimer and pentamer. If another order of magnitude in the accuracy of such measurements could be obtained, it would probably be possible to reach some definite conclusions concerning the concentrations of the various possible borate ions in aqueous boric acid solutions. In view of these difficulties associated with measurements on solutions, the nature of solid polyborate salts remains perhaps the most significant factor in an understanding of borate chemistry.

The present work comprises the preparation and identification of several quaternary ammonium polyborates. Most of these salts have the formula $QH_4B_5O_{10}$, where Q represents the quaternary ammonium radical, while a few correspond to this formula plus one H_3BO_3 molecule. In some cases the salt was obtained with water of crystallization, but this water could be removed by suitable heating *in vacuo*. Those salts found to have the formula $QH_4B_5O_{10}$ will be termed pentaborates while those with the additional boric acid molecule will be called hexaborates.

Experimental

Neutral Equivalents.—Acid neutral equivalents (A.N.E.) were determined by titration with standard HCl to brom cresol green end-point while base neutral equivalents (B.N.E.) were determined by titration with standard NaOH to phenolphthalein end-point in the presence of mannitol. The selection of indicators was based on the results of preliminary titrations performed with a *p*H meter. Values of neutral equivalents reported are the average of two or more determinations in many cases.

Calculated values of B.N.E. were obtained by assuming that each boron in the molecule would behave as a molecule

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[1] This research was performed in part under Contract No. DA-36-039-sc-71186 between the Signal Corps Engineering Laboratories, Department of the Army, and the Sprague Electric Co.

[2] W. H. Zachariasen, *Z. Krist.*, **98**, 266 (1937).

[3] A. F. Wells, "Structural Inorganic Chemistry," 2nd ed., Oxford University Press, London, 1950, p. 447.

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

[5] J. O. Edwards, THIS JOURNAL, **75**, 6151 (1953).

of boric acid and that one boron per molecule was already neutralized by the quaternary ammonium base. A pentaborate molecule thus has four titratable borons while a hexaborate has five. The combined values of A.N.E. and B.N.E. permit a clear distinction to be made among $QH_4B_5O_{10} \cdot QH_4B_5O_{10} \cdot H_3BO_3$ and $QH_4B_5O_{10} \cdot nH_2O$.

Elemental Analyses.—Analyses for carbon, hydrogen, nitrogen and boron were performed by the Clark Microanalytical Laboratory. The analytical laboratory reports that in some cases a black residue remained after ignition for the C–H determination and that the C–H values tended to be somewhat lower than expected in these cases. It is felt, however, that these values, coupled with the nitrogen and boron values and with the acid and base neutral equivalents, are sufficient to confirm the compositions of the salts.

Tetraethylammonium Pentaborate.—(a) Ammonium pentaborate (66 g., 0.24 mole) was dissolved in a minimum of boiling water and 370 ml. of Eastman Kodak Co. 10% aqueous tetraethylammonium hydroxide (0.25 mole) was added. Water and ammonia were removed by heating *in vacuo*.

(b) Boric acid (32 g., 0.52 mole) was dissolved in a minimum of boiling water and 160 ml. of 10% tetraethylammonium hydroxide (0.108 mole) was added. Water was removed by heating *in vacuo*.

The white solid obtained in each case was twice recrystallized from water, washed with acetone and dried *in vacuo* at 25°.

Anal. Calcd. for $C_8H_{20}NH_4B_5O_{10}$: C, 27.58; H, 6.94; N, 4.02; B, 15.53; A.N.E., 348.4; B.N.E., 87.1. Found (a): C, 27.74, H, 6.64; N, 4.10; A.N.E., 350.6. Found (b): C, 27.40; H. 6.62; N, 4.05; B, 15.56; A.N.E., 349.5; B.N.E., 88.2.

Tetramethylammonium Pentaborate.—Boric acid (77.3 g., 1.25 moles) was added to 250 ml. of Eastman Kodak Co. 10% aqueous tetramethylammonium hydroxide (0.25 mole). The mixture was heated to solution and water was removed *in vacuo*. The white solid obtained was twice recrystallized from water and dried at 25° *in vacuo*.

Anal. Calcd. for $C_4H_{12}NH_4B_5O_{10}$: C, 16.44; H, 5.52; A.N.E., 292.3; B.N.E., 73.1. Found: C, 16.53; H, 5.48; A.N.E., 293.8; B.N.E., 73.6.

Tetraallylammonium Pentaborate.—Tetraallylammonium bromide was prepared by refluxing for 2 hours a solution of 59.7 g. (0.436 mole) of triallylamine and 43 ml. (0.497 mole) of allyl bromide in 200 ml. of acetone. The resultant pink solution, from which white crystals had deposited, was cooled and treated with 200 ml. of ether. The precipitate was filtered, washed with ether and dried *in vacuo*. The yield was 94.5 g. (84%).

Tetraallylammonium bromide (67.9 g., 0.263 mole) was dissolved in water and silver oxide was added with vigorous stirring until the solution gave a negative halide test (with acidic silver nitrate). The solution was filtered and treated with boric acid (81.6 g., 1.32 moles). The mixture was heated and enough water was added to effect complete solution, the solution was filtered and then concentrated to dryness. The pink-white solid obtained was treated with charcoal and crystallized from water–isopropyl alcohol, then twice recrystallized from water–isopropyl alcohol and air-dried.

Anal. Calcd. for $C_{12}H_{20}NH_4B_5O_{10} \cdot H_2O$: A.N.E., 414.4. Found: A.N.E., 414.1.

The salt was then dried at 90° *in vacuo* for 2 hours.

Anal. Calcd. for $C_{12}H_{20}NH_4B_5O_{10}$: C, 36.36: H, 6.10; N, 3.53; B, 13.65; A.N.E., 396.4; B.N.E., 99.1. Found: C, 36.22; H, 6.16; N, 3.62; B, 13.45; A.N.E., 396.1; B.N.E., 99.7.

Triallyl-*n*-propylammonium Pentaborate.—Triallyl-*n*-propylammonium iodide was obtained by refluxing equimolar quantities of *n*-propyl iodide and triallylamine in acetonitrile for 2 hours, then cooling and adding ether. The iodide (17.7 g., 0.0575 mole) was dissolved in water and treated with silver oxide until a negative halide test was obtained. The solution was filtered, analyzed for hydroxide ion, and found to contain 0.055 equivalent. Boric acid (17 g., 0.275 mole) was added to the solution and the water was removed *in vacuo*. The white solid obtained was crystallized from water–acetone, three times recrystallized from water and air-dried.

Anal. Calcd. for $C_{12}H_{22}NH_4B_5O_{10} \cdot H_2O$: A.N.E., 416.5. Found: A.N.E., 414.3.

The salt was then dried *in vacuo* at 55° for 5 hours.

Anal. Calcd. for $C_{12}H_{22}NH_4B_5O_{10}$: C. 36.17; H. 6.56; A.N.E., 398.4; B.N.E., 99.6. Found: C, 36.00: H, 6.40; A.N.E., 397.4; B.N.E., 100.5.

Trimethylanilinium Pentaborate.—Trimethylanilinium iodide was prepared by mixing methyl iodide (142 g., 1 mole) and dimethylaniline (121 g., 1 mole) in 300 ml. of acetone. Heat was evolved and crystals separated immediately. On cooling and filtering, 240 g. of salt was obtained (91% yield).

The iodide was recrystallized from water-isopropyl alcohol and 16.7 g. (0.063 mole) of it was dissolved in 150 ml. of water. Silver oxide was added with vigorous stirring until the solution showed a negative halide test. After filtration, boric acid (19.7 g., 0.32 mole) was added to the solution. The mixture was diluted to 500 ml., heated to solution, filtered, and concentrated by heating *in vacuo*. The white solid was crystallized from water–isopropyl alcohol, twice recrystallized from water and dried at 40° *in vacuo*.

Anal. Calcd. for $C_9H_{14}NH_4B_5O_{10}$: C, 30.50; H, 5.12: A.N.E., 354.3: B.N.E., 88.6. Found: C, 31.39, 30.07; H, 4.72, 5.25; A.N.E., 355.9; B.N.E., 87.2.

Allyldimethylanilinium Pentaborate.—To a solution of 188 ml. (1.49 moles) of dimethylaniline in 500 ml. of acetone was added a solution of 136 ml. (1.49 moles) of allyl iodide in 350 ml. of acetone. The mixture was refluxed for 3 hours and 500 ml. of acetone was removed *in vacuo*. The reddish product (crystallized with difficulty) was washed with a mixture of equal volumes of acetone and ether (removing most of the color) and dried. The yield was 299 g. (69%) of allyldimethylanilinium iodide.

An aqueous solution of 299 g. (1.03 moles) of the iodide was treated with silver oxide until a negative halide test was obtained. The solution was filtered and the total amount of base was determined to be 0.85 equivalent. Boric acid (264 g., 4.25 moles) was added and the mixture was heated to effect solution. Carbon was added to decolorize the solution, the solution was filtered and water was removed *in vacuo*. Crystallization of the product from water–acetone afforded 176 g. of fine white crystals. The salt was twice recrystallized from water and air-dried.

Anal. Calcd. for $C_{11}H_{16}NH_4B_5O_{10}$: C. 34.73; H. 5.30: A.N.E., 380.4; B.N.E., 95.1. Found: C. 34.16; H, 5.61; A.N.E., 382.0; B.N.E., 96.4.

Trimethylfluorenylammonium Pentaborate.—Trimethylfluorenylammonium bromide was prepared by treating 12.3 g. (0.05 mole) of 9-bromofluorene[6] with 25 ml. of 25% trimethylamine in methanol. This was allowed to stand 15 minutes after which ether was added and the crystals were filtered. Recrystallization from isopropyl alcohol afforded 14.9 g. of salt (98% yield).

A solution of 14.9 g. (0.049 mole) of the bromide in 150 ml. of water was treated with silver oxide until a negative halide test was obtained. The resultant purple solution was filtered, diluted to 250 ml., analyzed and found to contain 0.044 equivalent of base. To this solution was added 13.7 g. (0.22 mole) of boric acid. The mixture was heated to solution, filtered and concentrated nearly to dryness *in vacuo*. The residue was crystallized from water–isopropyl alcohol and the crystals washed with ether; yield 14.5 g. The salt was twice recrystallized from water and dried *in vacuo* at 55°.

Anal. Calcd. for $C_{16}H_{18}NH_4B_5O_{10}$: C. 43.43; H. 5.01: N, 3.17: B. 12.23: A.N.E., 442.5; B.N.E., 110.6. Found: C, 42.12; H, 5.53; N, 3.07; B, 11.85; A.N.E., 444.7: B.N.E., 113.1.

Triethylfluorenylammonium Pentaborate.—A solution of 13.2 g. (0.054 mole) of 9-bromofluorene in 50 ml. of ethanol was treated with 15 ml. (0.108 mole) of triethylamine. The mixture was refluxed for 1 hour, cooled, and ether was added. The precipitate obtained was recrystallized from ethanol with addition of ether. White crystals were obtained in a yield of 15.1 g. (80.7%).

An aqueous solution of this salt was treated with silver oxide in the usual manner. After achieving a negative halide test the mixture was filtered and the solution was diluted to 500 ml. Analysis showed the solution to contain 0.0356 equivalent of base. Boric acid (11 g., 0.178 mole) was added and the dark solution was filtered through Celite

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[6] R. C. Fuson and H. D. Porter, THIS JOURNAL, **70**, 895 (1948).

and a sintered glass filter. Concentration to dryness gave a residue which was crystallized from water–isopropyl alcohol, then twice recrystallized from water and dried at 55° *in vacuo*.

Anal. Calcd. for $C_{10}H_{24}NH_4B_5O_{10}$: C, 47.10; H, 5.82; A.N.E., 484.5. Found: C, 47.13; H, 5.45; A.N.E., 487.0.

Trimethyl-1-acenaphthenylammonium Pentaborate.—A suspension of N-bromosuccinimide (8.9 g., 0.05 mole) and acenaphthene (7.7 g., 0.05 mole) in 100 ml. of carbon tetrachloride was heated in a water-bath at 85°. The vigorous reaction was completed in 10 minutes. The solution was cooled to room temperature and filtered. After removal of the solvent *in vacuo* the residue was dissolved in acetone and treated with trimethylamine (25 ml. of 25% solution in methanol). Removal of the solvent gave a solid which was dissolved in a mixture of ether and water. The ether layer was removed and the water layer was washed several times with ether. Concentration of the aqueous solution gave a yellow-white solid which was crystallized from isopropyl alcohol; m.p. 206–207° d.[7]

An authentic sample of trimethyl-1-acenaphthenylammonium bromide was obtained by preparing 1-acenaphthenol,[8] converting it to the bromide with phosphorus tribromide[9] and quaternizing with methanolic trimethylamine. A mixed melting point showed no depression.

An aqueous solution of 10 g. (0.034 mole) of the bromide was treated with silver oxide in the usual manner. Boric acid (10.5 g., 0.170 mole) was added and the solvent was removed *in vacuo*. The white residue was recrystallized from water–isopropyl alcohol, yielding 11.8 g. (80.3%). The salt was then three times recrystallized from water and air-dried.

Anal. Calcd. for $C_{15}H_{18}NH_4B_5O_{10}\cdot 2H_2O$: A.N.E., 466.5. Found: A.N.E., 463.6.

This salt holds water tenaciously. It was dried *in vacuo* for periods of 4–6 hours at various increasing temperatures during which treatment the A.N.E. constantly decreased. It was finally dried for 3 hours *in vacuo* at 90°.

Anal. Calcd. for $C_{15}H_{18}NH_4B_5O_{10}$: C, 41.85; H, 5.15; N, 3.25; B, 12.57; A.N.E., 430.4; B.N.E., 107.6. Found: C, 41.79; H, 5.38; N, 2.96; B, 12.25; A.N.E., 436.4; B.N.E., 108.4.

Benzyltrimethylammonium pentaborate was prepared from benzyltrimethylammonium hydroxide (38% aqueous solution, Eastman Kodak Co. technical grade) and boric acid using first 5 moles of boric acid, then 6 moles, to 1 mole of base.

(a) To an aqueous solution containing 0.205 mole of the quaternary ammonium base was added 63.4 g. (1.025 moles) of boric acid. The mixture was heated to solution, acetone was added and the mixture was cooled in an ice-bath. The solid product obtained was twice recrystallized from water and was dried *in vacuo* 1.5 hours at 90°.

(b) The previously described procedure was followed, but 76.1 g. (1.231 moles) of boric acid was used with 0.205 mole of base.

Anal. Calcd. for $C_{10}H_{16}NH_4B_5O_{10}$: A.N.E., 368.4. Found: (a) A.N.E., 367.5. Found (b): A.N.E., 367.8.

The two samples were combined.

Anal. Calcd. for $C_{10}H_{16}NH_4B_5O_{10}$: C, 32.60; H, 5.47; N, 3.80; B, 14.69; B.N.E., 92.1. Found: C, 32.23; H, 5.31; N, 3.70; B, 14.85; B.N.E., 92.9.

Benzyltriethylammonium Pentaborate.—(a) A solution of benzyltriethylammonium chloride[10] (35 g., 0.154 mole) in water was treated with silver oxide, filtered and diluted to 500 ml. Analysis indicated that the solution contained 0.123 equivalent of base. Boric acid (38 g., 0.615 mole) was added, the mixture was heated to solution, filtered and concentrated *in vacuo*. The residue was crystallized from water–acetone, yielding 40 g.

(b) An ion exchange method was used.[11] Forty grams of Dowex 2 was suspended in water and poured into a chromatographic column. The resin was washed with 2 liters of 1 *M* aqueous sodium hydroxide and then with distilled water until the washings were free of halide and hydroxide. An aqueous solution containing 10 g. (0.044 mole) of benzyltriethylammonium chloride was poured on the column. An eluate of 600–700 ml. was collected (until non-basic to phenolphthalein). A negative halide test was shown by this solution. The solution was diluted to 1 liter and analyzed, showing 0.0418 equivalent of base. Boric acid (12.8 g., 0.207 mole) was added, water was removed *in vacuo* and the residue was crystallized from water–acetone with ether added, yielding 11 g.

Each sample was twice recrystallized from water and air-dried.

Anal. Calcd. for $C_{13}H_{22}NH_4B_5O_{10}\cdot 3H_2O$: A.N.E., 464.5. Found (a): A.N.E., 461. Found (b): A.N.E., 461.

The two samples were combined and dried for 5 hours at 55° *in vacuo*.

Anal. Calcd. for $C_{13}H_{22}NH_4B_5O_{10}$: C, 38.04; H, 6.39; B, 13.18; A.N.E., 410.4; B.N.E., 102.6. Found: C, 37.86; H, 6.31; B, 13.7; A.N.E., 409; B.N.E., 104.7.

Benzyltri-*n*-butylammonium Pentaborate.—Benzyltri-*n*-butylammonium bromide was prepared by refluxing 23 ml. (0.19 mole) of benzyl bromide and 50 ml. (0.21 mole) of tri-*n*-butylamine in 50 ml. of acetonitrile mixed with 100 ml. of acetone for 6 hours. The solution was concentrated *in vacuo* and ether was added, yielding 62.5 g. of white crystals. The bromide was dissolved in 300 ml. of water and the solution was treated with silver oxide as usual. The solution was filtered, diluted to 500 ml., analyzed for base and divided into two equal portions, each containing 0.080 equivalent of base. These two portions were treated with (a) 25 g. (0.40 mole) and (b) 30 g. (0.49 mole) of boric acid. Each was heated to solution, filtered and concentrated *in vacuo*, yielding a sticky white material. Addition of acetone and ether with stirring, followed by filtration, gave a white powder in each case which was then crystallized by dissolving in acetone with a small amount of water and adding ether. The samples were twice recrystallized and air-dried.

Anal. Calcd. for $C_{19}H_{34}NH_4B_5O_{10}\cdot 3H_2O$: A.N.E., 548.7. Found (a): A.N.E., 549.7. Found (b): A.N.E., 542.7.

The samples were then dried for 2 hours *in vacuo* at 70°.

Anal. Calcd. for $C_{19}H_{34}NH_4B_5O_{10}$: A.N.E., 494.6. Found (a): A.N.E., 493.3. Found (b): A.N.E., 494.6.

The two samples were combined, recrystallized and redried *in vacuo* at 70°.

Anal. Calcd. for $C_{19}H_{34}NH_4B_5O_{10}$: C, 46.14; H, 7.71; B.N.E., 123.7. Found: C, 45.99; H, 7.28; B.N.E., 124.7.

Cinnamyltriethylammonium Hexaborate.—To a solution of 20 g. (0.101 mole) of cinnamyl bromide (b.p. 119°, 9 mm.) in 100 ml. of acetonitrile was added 25 ml. (0.18 mole) of triethylamine. Heat was evolved and after 2 hours standing the solution was concentrated *in vacuo*. Addition of ether and acetone with scratching gave 29 g. of white crystals.

The salt was dissolved in water and treated with silver oxide. The solution was filtered, diluted to 500 ml., analyzed for base and found to contain 0.085 equivalent. Boric acid (26 g., 0.424 mole) was added and the mixture was heated to solution, filtered and concentrated *in vacuo*. The residue was crystallized from water–isopropyl alcohol, twice recrystallized and dried *in vacuo* at 70°.

Anal. Calcd. for $C_{15}H_{24}NH_4B_5O_{10}\cdot H_3BO_3$: C, 36.15; H, 6.27; N, 2.81; B, 13.03; A.N.E., 498.3; B.N.E., 99.7. Found: C, 35.97; H, 5.95; N, 2.82; B, 13.55; A.N.E., 494.5; B.N.E., 100.8.

Benzyldimethylallylammonium Hexaborate.—Benzyldimethylallylammonium iodide was prepared by mixing 20 ml. (0.220 mole) of allyl iodide and 31 ml. (0.210 mole) of benzyldimethylamine in 200 ml. of acetone. The reaction was violent, and after 1 hour of standing ether was added to precipitate the salt. A solution of 15.1 g. (0.05 mole) of the iodide in water was treated with silver oxide in the usual manner and the solution was filtered. Boric acid (15.5 g., 0.25 mole) was added, the mixture was heated to solution, and the solution was concentrated to dryness. The white solid was twice recrystallized from water–isopropyl alcohol,

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[7] G. Wittig and H. Ludwig, *Ann.*, **589**, 55 (1954), give 208.5–209° d.

[8] L. F. Fieser and J. Cason, THIS JOURNAL, **62**, 432 (1940).

[9] W. E. Bachmann and J. C. Sheehan, *ibid.*, **63**, 204 (1941).

[10] S. D. Ross and M. Finkelstein, *ibid.*, **79**, 6547 (1957).

[11] R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **43**, 1088 (1951).

filtered and washed with ether. The crystals were dried *in vacuo* at 70°.

Anal. Calcd. for $C_{12}H_{18}NH_4B_5O_{10}\cdot H_3BO_3$: C, 31.59; H, 5.52; N, 3.07; B. 14.23; A.N.E., 456.3; B.N.E., 91.3. Found: C, 31.81; H, 5.65; N, 2.95; B, 14.08; A.N.E., 454.2; B.N.E., 92.1.

Benzyldimethyl-*n*-propylammonium Hexaborate.—Benzyldimethyl-*n*-propylammonium bromide was prepared by refluxing 36 ml. (0.40 mole) of *n*-propyl bromide and 60 ml. (0.43 mole) of benzyldimethylamine in 250 ml. of acetonitrile for 18 hours. The solvent was removed *in vacuo* and the crystalline product was dissolved in 200 ml. of water. This solution of the bromide was treated with silver oxide, filtered through Celite, diluted to 500 ml., analyzed for base and divided into three equal portions of 0.1005 equivalent each. These three portions were treated with (a) 24.7 g. (0.40 mole), (b) 30.9 g. (0.50 mole) and (c) 37.1 g. (0.60 mole) of boric acid.

In each case the mixture was heated to solution and concentrated by boiling. The crystalline products obtained were twice recrystallized from water and dried *in vacuo* at 90°.

Anal. Calcd. for $C_{12}H_{20}NH_4B_5O_{10}\cdot H_3BO_3$: C, 31.45; H, 5.94; N, 3.06; B, 14.17; A.N.E., 458.3; B.N.E., 91.7. Found: (a) A.N.E., 453.8; B.N.E., 94.9. Found (b): A.N.E., 457.3; B.N.E., 94.2. Found (c): C, 31.22; H, 5.43; N, 3.06; B, 13.97; A.N.E., 458.4; B.N.E., 92.9.

Discussion

It is of interest to note that the general formula for quaternary ammonium pentaborates is $QH_4B_5O_{10}$ in contrast to potassium and ammonium pentaborates which have two additional water molecules per pentaborate unit.[12] Some of the quaternary ammonium pentaborates crystallize from aqueous solution with additional water, but this water is readily removed in all cases except one, trimethyl-1-acenaphthenylammonium pentaborate, from which the water is removed with difficulty.

It is also interesting to note that tetraallylammonium and triallyl-*n*-propylammonium pentaborates, differing only in the interchange of an allyl and a propyl radical, both appear to crystallize with one water molecule, while tetraethylammonium pentaborate crystallizes without water, and that benzyltriethylammonium pentaborate apparently crystallizes with three water molecules as does benzyltri-*n*-butylammonium pentaborate which differs from it in having three butyl groups in place of three ethyl groups.

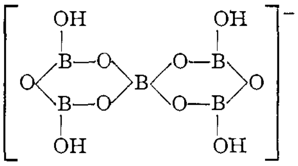
In changing the cation from benzyltriethylammonium to cinnamyltriethylammonium, three water molecules are replaced by a single boric acid molecule, and in replacing the phenyl group of allyldimethylanilinium, whose pentaborate crystallizes with neither water nor boric acid, by a benzyl group, benzyldimethylallylammonium hexaborate is obtained. Replacing the allyl radical of this compound by *n*-propyl has no effect.

It should also be noted that attempts to prepare both the pentaborate and the hexaborate of benzyltrimethylammonium, benzyltri-*n*-butylammonium and benzyldimethyl-*n*-propylammonium by varying the ratios of acid to base used failed, the first two always appearing as pentaborates and the last as a hexaborate.

Clearly the nature of the cation determines whether the salt will crystallize as $QH_4B_5O_{10}$, $QH_4B_5O_{10}\cdot nH_2O$ or $QH_4B_5O_{10}\cdot H_3BO_3$, but it is not at all clear just what features of the cation are significant. It seems likely that size and symmetry of the quaternary ammonium ion dictate the nature of spaces in the crystal lattice and that the nature of the spacing determines whether boric acid, water or neither will crystallize with salt. It also seems quite likely that boric acid or water molecules will form hydrogen bonds with the pentaborate ions.

The concept of a pentaborate with a boric acid molecule of crystallization, as opposed to a salt containing an integral hexaborate ion, is supported by the fact that the added unit is H_3BO_3 rather than HBO_2. Attempts to remove water from the hexaborates by heating them as high as 90° *in vacuo* have all failed. Such treatment was always successful in removing water from the hydrated pentaborates, thus indicating that the hexaborates do not contain an $H_5B_6O_{12}^-$ ion plus water of crystallization.

For the pentaborate ion, $H_4B_5O_{10}^-$, which appears to be present in all of these salts, we would propose the structure



This structure is essentially that proposed by Zachariasen[2,3] for this structural element in potassium pentaborate. It has the virtue of distinguishing one boron atom from the other four, and accounts for the fact that the anion is singly charged.

Whether or not the hexaborates are really pentaborates plus boric acid, it is apparent that the pentaborate ion is a most important species of polyborate.

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[12] Drying for 5 hours *in vacuo* at 88° failed to remove water from $KH_4B_5O_{10}\cdot 2H_2O$.