drawn was that the COOH, $COOC_2H_5$, and NO_2 groups were adjacent to the pair of equivalent protons responsible for the low-field multiplet; *i.e.*, the order of the multiplets was reversed. The fact that the high-field multiplet fell in the region previously ascribed to the pair of protons adjacent to the boronic acid group supports these conclusions. Thus the chemical shifts measured for the compounds containing the three groups were assigned a negative sign.

An inspection of the data reported by Martin and Dailey[4] and Richards and Schaeffer[3] revealed that correlations of substituent effects were possible for the proton spectra of other disubstituted benzenes. Using the method discussed in the present study, internal chemical shifts could be calculated from their data from which relative shifts were derived. The relative shifts for selected compounds were found to be linear with σ provided (a) the same reference substituent was present in each compound in the series, and (b) the substituents *para* to the reference group on the benzene ring were exerting a greater degree of inductive release of electron density than was the reference group.

A future paper will discuss these findings and their implications in detail. For the present it should suffice to state that to be effective in a study of this type the reference group must exert a relatively constant inductive influence on the separation of the multiplets. The principle role of the reference group must be to reduce the number of ring protons so that a complete spin analysis is possible without interacting with the *para* substituents in an inconsistent manner. So long as the inductive effect of the reference group may be classified as electron withdrawing, relative to the *para* substituent, its influence on the separation of the multiplets is virtually constant. The relative chemical shifts within a series of *para* substituents reflect only the electron-donating capabilities of the latter and may be correlated with known substituent phenomena.

The generalization holds for several series in addition to the phenylboronic acids. The series include the benzoic acids and the nitrobenzenes, and, with few exceptions, the relative chemical shifts determined for these series correlate well with σ constants. The chemical shifts of the 4-nitrophenylboronic acid and (phenylboronic acid)4-carboxylic acid correlate well within their respective series when calculated relative to their parent compounds—nitrobenzene and benzoic acid, respectively. That is, they correlate well based on the assumption that the σ constant for the boronic acid group should be slightly less positive than that of the carboxylic acid group; the σ constant for the boronic acid group cannot be determined directly. Their chemical shifts are positive and are of the proper order of magnitude to be treated by the same method given in eq. 3, adjusted for the proper reference shift.

Although much emphasis has been given the correlation of the relative proton chemical shifts with σ, note should be made that the boron-11 shifts for the series of phenylboronic acids correlated surprisingly well with σ. The linear plot fit ten of the eleven relative chemical shifts within the experimental error. Because it may be possible to prepare phenylboronic acids with *para* substituents other than those reported here, future studies may extend the range of the correlation still further. If the appropriate compound could be prepared, it may be possible to use its relative boron-11 chemical shift in conjunction with Fig. 4 to predict the σ constant when no other data are available.

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Chemistry of Boranes. XV.[1] Synthesis of Diborane from Boric Oxide

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A direct synthesis of diborane from boric oxide has been achieved by hydrogenation of the oxide in the presence of aluminum and aluminum trichloride. Very pure diborane is obtained from this reaction in 40–50% conversions at temperatures above 150° and hydrogen pressures of 750 atm. This hydrogenation is believed to proceed through an aluminum chlorohydride intermediate. Amine boranes, aminoboranes, and borazines were obtained directly from boric oxide when the hydrogenation was effected in the presence of secondary or tertiary alkylamines.

Diborane Synthesis.—There are a large number of routes to diborane[2] which are based on boron halides or boron esters as starting materials; however, no synthesis of this hydride directly from boric oxide has been described. We have found that the oxide can be converted to diborane in good yields by reaction with aluminum, aluminum chloride (or an $AlCl_3$–NaCl melt), and hydrogen. This reaction, when effected at 175° and 750 atm. hydrogen pressure, gave diborane in conversions as high as 50%. The

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[1] Chemistry of Boranes. XIV: W. R. Hertler and M. S. Raasch, *J. Am. Chem. Soc.*, in press.

[2] For partial review of this subject, see D. T. Hurd, "Chemistry of the Hydrides," John Wiley and Sons, New York, N. Y., 1952, pp. 76–77; N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, New York, N. Y., 1956, pp. 49–51; Gmelin's "Handbuch Der Anorganischen Chemie," 8th Ed., Verlag Chemie, G.M.B.H., 1954, pp. 97–105.

TABLE I

SYNTHESIS OF DIBORANE

Boron compd.	NaCl, g.	$AlCl_3$, g.	Al, g.	Temp., °C.	H_2 press., atm.	Time, hr.	Conv. to B_2H_6, %
BCl_3 (30 g.)	90	133	20	170	400	5	29
BF_3 (18 g.)	30	113	20	170	800	5	22
$(CH_3O)_3B_3O_3$ (14 g.)	34[a]	226	20	180	800	5	10
$B(OCH_3)_3$ (21 g.)	30	113	20	170	800	5	20
KB_5O_8 (12 g.)	30	112	20	180	800	5	7
$Na_2B_4O_7$ (9.0 g.)	30	112	20	180	700	5	30
H_3BO_3 (11.1 g.)	25	118	20	180	700	5	7
B (10 g.)	30	113	20	180	800	5	0

[a] KCl used instead of NaCl.

purity of the diborane was at least 98% (hydrogen and pentaborane contaminants); all samples of diborane obtained by this method were sufficiently free of impurities to resist spontaneous inflammation in air. Other boron compounds, *e.g.*, borates and boron halides, were also converted to diborane under these conditions.

Although the mechanism of this reaction has not been elucidated, a number of facts regarding the reaction have been worked out.[3] Conclusions based on experimental studies are given below.

(1) Although boron trichloride can be hydrogenated to diborane (Table I), the hydrogenation of boric oxide in the aluminum chloride–sodium chloride melt does not appear to proceed through this route. It was shown experimentally that boric oxide and aluminum chloride (as an $AlCl_3$–NaCl melt) do not form boron trichloride at 185°; a reaction does take place with the formation of a nonvolatile oxychloride which may be an intermediate.

(2) The hydrogenation is not a stepwise conversion of boric oxide to elemental boron to diborane. Boron was not found in residual reaction mixtures, and it was independently established that elemental boron is not hydrogenated under the above synthesis conditions.

(3) Aluminum appears to form a volatile hydride under the conditions employed for the diborane synthesis. A mixture of aluminum and aluminum trichloride absorbs hydrogen at 180° to produce a species that transforms boron oxide to diborane. Aluminum metal transfer occurs under these reaction conditions. Attempts to isolate and characterize this aluminum hydride were not successful. We suggest that the aluminum intermediate is a chlorohydride.

$$2x\mathrm{Al} + (6 - 2x)\mathrm{AlCl_3} + 3x\mathrm{H_2} \rightleftharpoons 6(\mathrm{AlH}_x\mathrm{Cl}_{3-x}) \quad (1)$$

Similar evidence for an aluminum hydride intermediate has been presented for the analogous silane synthesis.[3]

(4) It was established that an aluminum hydride ($LiAlH_4$) does react with boric oxide under the melt synthesis conditions to form diborane. Thus, an (AlH_x-Cl_{3-x}) species is a plausible reactant in the diborane synthesis.

$$6(\mathrm{AlH}_x\mathrm{Cl}_{3-x}) + x\mathrm{B_2O_3}\ (\text{or BOCl}) \longrightarrow x\mathrm{B_2H_6} + 6(\mathrm{AlO}_{x/2}\mathrm{Cl}_{3-x}) \quad (2)$$

(5) Aluminum borohydrides would be expected to form from diborane and aluminum hydrides. Thus, the diborane formed in the above synthesis could further react as follows.

$$2(\mathrm{AlH}_x\mathrm{Cl}_{3-x}) + x\mathrm{B_2H_6} \rightleftharpoons 2[\mathrm{Al(BH_4)}_x\mathrm{Cl}_{3-x}] \quad (3)$$
$$\mathrm{Al(BH_4)}_x\mathrm{Cl}_{3-x} + \mathrm{Cl^-} \rightleftharpoons [\mathrm{Al(BH_4)}_x\mathrm{Cl}_{4-x}]^-$$

This reaction, which would compete with reaction 2, would be favored by low boric oxide concentration and high (AlH_xCl_{3-x}) concentration. These effects were observed experimentally. It is critical that excess boron oxide be present for high-yield diborane synthesis.

Diborane was added to a melt that contained aluminum but no boric oxide. When this system was heated under hydrogen pressure to 150° and then cooled, no diborane could be recovered. However, when this experiment was repeated with both aluminum and boric oxide absent, the diborane was recovered. These results are consistent with the postulated side reaction (3).

Synthesis of Borane Derivatives.—Hydrogenation of boric oxide in the presence of secondary or tertiary amines and aluminum–aluminum trichloride led to the formation of amine boranes, aminoboranes, and borazines. For example, trimethylamine gave predominantly trimethylamine borane with lesser amounts of the dimethylaminoborane dimer and N-trimethylborazine.

Experimental

Purity of Reactants.—Boric oxide used for these experiments was 100 mesh, commercial "boric acid anhydride." This is the glassy form of the oxide. The porous form prepared by slow dehydration of boric acid without fusion gave equivalent results. Anhydrous aluminum chloride, powdered aluminum metal, and sodium chloride of reagent grade quality were suitable. Granulated aluminum and aluminum turnings were also active but conversion was slower. The hydrogen was 99.8–99.9% pure, with water (50–150 p.p.m.) and nitrogen or air (0.1–0.2%) the only impurities detected by mass spectrometry.

Hydrogenation of Boric Oxide.—A stainless steel pressure vessel of 400-ml. capacity was thoroughly cleaned, dried, and flushed with nitrogen. Ten $^3/_8$-in. stainless steel balls were introduced into the vessel to aid in mixing. Boric oxide (6.25 g., 0.09 mole), aluminum chloride (113 g., 0.85 mole), powdered aluminum (20 g., 0.74 g.-atom), and sodium chloride (25 g., 0.42 mole) were charged to the tube maintained under an atmosphere of nitrogen. The vessel was evacuated, pressured with hydrogen to 200 atm., and then heated with shaking to 180°.

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[3] This is closely related to the synthesis of silane from silica: H. L. Jackson, F. D. Marsh, and E. L. Muetterties, *Inorg. Chem.*, **2**, 43 (1963). See also A. L. McClelland, U. S. Patent 3,088,804 (May 7, 1963).

The reaction vessel was shaken at this temperature and 700–775 atm. for 5 hr. Additional hydrogen was added during reaction to maintain the pressure. At the end of this time, the vessel was cooled and the gases were bled through two liquid nitrogen cooled traps provided with plugs of glass wool to prevent the finely divided solid diborane from being carried through the traps with the hydrogen. The "crude" diborane was transferred to a vacuum system, evacuated at −196° with a diffusion pump to remove noncondensable gases, then transferred to a known volume, and allowed to vaporize, and its pressure was determined. The gas amounted to 0.046 mole. The gas was condensed again and then allowed to vaporize slowly. By this technique, the product was divided into three approximately equal samples which were analyzed by mass spectrometry. The most volatile fraction comprised 99–99.7% B_2H_6, 0.2–0.4% max. H_2, and possibly 0.1–0.2% B_5H_9. The least-volatile fraction contained greater quantities of the B_5 compound: 96–97% B_2H_6, 0.5–1.4% max. H_2, 2.0–2.5% B_5H_9. All of the diborane fractions were sufficiently pure that they did not ignite spontaneously in air. The conversion to diborane amounted to 50% based on the boric oxide employed. The residual melt, when allowed to react with fresh hydrogen under the above conditions, gave an additional 20% conversion of the boric oxide to diborane, bringing the total conversion to 70%. Other boron compounds (see Table I) were successfully substituted in the diborane synthesis, but elemental boron did not react under these conditions.

Residual melts from the boric oxide hydrogenation were found to contain melt-soluble hydrides. The amount of hydrogen evolved by hydrolysis in methanol–water[4] of filtered melts indicated that from 1 to 6% of the boron charged could be present as hydrides. Heating the residual melts under vacuum liberated diborane and very small amounts of higher boranes, *e.g.*, pentaborane, in amounts corresponding approximately to the hydrolytic hydride determination.

The major portion of the unreacted boron was insoluble in the melt, nonhydridic, and water-soluble. Flame photometry demonstrated that the melt-insoluble fractions contained 3.5–6.8% boron and, therefore, contained the major part of the boron not converted to diborane. X-Ray diffraction experiments on this material demonstrated that crystalline aluminum oxide was not present.

Effect of Hydrogen Pressure.—The optimum hydrogenation pressure for shaker tube studies carried out at 170–180° was in the range of 700–800 atm., yielding 40–50% conversion of boric oxide to diborane in 4–5 hr. operating time. Under similar conditions of temperature and reaction time but at 150–200 atm., the conversion fell to 5–12% in 5 hr. but by extending the reaction time to 15 hr., a 23% conversion of boric oxide to diborane was obtained.

At pressures above 800 atm. the relative concentrations of aluminum and boric oxide play a very important role in the diborane synthesis. Use of hydrogen pressures of 1600 atm. or higher with the typical reaction mixtures described above resulted in further reactions which completely consumed the diborane and none was isolated. Rehydrogenation of such melts at 800 atm. gave no diborane. Furthermore, melts that had given diborane at 800 atm. did not give additional diborane on rehydrogenation at 1600 atm. as they would on rehydrogenation at 800 atm. These unexpected reactions at high pressure proved to be associated with the use of excess aluminum. When the boric oxide was used in excess, by increasing the quantity charged to 62.5 g., diborane synthesis did occur at 1600 atm. and the quantity of diborane was equivalent to that obtained at 800 atm.

Reaction of Boric Oxide with Aluminum Chloride.—A mixture of 113 g. (0.85 mole) of aluminum chloride, 30 g. (0.42 mole) of sodium chloride, and 6.25 g. (0.09 mole) of boric oxide was heated at 185° for periods up to 72 hr. A slow stream of helium was bubbled through the melt and the exit gas passed through two traps in series cooled to −78°. In four experiments the amount of condensable gases varied from 0.0003 to 0.0029 mole. Mass spectrometer analysis demonstrated that the volatile product contained 97% hydrogen chloride (probably because of traces of moisture) and no boron chloride. A white, insoluble solid precipitated from the melt in these experiments.

In experiments aimed at determining the composition of the precipitate mentioned above, a mixture of 113 g. of aluminum chloride, 30 g. of sodium chloride, and 6.25 g. of boric oxide was heated to 185° for a period of 6 hr. with vigorous stirring every 15 min. The white precipitate, separated from the melt by filtration under anhydrous conditions through a sintered glass funnel, weighed 21.5 and 22.5 g. in duplicate experiments. Analysis of this precipitate indicated that the approximate composition was $BOCl \cdot AlOCl$ (analyses corresponded to $AlB_{1.03}O_{2.03}Cl_{2.28}$). If all of the boric oxide had been converted to the mixed oxychloride, there would have been 26.8 g. of product. Some of the aluminum oxychloride must have been present in the aluminum chloride initially since the oxygen added as B_2O_3 was less than that required for the mixed oxychloride filtered off. The melt, after filtration to remove the precipitate, contained the equivalent of 0.3 g. of B_2O_3 per 100 g. of the aluminum chloride–sodium chloride melt.

Evidence for an Aluminum Hydride Intermediate.—A mixture of 22.8 g. of aluminum, 113 g. of aluminum chloride, and 30 g. of sodium chloride in a stainless steel pressure vessel was heated to 155° at ~800 atm. hydrogen pressure for 14.5 hr. At the end of this time the tube was cooled and the gases were bled off. Subsequently, a 10-g. sample of the melt was placed in a totally enclosed evacuated system. The melt was fused by heating to 185°. At this temperature hydrogen was liberated and its volume determined with a gas buret. The hydrogen liberated amounted to 4.41 ml./g. (0.002 mole of H_2/mole of aluminum charged) of initial product at STP. When the pressure hydrogenation was carried out at 100°, there was obtained 5.05 ml. of hydrogen/g. and at 200° only 1.51 ml. of hydrogen/g. was obtained. These quantities of hydrogen are orders of magnitude larger than would be expected on the basis of solubility. The hydride appeared to be volatile because in experiments with similar mixtures in a vertically positioned nonagitated tube aluminum was plated out at the top (cooler part) of the tube.

Side Reaction in Diborane Synthesis.—Evidence for reaction 3 was obtained by adding diborane to an aluminum-containing aluminum chloride–sodium chloride melt under conditions used for the synthesis of diborane from boric oxide. Diborane (0.039 mole) was added to a mixture of 20 g. of aluminum, 113 g. of $AlCl_3$, and 23 g. of NaCl and treated with hydrogen at 700 atm. for 5 hr. at 180°. The hydrogen, bled down through traps in the usual manner, contained less than 0.3% of the diborane charged. Two additional portions of diborane (0.059 and 0.064 mole) were in turn added to the residual mixture and similarly treated with hydrogen. No diborane was recovered. Samples of the melt after filtration through sintered glass (to remove undissolved aluminum) when hydrolyzed with methanol–water gave hydrogen, indicating the presence of dissolved hydrides. On the other hand, in the absence of aluminum, 40–50% of the diborane was recovered when a mixture of sodium chloride–aluminum chloride with diborane was heated under 700 atm. hydrogen pressure for 5 hr. Very little hydridic material was found in the melt; the hydride value determined on the melt accounted for less than 5% of the boron.

Reduction of Boric Oxide with Lithium Aluminum Hydride.—Solid lithium aluminum hydride (5.0 g., 0.13 mole) was added slowly to a mixture of 3.1 g. (0.045 mole) of boric oxide, 56 g. (0.43 mole) of aluminum chloride, and 15 g. (0.21 mole) of sodium chloride in a glass flask maintained at 170–180°. The gases from this mixture were led through a liquid nitrogen trap. Analysis of the condensable gases with a mass spectrometer indicated a 0.2% conversion of boric oxide to diborane. Low

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(4) Methanol–water (3:1) in the presence of aluminum chloride liberated hydrogen quantitatively from decaborane and from a polymeric higher hydride and was assumed to give complete hydrolysis of the hydride functions in the residual melts from boric oxide hydrogenation.

conversion was due to a competing reaction, thermal decomposition of lithium aluminum hydride.

Hydrogenation of Boric Oxide in Trimethylamine.—A stainless steel shaker tube of 400-ml. capacity was charged with 12.5 g. (0.18 mole) of boric oxide, 20 g. (0.74 g.-atom) of aluminum, 10 g. (0.075 mole) of aluminum chloride, and 20 stainless steel balls. The vessel was evacuated and cooled and 50 g. (0.85 mole) of trimethylamine was introduced. Hydrogen pressure was applied, and the vessel and contents were heated to 275°. The hydrogen pressure was adjusted to 800–900 atm. These conditions were maintained for 10 hr. At the end of this time the vessel was cooled and vented. The solid residues from four similar runs were combined and heated under vacuum to 250–300°. The volatile portion was collected in a liquid nitrogen trap. Distillation of this material gave 0.98 g. of N-trimethylborazine and 4.02 g. of $[(CH_3)_2NBH_2]_2$. The residue, ~10 g., was $(CH_3)_3NBH_3$. All of these materials were identified by comparison of their B^{11} and H^1 n.m.r. and infrared spectra with authentic samples.

Anal. Calcd. for $[(CH_3)_2NBH_2]_2$: C, 40.4; H, 14.2; N, 24.6; B, 19.02. Found: C, 40.1; H, 13.3; N, 24.6; B, 17.2.

Anal. Calcd. for $(CH_3)_3NBH_3$: C, 49.4; H, 16.6. Found: C, 48.6; H, 16.1.

Similar reactions were carried out under the conditions given above with dimethylamine, pyridine, dimethylaniline, and N-methylmorpholine. In all cases an amine borane appeared to be formed as evidenced by the reduction of silver nitrate by the crude products, but the individual components were not isolated.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Carbonate Ion Dissociation in Fused Alkali Nitrates

BY R. N. KUST

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The equilibrium constant K for the dissociation of carbonate ion in fused equimolar sodium–potassium nitrate solvent, according to the reaction $CO_3^{-2} \rightleftarrows CO_2 + O^{-2}$, was determined potentiometrically with an oxygen–platinum indicator electrode in conjunction with a silver–silver nitrate (1.0 M $AgNO_3$ in equimolar $(Na,K)NO_3$) reference electrode. Values of K obtained were $(3.9 \pm 0.5) \times 10^{-6}$ at 523°K. and $(5.6 \pm 0.2) \times 10^{-5}$ at 580°K. $\Delta H°$ and $\Delta S°$ for the dissociation were constant over the temperature range studied and were found to be 27.0 ± 0.1 kcal. and 27.1 ± 0.1 e.u., respectively. Values for $\Delta G°$ at 523 and 573°K. are 12.9 ± 0.1 and 11.5 ± 0.1 kcal., respectively.

Introduction

According to the Lux acid–base theory which is usually used in the description of melts containing oxyanions, a base is an oxide ion donor and an acid is an oxide ion acceptor.[1] In fused alkali nitrates, several acids have been investigated—pyrosulfate,[2] dichromate,[3] transition metal ions,[4,5] to name a few. Little has been done, however, in the characterization of bases in fused alkali nitrates. Most oxyanions are potential bases, the degree of basicity being inversely proportional to the stability of the oxyanion with respect to dissociation according to the reaction

$$MO_x^{-y} \rightleftarrows MO_{x-1}^{-y+2} + O^{-2} \qquad (1)$$

The carbonate ion displays significant basicity in a nitrate solvent. This paper is a report on the determination of the equilibrium constant for the reaction

$$CO_3^{-2} \rightleftarrows CO_2 + O^{-2} \qquad (2)$$

The method of determination consisted of the maintenance of a constant CO_2 partial pressure over the solvent in the reaction vessel and the measurement of the O^{-2} ion concentration with an oxygen–platinum electrode developed previously.[6]

Experimental

All chemicals used were reagent grade. The solvent of equimolar sodium–potassium nitrates was prepared by fusing the proper proportions of the two salts, mixing well, filtering through a fine grade fritted glass disk, and molding into slugs of about 100 g. All reagents were dried at 110° and were stored over magnesium perchlorate.

The reaction vessel and electrodes were similar to those previously described.[6] An oxygen–platinum electrode was used as the indicator electrode and a silver–silver nitrate (1.0 M $AgNO_3$ in equimolar Na,KNO_3) electrode was used as the reference electrode. The flow rates of carbon dioxide and oxygen were measured with floating ball type flow meters manufactured by Roger Gilmont Instruments, Inc.

Potential measurements were made with a Leeds and Northrup K-3 universal potentiometer. A Keithley Model 603 electrometer-amplifier was connected in series with the electrochemical cell and was used as a null indicator.

Results and Discussion

The stoichiometry of reaction 2 was verified by adsorbing on Ascarite the CO_2 gas evolved when a known

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