TABLE I

OBSERVED AND CALCULATED RATES

| [Ag(II)] $\times 10^5$ | [Ag(I)] $\times 10^2$ | [Tl(I)] $\times 10^4$ | $R_{obs}$ $\times 10^6$ | $R_{cal}$ $\times 10^6$ | [Ag(II)] $\times 10^5$ | [Ag(I)] $\times 10^2$ | [Tl(I)] $\times 10^4$ | $R_{obs}$ $\times 10^6$ | $R_{cal}$ $\times 10^6$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.593 | 2.45 | 8.19 | 0.55 | 0.58 | 1.90 | 1.65 | 1.59 | 1.0 | 1.6 |
| 0.593 | 2.45 | 17.3 | 0.92 | 0.97 | 1.94 | 2.45 | 17.6 | 8.6 | 5.1 |
| 0.593 | 2.45 | 17.5 | 0.84 | 0.97 | 2.17 | 1.64 | 4.12 | 3.0 | 3.7 |
| 1.07 | 1.64 | 4.06 | 1.1 | 1.2 | 2.37 | 0.146 | 1.64 | 6.2 | 7.4 |
| 1.19 | 0.147 | 1.58 | 2.3 | 3.1 | 2.37 | 0.146 | 1.74 | 6.8 | 7.5 |
| 1.19 | 0.147 | 1.68 | 2.1 | 3.2 | 2.37 | 0.266 | 1.59 | 3.5 | 6.2 |
| 1.19 | 0.147 | 3.62 | 4.4 | 3.9 | 2.37 | 0.433 | 3.87 | 4.8 | 7.0 |
| 1.19 | 0.226 | 2.13 | 2.5 | 3.0 | 2.37 | 0.828 | 1.00 | 1.7 | 2.6 |
| 1.19 | 0.267 | 1.53 | 1.1 | 2.4 | 2.37 | 0.828 | 1.55 | 2.1 | 3.5 |
| 1.19 | 0.445 | 1.07 | 2.4 | 1.4 | 2.37 | 1.57 | 0.97 | 1.9 | 1.5 |
| 1.19 | 0.434 | 3.81 | 1.7 | 2.9 | 2.37 | 1.69 | 1.34 | 2.5 | 1.9 |
| 1.19 | 0.829 | 0.94 | 0.48 | 0.80 | 2.37 | 1.69 | 1.39 | 2.4 | 2.0 |
| 1.19 | 0.829 | 1.49 | 0.97 | 1.2 | 2.37 | 1.73 | 1.62 | 1.9 | 2.2 |
| 1.19 | 0.829 | 3.47 | 1.7 | 2.0 | 2.37 | 1.69 | 1.66 | 1.9 | 2.2 |
| 1.19 | 0.829 | 3.75 | 1.9 | 2.1 | 2.37 | 1.56 | 3.49 | 3.4 | 3.9 |
| 1.19 | 1.57 | 0.91 | 0.55 | 0.44 | 2.37 | 1.69 | 4.05 | 3.3 | 4.1 |
| 1.19 | 1.69 | 1.28 | 0.80 | 0.57 | 2.37 | 1.69 | 4.31 | 3.6 | 4.2 |
| 1.19 | 1.69 | 1.33 | 0.80 | 0.59 | 2.37 | 1.67 | 7.79 | 4.8 | 5.7 |
| 1.19 | 1.73 | 1.56 | 0.47 | 0.66 | 2.37 | 1.62 | 8.04 | 6.5 | 5.8 |
| 1.19 | 1.69 | 1.60 | 0.60 | 0.69 | 2.37 | 1.57 | 8.42 | 6.4 | 6.0 |
| 1.19 | 1.75 | 2.46 | 1.7 | 0.96 | 2.37 | 1.70 | 8.75 | 7.2 | 5.9 |
| 1.19 | 1.56 | 3.43 | 1.0 | 1.4 | 2.37 | 1.69 | 8.77 | 3.7 | 5.9 |
| 1.19 | 1.69 | 3.99 | 1.1 | 1.4 | 2.37 | 1.57 | 17.1 | 12.0 | 7.4 |
| 1.19 | 1.69 | 4.25 | 0.97 | 1.5 | 2.37 | 2.46 | 1.71 | 1.1 | 1.7 |
| 1.19 | 1.66 | 7.49 | 2.3 | 2.1 | 2.37 | 2.45 | 3.78 | 2.8 | 3.1 |
| 1.19 | 1.67 | 7.73 | 1.7 | 2.2 | 2.37 | 2.46 | 3.90 | 2.3 | 3.2 |
| 1.19 | 1.63 | 8.07 | 4.6 | 2.2 | 2.37 | 2.46 | 10.6 | 8.2 | 5.5 |
| 1.19 | 1.57 | 8.37 | 1.7 | 2.3 | 2.37 | 2.46 | 10.8 | 7.4 | 5.5 |
| 1.19 | 1.70 | 8.69 | 2.4 | 2.3 | 2.37 | 2.46 | 11.0 | 6.6 | 5.6 |
| 1.19 | 1.57 | 17.0 | 2.4 | 3.2 | 2.37 | 3.16 | 8.31 | 5.5 | 4.3 |
| 1.19 | 2.46 | 1.66 | 0.50 | 0.51 | 2.93 | 1.69 | 4.34 | 5.4 | 5.7 |
| 1.19 | 2.45 | 3.72 | 0.97 | 1.0 | 2.85 | 2.45 | 8.30 | 7.1 | 6.3 |
| 1.19 | 2.46 | 3.84 | 0.82 | 1.0 | 3.28 | 1.73 | 1.67 | 3.0 | 3.6 |
| 1.19 | 2.47 | 10.5 | 3.0 | 2.1 | 3.56 | 0.265 | 1.65 | 8.1 | 10.3 |
| 1.19 | 2.47 | 10.8 | 2.2 | 2.1 | 3.56 | 0.826 | 1.06 | 4.1 | 5.0 |
| 1.19 | 2.46 | 10.9 | 2.0 | 2.1 | 3.56 | 1.57 | 1.03 | 3.7 | 3.0 |
| 1.19 | 2.46 | 17.0 | 3.0 | 2.6 | 3.56 | 1.69 | 1.40 | 4.0 | 3.7 |
| 1.19 | 2.46 | 17.4 | 3.0 | 2.7 | 3.56 | 1.69 | 1.45 | 4.1 | 3.8 |
| 1.19 | 2.45 | 24.4 | 4.4 | 3.1 | 3.56 | 1.69 | 1.72 | 4.0 | 4.3 |
| 1.19 | 3.16 | 0.94 | 0.28 | 0.24 | 3.56 | 1.73 | 1.69 | 3.0 | 4.1 |
| 1.19 | 3.16 | 3.37 | 0.59 | 0.76 | 3.56 | 2.46 | 1.77 | 2.9 | 3.3 |
| 1.19 | 3.16 | 3.55 | 0.75 | 0.80 | 3.56 | 2.45 | 3.83 | 6.1 | 5.6 |
| 1.19 | 3.16 | 8.25 | 1.3 | 1.5 | 3.56 | 2.46 | 3.96 | 4.7 | 5.7 |
| 1.19 | 3.16 | 16.9 | 2.2 | 2.3 | 3.56 | 3.15 | 1.06 | 1.8 | 1.7 |
| 1.19 | 4.66 | 1.05 | 0.21 | 0.18 | 3.56 | 3.15 | 3.67 | 4.6 | 4.7 |
| 1.19 | 4.61 | 35.5 | 2.5 | 2.8 | 3.56 | 4.66 | 1.16 | 1.3 | 1.3 |
| 1.42 | 2.45 | 17.5 | 4.4 | 3.4 | 4.27 | 1.73 | 1.72 | 4.4 | 5.4 |
| 1.74 | 1.73 | 1.59 | 1.1 | 1.3 | 4.74 | 2.46 | 1.83 | 4.8 | 5.2 |
| 1.62 | 2.45 | 8.24 | 3.0 | 2.9 | 5.93 | 3.15 | 1.17 | 3.4 | 4.1 |
| 1.68 | 2.45 | 17.4 | 5.5 | 4.3 | 6.32 | 4.65 | 1.30 | 4.4 | 3.6 |
|  |  |  |  |  | 6.44 | 0.873 | 1.06 | 11.0 | 10.8 |

$$\mathrm{NO_3} + \mathrm{Tl(I)} \underset{4}{\overset{3}{\rightleftarrows}} \mathrm{NO_3} + \mathrm{Tl(II)} \qquad (\mathrm{B'})$$

$$\mathrm{Ce(IV)} + \mathrm{Tl(II)} \xrightarrow{5'} \mathrm{Ce(III)} + \mathrm{Tl(III)} \qquad (\mathrm{C'})$$

$$\mathrm{Ce(IV)} + \mathrm{Tl(I)} \underset{7}{\overset{6}{\rightleftarrows}} \mathrm{Ce(III)} + \mathrm{Tl(II)} \qquad (\mathrm{D'})$$

From an argument similar to that presented elsewhere,[17] we see that the equilibrium constant in 6 $F$ $HNO_3$ for the reaction

$$\mathrm{Ce(III)} + \mathrm{Ag(II)} \rightleftarrows \mathrm{Ce(IV)} + \mathrm{Ag(I)} \qquad (5)$$

can be obtained from the rate constants for reactions A and A′ and is equal to $k_1k_2'/(k_2k_1')$. This combination of constants can be obtained from the data presented here and from published values.[11] The ratio $k_2'/k_2$ can be calculated from the ratios of $k_2/k_3$ and $k_2'/k_3$ assuming in the latter case that the ratio is independent of temperature. The value for $k_2'/k_2$ is 2.6. Preliminary measurements performed by Mr. Eugene Zeltmann to determine $k_1'$ at 35.2° permit us to estimate the value of this constant at 26.2° to be $2.8 \times 10^{-7}$. We thus obtain a value for the equilibrium constant for reaction 5 at 26.2° in 6.18 $F$ $HNO_3$ of $3.8 \times 10^6$, which is to be compared with a value of $2.34 \times 10^5$ determined by Mr. Zeltmann by emf measurements. Considering the assumption that $k_2'/k_3$ is temperature independent and the scatter in the present data, the agreement is within probable error.

The mechanisms proposed for the Ce(IV)–Tl(I) and Ag(II)–Tl(I) reactions appear to bear out the proposal made by Uri[18] that reactions involving strongly oxidizing cations would be expected to occur *via* free-radical intermediates. It would be of interest to investigate the Ag(I)-catalyzed reaction of Ce(IV) with Tl(I) in nitric acid to see if the catalysis is perturbed by the reaction of Ag(II) to form $NO_3$ radical.

[17] J. W. Gryder and R. W. Dundon, *J. Am. Chem. Soc.*, **88**, 275 (1966).
[18] N. Uri, *Chem. Rev.*, **50**, 375 (1952).

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# A New Route to Boron Nitride

BY J. ECONOMY AND R. ANDERSON

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A new synthesis is described for preparation of boron nitride from the reaction of an alkyl polyborate–ammonia complex $(RO)_3B_{25}O_{36}\cdot(NH_3)_8$ with ammonia in the temperature range of 400–800°. The ammonia complex is obtained *via* a novel disproportionation of a trialkoxyboroxine to the corresponding trialkoxyborane and the ammonia complex. Boron nitride obtained under these conditions possesses a turbostratic structure.

## Introduction

A number of preparations for boron nitride have been reported in the literature during the past 120 years.[1-6] In most of these reactions ammonia is utilized as a reactant and temperatures of 900–1500° are required for completion of reaction.

The present work describes a new route for preparation of boron nitride by the reaction of an alkyl polyborate–ammonia complex of slightly variable composition $(RO)_3B_{25}O_{34}\cdot(NH_3)_8$ with ammonia in the temperature

[1] A. A. Giardini, U. S. Department of the Interior, Bureau of Mines' Information Circular, No. 7664, U. S. Government Printing Office, Washington, D. C., 1953.
[2] P. Popper, Ed., "Special Ceramics," Heywood and Co., London, 1960, Chapter 8.
[3] K. M. Taylor, U. S. Patent 2,808,314 (1957); U. S. Patent 2,855,316 (1958); U. S. Patent 2,888,325 (1959).
[4] T. Renner, *Z. Anorg. Allgem. Chem.*, **298**, 22 (1958).
[5] H. Tagawa and O. Itouji, *Bull. Chem. Soc. Japan*, **35**, 1536 (1962).
[6] T. E. O'Connor, *J. Am. Chem. Soc.*, **84**, 1753 (1962).

range of 400–800°. Boron nitride prepared in this manner does not possess a well-defined crystallographic structure and appears to resemble closely the turbostratic structure prepared *via* the urea–boric acid route recently reported in the literature.[6,7] Data are presented which demonstrate that the turbostratic boron nitride can be obtained from other synthetic routes and is not limited to this new approach or to the urea–boric acid process. The nature and mode of formation of the alkyl polyborate–ammonia complex are also discussed.

## Experimental Section

The trialkoxyboroxines were prepared by the reaction of boric oxide or boric acid with the appropriate alcohol in an organic solvent. The reaction was forced to completion by the azeotropic removal of the water of reaction. The trialkoxyboroxine was then treated *in situ* with ammonia to produce a precipitate of the alkyl polyborate–ammonia complex and the soluble trialkoxyborane. The complex was treated with ammonia in two steps at elevated temperatures to produce boron nitride. All of the intermediates are sensitive toward water and must be handled in an inert atmosphere.

**Reaction of Triisopropoxyboroxine with Ammonia.**—In a 3-l. reaction vessel equipped with a mechanical stirrer and a packed distillation column (2.5-cm diameter × 30-cm length) topped with a 100-ml Dean–Stark trap were placed 69.6 g of boric oxide (98.8%), 151 g of isopropyl alcohol, and 130 ml of heptane. The mixture was heated and 69 ml of water was removed as the water layer of the ternary azeotrope. A small sample of the clear liquid was removed, and the solvent was evaporated leaving a white residue of triisopropoxyboroxine (mp 50°, lit.[8] 50°). *Anal.* Calcd for $(i\text{-}C_3H_7OBO)_3$: B, 12.6. Found: B, 12.8.

The distillation column was replaced with a reflux condenser, and a gas-inlet tube extending below the surface of the liquid was installed. The solution was heated to reflux temperature, and ammonia was added at a rate of 0.7 g/min for 1.3 hr. A readily filterable precipitate was obtained under these conditions (lower reaction temperatures or more concentrated solutions lead to a gellike product). The resulting slurry was filtered hot, washed twice with 1 l. of hot, dried heptane and once with 1.5 l. of hot, dried petroleum ether (bp 30–60°) under an ammonia atmosphere. The isopropyl polyborate–ammonia complex was dried for 24 hr at 200° under vacuum and a nitrogen bleed (60.2-g yield). *Anal.* Calcd for $(i\text{-}C_3H_7O)_3B_{25}O_{36}\cdot(NH_3)_8$: B, 23.32; N, 9.66; C, 9.31; H, 3.88. Found: B, 23.89; N, 10.03; C, 9.44; H, 4.06.

The isopropyl polyborate–ammonia complex does not possess a clear-cut stoichiometry, and the formula $(i\text{-}C_3H_7O)_3B_{25}O_{36}\cdot(NH_3)_8$ is representative of a number of analyses that were taken. Fractional distillation of the filtrate gave a 90% recovery of $i\text{-}C_3H_7O\text{–}$ as triisopropoxyborane (bp 138–140°, lit.[9] 140°). The triisopropoxyborane reacts quantitatively with boric oxide to reform triisopropoxyboroxine.

**Comparative Reactivity of Various Trialkoxyboroxines with Ammonia.**—Isopropyl-, *n*-propyl-, *sec*-butyl-, and *n*-butyltrialkoxyboroxines were prepared and treated with ammonia in the same manner as in the preceding experiment. In this set of experiments the slurries were filtered hot and vacuum dried at 150°. The results are summarized in Table I.

**Preparation of Boron Nitride from the Isopropyl Polyborate–Ammonia Complex.**—Boron nitride was prepared from the isopropyl polyborate–ammonia complex by allowing the complex to react with ammonia in two steps. In the first step the complex containing 9% nitrogen was dispersed in a preheated ammonia stream and blown through a heated Pyrex tube (4 ft × 2 in.). The results of four experiments are shown in Table II.

Table I

Preparation of Alkyl Polyborate–Ammonia Complexes

| Trialkoxy-boroxine | Analysis of complex B | Analysis of complex N | Calcd composition of complex B | Calcd composition of complex N | % OR recovered in filtrate |
|---|---|---|---|---|---|
| Isopropyl | 23.61 | 8.73 | 23.33 | 9.66 | 88.2 |
| *n*-Propyl | 24.31 | 8.38 | 23.33 | 9.66 | 90.2 |
| *sec*-Butyl | 22.52 | 7.02 | 22.51 | 9.32 | 91.8 |
| *n*-Butyl | 22.34 | 7.99 | 22.51 | 9.32 | 88.7 |

Table II

Nitriding of Isopropyl Polyborate–Ammonia Complex

| Reaction temp, °C | Contact time, sec | Nitrogen content of powder obtained, % |
|---|---|---|
| 500 | 4 | 17.47 |
| 500 | 16 | 23.75 |
| 610 | 4 | 19.83 |
| 610 | 16 | 26.86 |

In the second step ammonia was passed over the partially nitrided powder in a Vycor tube to produce boron nitride. In Table III the boron and nitrogen content obtained at various temperatures and times is shown.

Table III

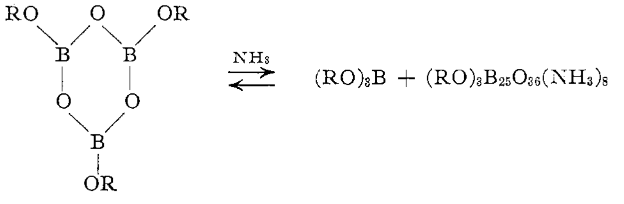
Preparation of BN from 23.7% N Powder

| Temp, °C | Time, hr | % B (43.57 theoret) | % N (56.43 theoret) |
|---|---|---|---|
| 600 | 24 | 39.88 | 53.16 |
| 700 | 2.5 | 38.97 | 57.51 |
| 700 | 16 | 39.28 | 59.20 |
| 800 | 2 | 40.00 | 57.04 |
| 800 | 6 | 41.75 | 55.52 |

**X-Ray Analysis of Boron Nitride.**—The X-ray diffraction studies were made using twin North American Philips diffractometers (using wide-range goniometer and Geiger counters). Copper radiation was used with a nickel filter at a scanning speed of 1°/min.

## Discussion

Preparation of boron nitride *via* this route depends on the formation of the alkyl polyborate–ammonia complex which at elevated temperatures can react further with ammonia to produce boron nitride. The alkyl polyborate–ammonia complex is obtained as an insoluble precipitate from the reaction of a trialkoxyboroxine with ammonia. In this reaction the trialkoxyboroxine disproportionates forming the ammonia complex and trialkoxyborane. In the disproportionation the ratio of boron in the ammonia complex to boron in the trialkoxyborane approaches a value of 2:1.



$$\xrightleftharpoons{NH_3} (RO)_3B + (RO)_3B_{25}O_{36}(NH_3)_8$$

Approximately 90% of the alkyl group originally present in the trialkoxyboroxine is recovered as tri-

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[7] J. Thomas, Jr., N. E. Weston, and T. E. O'Connor, *J. Am. Chem. Soc.*, **84**, 4619 (1962).

[8] F. J. Dykstra, U. S. Patent 2,862,879 (1958).

[9] M. F. Lappert, *Chem. Rev.*, **56**, 969 (1956).

alkoxyborane while the remaining 10% is present in the ammonia complex. The driving force to the disproportionation depends on maintaining an atmosphere of ammonia throughout the entire reaction. The reversible nature of the reaction can be demonstrated by refluxing the reaction mixture in the absence of additional ammonia. The precipitate of the alkyl polyborate–ammonia complex reacts with the trialkoxyborane reforming the trialkoxyboroxine. Attempts to form either a complex or an amide from the reaction of triisopropoxyborane with ammonia were unsuccessful. No reaction was observed from room temperature up to the decomposition point of the trialkoxyborane.

The alkyl polyborate–ammonia complex reacts very rapidly with ammonia at elevated temperatures. Thus, at 500° the nitrogen in the structure increases from 9 to 24% in a matter of 16 sec. The alkyl group is eliminated as olefin in this step. Final conversion of the partially nitrided product (24%) can be carried out at higher temperatures in a stream of ammonia. Thus, at 800° a B + N content of 97% is obtained within 2–6 hr.

Since very little has been reported in the literature as to the chemistry of the trialkoxyboroxines, some work was carried out to determine the scope of the disproportionation reaction. Several different alcohols such as isopropyl, *n*-propyl, *sec*-butyl, and *n*-butyl were used for the preparation of the trialkoxyboroxine. No significant differences were noted with the various trialkoxyboroxines in the reaction with ammonia, and the yield of trialkoxyborane from the disproportionation varied slightly from 88 to 92%. Preliminary experiments using other amines such as aniline, triethylamine, and pyridine in place of ammonia were performed. It was found that these amines also reacted with the trialkoxyboroxines producing an insoluble alkyl polyborate–amine complex. No reaction was observed between the trialkoxyboroxines and urea or dimethylacetamide.

**Nature and Mode of Formation of the Alkyl Polyborate–Ammonia Complex.**—A number of factors, such as choice of solvent, reaction temperature, concentration of ammonia, and drying temperature, can influence both the degree of complexing with ammonia and the amount of isopropyl group that remains. The isopropyl polyborate–ammonia complex loses practically all of the isopropyl groups as propylene on heating at temperatures of 270–300° under ammonia. In the absence of additional ammonia the complex at 325° forms a highly viscous melt which liberates ammonia.

The complex was insoluble in practically all solvents but appeared to dissolve in pyridine. A molecular weight determination (Mecholab vapor pressure osmometer) carried out from a pyridine solution showed a molecular weight of 61.2. This indicates that the complex dissociated almost completely to ammonia, a trialkoxyborane, and a $(BO_{1.5})_x$ pyridine complex (where $x$ approaches 3). This type of dissociation is not observed with boric oxide which is insoluble in pyridine.

TABLE IV

X-RAY DIFFRACTION DATA FOR BORON NITRIDE PREPARED BY VARIOUS SYNTHETIC ROUTES

| Synthetic route | $d(002)$,[a] A | $L_a$, A | $L_c$, A |
|---|---|---|---|
| 1. $NH_2CONH_2$–$H_3BO_3 + NH_3$[7] | | | |
| a. Turbostratic, 500–950° | 3.56 | 46 | 14 |
| b. Mesographitic, 1400–1850° | 3.46 | 103 | Large |
| c. Graphitic, 1850° | 3.33 | 500 | Large |
| 2. $BCl_3 + NH_3$, 900° [b] | 3.612 | 45 | 12 |
| 3. $BCl_3 \cdot 4NH_3$, decompn at 800° [b] | 3.624 | 56 | 14 |
| 4. $B_2O_3 + NaNH_2$[5] | 3.44 | ... | 22 |
| 5. $(i\text{-}C_3H_7O)_3B_{25}O_{36} \cdot (NH_3)_8 + NH_3$ | | | |
| a. 600° | 3.75 | ... | 20 |
| b. 800° | 3.56 | 59 | 10 |
| 6. $B_2O_3 + NH_3$ on calcium phosphate[b] | | | |
| a. 800° | 3.389 | 71 | 45 |
| b. 1000° | 3.339 | 290 | 66 |

[a] In one case[7] this value was reported as (004), but for purposes of comparison all values have been expressed as (002). [b] H. Tagawa and K. Ishii, *Bull. Chem. Soc. Japan*, **35**, 1425 (1962).

From infrared studies of the ammonia complex, it was not possible to determine whether the boric oxide is present in the form of $(BO)_3$ rings joined by oxygen links or as an open-chain network. However, it should be noted that the ratio of boron to nitrogen in the complex $(i\text{-}C_3H_7O)_3B_{25}O_{36} \cdot (NH_3)_8$ is almost exactly 3:1. In fact, as can be seen from Table I the B:N ratio for the complexes derived from four different esters also approaches a value of 3:1. It, therefore, seems reasonable to postulate that the ammonia is complexed with a cyclic $(BO)_3$ structure in a 1:1 ratio and that the rings are linked *via* oxygen atoms. Additional support for this contention is found in the literature,[10] where it is reported that cyclic boroxines $(RBO)_3$ also form a 1:1 complex with ammonia.

From the available information it would appear that in the disproportionation reaction the trialkoxyboroxine initially forms an unstable 1:1 complex with ammonia. The complex may equilibrate in a stepwise manner with the corresponding open-chain structure and the monomeric O═B—OR intermediate. The O═B—OR unit could react with alkoxyl groups present in the alkyl polyborate–ammonia complex forming an –O–B(OR)$_2$ unit. This intermediate could then undergo a double displacement reaction with another alkoxyl grouping yielding the trialkoxyborane and two boroxine rings linked by oxygen. The alkoxy and –O–B(OR)$_2$ groups continue to react in this manner building up a network of six-membered rings, each complexed with a molecule of ammonia and interconnected by oxygen. The reaction would then terminate when the product precipitates from solution.

**Structure of BN.**—The boron nitride obtained *via* this route displays an X-ray pattern very similar to that produced by turbostratic boron nitride. The term "turbostratic" was introduced originally by Biscoe and Warren[11] to described an intermediate form of carbon in which a number of graphite layers are stacked together roughly parallel and equidistant but show random rotation and translation about the layer normal.

(10) A. B. Burg, *J. Am. Chem. Soc.*, **62**, 2228 (1940).

(11) J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).

Thomas, *et al.*,[7] assigned this type of structure to boron nitride prepared from urea–boric acid and ammonia. It now appears that boron nitride derived from a number of different routes possesses the turbostratic structure. In Table IV X-ray data reported by others for boron nitride prepared by five different methods are compared with data for samples prepared by the new routes. The interlayer spacings and the $L_a$ and $L_c$ dimensions which represent the width of the graphite-like layer and the thickness of the parallel packet of layers, respectively, are used to define the turbostratic phase.[11] Values of $d(002)$, $L_a$, and $L_c$ for the turbostratic, mesographitic, and graphitic phases are shown for route 1. Routes 2–5 yield products which closely resemble the turbostratic phase. Route 6 yields products which more nearly resemble the mesographitic and graphitic phases, depending on temperature of reaction. In the latter case, it would appear that, if a lower reaction temperature could be used, a more random structure approaching the turbostratic phase would result.

Boron nitride prepared *via* these routes undoubtedly differs in the ease of conversion to graphitic boron nitride. As pointed out by Thomas, *et al.*,[7] both boric oxide and boron nitride seed crystals play important roles in this transformation. Tagawa and Ishii[12] also indicate that boron nitride prepared in a solid–gas reaction crystallizes more readily than boron nitride formed in the gas phase.

(12) See footnote *b* of Table IV.

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# The Divalency of Tin Ions Formed during Anodic Dissolution and the Behavior of the Tin Anode[1]

By M. E. Straumanis and M. Dutta

*Received November 19, 1965*

Tin was found to form solely $Sn^{2+}$ ions when dissolved anodically without the use of an external current from tin amalgam in aqueous solutions of HCl, $H_2SO_4$, $HClO_4$, $H_3PO_4$, $HNO_3$, and HF. Darkening of the surface of a solid tin anode was observed during electrolytic dissolution up to current densities of 1200 ma cm$^{-2}$ in HCl, $H_2SO_4$, and $HClO_4$, but there was no spalling of particles. The black entities protruding from the anodic surface were in contact with the surface of the anode and consisted of metallic tetragonal tin. They were formed owing to the uneven electrolytic surface attack of the tin anode.

## Introduction

In 1916, Newbery,[2] working on the anodic polarization of tin in sulfuric acid, observed the formation of a black coating on the anodic surface. The same observation was also made by Vaubel while dissolving tin anodically in hydrochloric acid.[3] He noted a black powder on the anode which dissolved very slowly even in concentrated acid. Therefore, it was assumed that the powder represented a peculiar modification of the metal. Jeffery,[4] electrolyzing a potassium oxalate solution with a tin anode, found that it became covered with a fine black adherent film at low current densities which spalled at higher ones.

Similar observations were also made during anodic dissolution of tin in an NaOH solution by Vallesi,[5] who found a black, powdery tin layer on the anode. The same experiments were later repeated by Nakai and Kato.[6]

The anodic formation of a black layer on the dissolving tin resembles a phenomenon called partial "surface disintegration" which has been frequently observed in our laboratories. A spalling of finest metallic particles occurs at the dissolving anode. The particles are recognizable as such only at high optical magnifications. Surface disintegration occurs also when a metal is simply dissolved in an acid, *e.g.*, Be in HCl[7] and Fe in $H_2SO_4$.[8] Partial disintegration of other metals can nearly always be enforced by anodic dissolution. It could thus be shown that the metals beryllium,[9] magnesium,[10] gallium,[11] indium,[12] aluminum,[13] thallium,[14] and zinc[15] partially disintegrate when dissolved anodically. The possibility of disintegration (metallic chunk formation) during corrosion

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(1) Extract from the thesis submitted by M. Dutta to the Graduate School of the University of Missouri at Rolla in partial fulfillment of the requirements for an M.S. degree.

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