

130. Two Lower Oxides of Boron.

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The residue obtained after repeated extraction of magnesium boride by water slowly reacts with aqueous ammonia to afford two ammonium salts, $(\text{NH}_4)_2\text{B}_2(\text{OH})_2$ and $(\text{NH}_4)_2\text{B}_4\text{O}_6$. When these are heated in a vacuum they afford the oxides B_2O_2 and B_4O_5 respectively. The properties of these salts and oxides are described.

IN 1916 Travers, Ray, and Gupta (Monograph, H. K. Lewis & Co., London) showed that when the residue from repeated extraction of crude magnesium boride with water was treated with concentrated aqueous ammonia in an atmosphere of hydrogen, the solution contained a substance of the composition $\text{H}_{12}\text{B}_4\text{O}_6 \cdot 2\text{NH}_3$. The present work was undertaken with the object of isolating this compound or its potassium salt. In the same monograph it was also shown that when the ammoniacal solution was evaporated to dryness in a vacuum, and gently heated, an oxide of boron, B_4O_5 , was left, together with a small quantity of magnesia. Similarly, when a solution containing the borohydrate $\text{H}_6\text{B}_2\text{O}_2$ was strongly heated in a vacuum, the oxide B_2O_2 , mixed with magnesia, was obtained.

In reviewing other evidence for the existence of the sub-oxide B_2O_2 , Wiberg and Ruchmann (*Ber.*, 1937, 70, 1393) stated that in the main it is indirect, the pure compound not having been isolated. Stock, Brandt, and Fischer (*Ber.*, 1925, 58, 643) showed that when the chloride, B_2Cl_4 , was hydrolysed no hydrogen was evolved, indicating that reaction occurred according to the equation $\text{B}_2\text{Cl}_4 + 2\text{H}_2\text{O} = \text{B}_2\text{O}_2 + 4\text{HCl}$. The oxide B_2O_2 should form the acid $\text{B}_2(\text{OH})_4$ with water, and Wiberg and Ruchmann (*loc. cit.*) isolated the esters corresponding to this acid. The methyl ester $\text{B}_2(\text{OMe})_4$ had been prepared by Wiberg and Smedsrud (*Z. anorg. Chem.*, 1935, 225, 204) by the action of sodium amalgam on the chloride $\text{B}(\text{OMe})_2\text{Cl}$, and the free acid was isolated as a white solid, soluble in water, by hydrolysis of the ester. Its formation from $\text{H}_6\text{B}_2\text{O}_2$ is discussed by Wiberg (*Ber.*, 1936, 69, 2832). No other work is on record regarding the oxide B_4O_5 .

Wiberg (*Z. anorg. Chem.*, 1930, **191**, 57) has suggested constitutions for several of the oxides. We were unable to isolate the 4-boron borohydrate.

EXPERIMENTAL.

The residues obtained by repeated and prolonged treatment with water of crude magnesium boride, prepared by Ray's method (J., 1922, **121**, 1088), were kept in contact with successive portions of a fairly concentrated solution of ammonia in an atmosphere of hydrogen, each portion being decanted and replaced after 24—48 hours, for preliminary experiments had shown that the concentration of boron compounds in the solution never rose beyond a limiting value. The ammoniacal liquors thus obtained were filtered through Allihn's apparatus in an atmosphere of hydrogen, and concentrated in a vacuum at room temperature. As soon as crystals began to separate, they were quickly removed, because they were always contaminated with traces of magnesia. The filtrates from several experiments were collected and fractionally crystallised in a vacuum. By repeating this process 4 or 5 times, two colourless compounds were isolated, both being *ammonium* salts of well-defined crystalline form; they were stable in presence of ammonia solution, and when dry they were stable if kept below 0°. With rise of temperature the crystals rapidly lost ammonia and fell into powder.

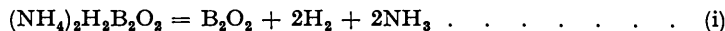
The ammonia was estimated by distillation with sodium hydroxide and absorption in standard acid. For estimating boron, a weighed quantity of the substance was heated with concentrated nitric acid in a sealed tube, and the boric acid formed was distilled with methyl alcohol into weighed lime [Found : (i) NH_3 , 38.9, 38.9, 38.85; B, 24.0, 23.9, 23.9. $(\text{NH}_4)_2\text{B}_2(\text{OH})_2$ requires NH_3 , 37.0; B, 23.9%. (ii) NH_3 , 19.1, 19.0, 18.9; B, 25.1, 25.0, 24.95. $(\text{NH}_4)_2\text{B}_4\text{O}_6$ requires NH_3 , 19.3; B, 25.0%].

Neither compound reacts with dilute sulphuric acid. The salt $(\text{NH}_4)_2\text{B}_2(\text{OH})_2$ does not give a precipitate with barium, calcium, or magnesium salts, but $(\text{NH}_4)_2\text{B}_4\text{O}_6$ yields white crystalline precipitates with these salts. The general behaviour, the action of acids, and the iodine absorption of the acidified solution indicate that $(\text{NH}_4)_2\text{B}_2(\text{OH})_2$ is the ammonium salt corresponding to the potassium compound $\beta\text{-K}_2\text{B}_2(\text{OH})_2$ already described by Ray (*Trans. Faraday Soc.*, 1937, **33**, 1261).

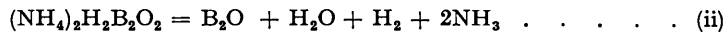
The action of heat on these ammonium salts was studied in the following manner: A small quantity of the substance was weighed into a wide Pyrex-glass tube provided with a ground glass joint at one end, and stop-cocks at both ends. One end of the tube was connected to a Töpler pump through two weighed U-tubes filled with dry calcium chloride. The tube was immersed in a freezing mixture, and the apparatus freed from air. The freezing mixture was then removed and the substance carefully heated. Considerable swelling took place, and finally the crystals fell into powder. The gases evolved were pumped out and measured, and the tube was then cooled in a current of dry hydrogen. Analyses of the evolved gases showed that, on heating, $(\text{NH}_4)_2\text{B}_2(\text{OH})_2$ gave a mixture of almost equal volumes of ammonia and hydrogen, whereas $(\text{NH}_4)_2\text{B}_4\text{O}_6$ gave only ammonia. The results, representing the mean of several experiments, are summarised in the following table:

Substance.	One g. yields			
	NH_3 , c.c. at N.T.P.	H_2 , c.c. at N.T.P.	H_2O , g.	Residue, g.
$(\text{NH}_4)_2\text{B}_2(\text{OH})_2$	482	478	0.0038	0.5812
$(\text{NH}_4)_2\text{B}_4\text{O}_6$	260	nil	0.1023	0.7046

Since the composition and properties of $(\text{NH}_4)_2\text{B}_2(\text{OH})_2$ are analogous to those of $\beta\text{-K}_2\text{B}_2(\text{OH})_2$, the former is assigned the double formula for the reasons set forth in the latter case (*loc. cit.*). The ammonium salt might decompose on heating in either of two ways:



or



but the experimental results show that the change is represented by (i), for the small quantity of water formed is equivalent to the decomposition of only 2% of the compound in the manner represented by (ii).

The decomposition of the compound $(\text{NH}_4)_2\text{B}_4\text{O}_6$ is represented by the equation $(\text{NH}_4)_2\text{B}_4\text{O}_6 = \text{B}_4\text{O}_6 + \text{H}_2\text{O} + 2\text{NH}_3$. The oxide thus formed is perfectly colourless, whereas B_2O_2 is slightly brown. Both oxides are readily soluble in water to give colourless solutions, but B_2O_2 leaves a trace of insoluble brown residue, too little for investigation: it may be either the oxide B_2O [see (ii)] or a solid solution of oxygen in amorphous boron. The clear solutions when

evaporated in a vacuum gave crystalline deposits of the free acids, which when heated in a vacuum gave the pure oxides. The boron contents of the pure oxides were determined by oxidation as above, the boric acid formed being washed into weighed lime. The results of three concordant determinations in each case were : in B_2O_2 , found 40.7 (calc. : B, 40.7%) ; in B_4O_6 , found 35.5 (calc. : B, 35.5%). The ratios B_2O_2/B_2O_3 and B_4O_6/B_2O_3 were respectively 0.7715 and 0.8857 (calc. : 0.7714, 0.8857).

The aqueous solutions of both oxides are slowly oxidised by air, and also by potassium permanganate to form boric acid. They possess reducing properties like the borohydrate solutions. When a solution of B_2O_2 was shaken in a vacuum with magnesium or barium hydroxide, the hydroxide went into solution, and from the filtered solution the *magnesium* or the *barium* salt could be crystallised out [Found : (i) Mg, 35.6 ; B, 16.3. $Mg_2B_2O_4$ requires Mg, 35.8 ; B, 16.4%. (ii) Ba, 76.1 ; B, 6.0. $Ba_2B_2O_4$ requires Ba, 76.1 ; B, 6.1%]. The solution of B_4O_6 , on the other hand, gave precipitates with magnesium and *barium* salts ; the latter was filtered off out of contact with air, washed with air-free water and dried in a vacuum (Found : Ba, 49.4 ; B, 15.8. BaB_4O_6 requires Ba, 49.8 ; B, 15.9%).

In conclusion, we wish to record our thanks to Dr. M. W. Travers, F.R.S., for his interest in the work.

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