

### 1225. *The Reduction of Boric Oxide to Boron Monoxide*

By D. NICHOLLS

RECENT interest in boron monoxide has been aroused by its uses in synthesis and by its importance in high-temperature vaporisation reactions from systems containing boron and oxygen. Two forms of the monoxide exist; the low temperature form is produced in the dehydration of tetrahydroxydiboron at 220°. Boron monoxide prepared in this way reacts with boron trichloride at 200° to give diboron tetrachloride,<sup>1</sup> and with sulphur tetrafluoride to give diboron tetrafluoride.<sup>2</sup> The high-temperature form, prepared initially<sup>3</sup> from boron and zirconium(IV) oxide at 1800°, and more recently<sup>4</sup> from boron and boric oxide at 1050°, is predominantly dimeric in the vapour phase<sup>5</sup> but condenses to an amber solid in which it is apparently polymeric. Hydrogenation of this form of boron monoxide above 1000° yields diborane.<sup>6</sup> Recently, B<sub>2</sub>O<sub>2</sub> has been shown to be present in the vapour over mixtures of boric oxide and carbon;<sup>7</sup> we here confirm the isolation of polymeric boron monoxide from the carbon and boron reductions of boric oxide, and report on the reduction of boric oxide with some other compounds of boron and titanium.

The analytical data for the boron monoxide prepared in the reaction of boric oxide with a variety of reducing agents are given in the Table. All the reactions were carried out in vacuo (10<sup>-3</sup> mm. Hg), and the sublimate of (BO)<sub>x</sub> was collected on a water-cooled cold finger which reached into the hot zone of the reaction tube. Boron monoxide of varying purity condensed as an amber glass in all the reactions except that of boron nitride with boric oxide. The characteristic reactions of the polymeric monoxide, *i.e.*, its dissolution in water with evolution of hydrogen containing traces of boranes, and the production of a solution which decolourises acid permanganate and reduces silver ions to the metal, were observed in all the sublimate having more than 31% of boron. The percentage of boron

<sup>1</sup> A. L. McCloskey, J. L. Boone, and R. J. Brotherton, *J. Amer. Chem. Soc.*, 1961, **83**, 4750.

<sup>2</sup> R. J. Brotherton, A. L. McCloskey, and H. M. Mansevit, *Inorg. Chem.*, 1963, **2**, 41.

<sup>3</sup> E. Zintl, W. Morawietz, and E. Gastinger, *Z. anorg. Chem.*, 1940, **245**, 8.

<sup>4</sup> F. A. Kanda, W. Katz, A. J. King, and V. A. Russell, *J. Amer. Chem. Soc.*, 1956, **78**, 1509.

<sup>5</sup> M. G. Inghram, R. F. Porter, and W. A. Chupka, *J. Chem. Phys.*, 1956, **25**, 498.

<sup>6</sup> L. Barton and D. Nicholls, *Proc. Chem. Soc.*, 1964, 242.

<sup>7</sup> P. Rentzepis, D. White, and P. N. Walsh, *J. Phys. Chem.*, 1960, **64**, 1784.

in the volatile products is in every case less than that theoretically required for  $B_2O_2$  (40.3%), but the figures are typical of those found by other workers<sup>3</sup> in the preparation of the high-temperature form of the monoxide. The main difficulty encountered here is the volatilisation of boric oxide. In order to avoid contamination from the latter, the starting materials must be absolutely anhydrous, and the reactions preferably carried out

## The reduction of boric oxide

Reductant	Temp. (°C)	% B in sublimate	Residue (X-ray powder photograph or analysis)	Comments
C .....	1150	37.4		With excess graphite Yield of $B_2O_2$ , 1% in 3 hr.
	1550	33.7	$B_4C$	With excess graphite
B .....	1150	37.0		
$B_4C$ .....	1250	39.8		$B_4C : B_2O_3 = 1 : 1$ Yield of $B_2O_2$ , 16% in 3 hr.
BN .....	1200	30.2		Sublimate has no reducing properties
Ti .....	1220		$\alpha-Ti_2O_3 + TiB_2$	Ti : $B_2O_3 = 1 : 1$ Sublimate pyrophoric, and gave chemical tests for $B_2O_2$
TiC .....	1400	39.8		TiC : $B_2O_3 = 1 : 2$ Reaction begins 1200°
	1640	38.7	TiO	
$TiB_2$ .....	1200		$\alpha-Ti_2O_3$	Sublimate of $B_2O_2$
	1600	39.0	Ti, 45.5; B, 9.14%	$TiB_2 : B_2O_3 = 1 : 4$ $Ti_3O_5 + B_2O_3$ mixture requires Ti, 44.9; B, 10.1%

below 1200°; the reactions of titanium carbide and diboride with boric oxide are very slow at this temperature, however. A further disadvantage of working at higher temperatures is that radiant heat from the furnace tube walls can cause disproportionation (blackening) of the boron monoxide on the cold finger. This disproportionation occurs around 400° and provides a route to elemental boron by carbon reduction of boric oxide (a reaction performed industrially for the preparation of boron carbide):  $B_2O_3 + C$  (at 1200°) gives  $B_2O_2 + CO$ ; collection at 20° and then heating to above 400° gives  $2/3 B + 2/3 B_2O_3$ . When a sample of  $(BO)_x$  containing 37% of boron was heated in dry hydrogen up to 1000°, a black glassy material was produced, having virtually the same weight as the starting material. On leaching with water at room temperature an insoluble brown powder was obtained having 64.4% of boron. Obviously a large amount of oxygen is still present but the boron could be easily upgraded by vacuum heating to around 1200°.

Whilst the carbon reduction gives only low yields of  $(BO)_x$  at 1150°, better yields are obtainable at higher temperatures, but the boric oxide content of the sublimate increases and by 1550° boron carbide is being formed. In the presence of excess boric oxide, however, the boron carbide reacts to form boron monoxide and carbon monoxides:  $B_4C + 5B_2O_3 \rightarrow 7B_2O_2 + CO$ . This reaction begins above 900° and is rapid at 1250°, when good yields of boron monoxide can be obtained.

In the reaction of boric oxide with titanium, the yellow sublimate obtained at 1220° was pyrophoric in air but sufficient was salvaged to observe the characteristic reactions of  $(BO)_x$ . The violet residue in the reaction vessel contained  $\alpha-Ti_2O_3$  and  $TiB_2$  phases. From available thermochemical data<sup>8</sup> we calculate for the reaction,  $3Ti + B_2O_3 \rightarrow TiB_2 + Ti_2O_3$ , that  $\Delta G^\circ$  at 1500°K = -109 kcal., so this appears to be the most likely reaction occurring. Our reaction mixture had an excess of boric oxide

<sup>8</sup> A. N. Krestovnikov and M. S. Vendrikh, *Izvest. V.V.Z. Tsvet. Metall.*, 1959, 2, 54; J. P. Coughlin, Bureau of Mines, Bulletin 542, 1954.

over that required by the above reaction, so that the formation of boron monoxide probably arises from some reaction of the excess boric oxide with the formed titanium diboride. Indeed, we find that boric oxide reacts with titanium diboride above 1200° to produce boron monoxide and titanium(III) oxide in accordance with the equation:  $2\text{TiB}_2 + 7\text{B}_2\text{O}_3 \longrightarrow \text{Ti}_2\text{O}_3 + 9\text{B}_2\text{O}_2$ . When a 1:4 ( $\text{TiB}_2:\text{B}_2\text{O}_3$ ) ratio of reactants was used the residue at 1600° corresponded to the 1:1 ( $\text{Ti}_2\text{O}_3:\text{B}_2\text{O}_3$ ) mixture expected, the boron figure being slightly reduced from the theoretical because of volatilisation of boric oxide. Titanium carbide begins to react with boric oxide at 1200°, the reaction is rapid at 1400°, and after a few minutes at 1640° all the carbon in the carbide had been evolved as carbon monoxide. The reaction occurring under continuous evacuation appears to be:  $\text{TiC} + 2\text{B}_2\text{O}_3 \longrightarrow \text{TiO} + 2\text{B}_2\text{O}_2 + \text{CO}$ . At atmospheric pressure this reaction is thermodynamically unfavourable ( $\Delta G^\circ_{1900^\circ\text{K}} = +230$  kcal., assuming  $\Delta G^\circ_{1900^\circ\text{K}} \text{B}_2\text{O}_2 = -80$  kcal./mole).

*Experimental.*—The apparatus used in the high-temperature reactions consisted of an impervious alumina combustion tube to the ends of which Pyrex ground-glass sockets had been attached by means of Araldite epoxy-resin; these joints were water-cooled. At one end of the tube a silica (or copper) water-cooled cold finger reached into the hot zone so that it came to within a few centimetres of the boat containing the reaction mixture. At the other end of the tube was a glass window through which the temperature of the reaction mixture was measured with an optical pyrometer. A connection from the tube to a high-vacuum system enabled reactions to be carried out at up to 1650° and  $10^{-3}$  mm. Hg. The heating was provided by a conventional molybdenum wound tubular resistance furnace. Except in the case of the reaction between boric oxide and carbon, where a graphite boat was used, the reaction mixtures were contained in recrystallised alumina vessels. The finely ground mixtures were dried for at least 3 hr. at 600—900° *in vacuo*.

RESEARCH LABORATORIES, BORAX CONSOLIDATED LTD., CHESSINGTON, SURREY.

[Present address: DONNAN LABORATORIES, THE UNIVERSITY,  
VINE STREET, LIVERPOOL 7.]

[Received, April 23rd, 1965.]