

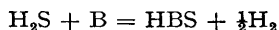
The Synthesis of Thioborine, HBS

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PREVIOUS reports of the action of hydrogen sulphide on boron at high temperatures^{1,2} indicated that compounds relatively rich in sulphur were formed, such as thiometaboric acid, HBS₂, and boron sulphide, B₂S₃.

We have found that the action of hydrogen sulphide on boron at 1150–1300° under low pressure gives good yields of a gaseous species, thought to be thioborine, HBS.



In our experiments, hydrogen sulphide gas was passed at the rate of 8–10 ml./min. (measured at STP) through a heated column of granular crystalline boron contained in a vertically mounted, $\frac{1}{4}$ -in. bore recrystallised alumina furnace tube. The gas pressure above the boron was maintained below 1 mm. by vacuum pumping.

The gas pumped from the hot zone was monitored with a Bendix time-of-flight mass spectro-

meter. The dominant ions in the mass spectrum, both at 50 ev and 15 ev, were at m/e 43 and 44, corresponding to H¹⁰BS⁺ and H¹¹BS⁺ respectively. These ions were only minor species in the work of Edwards, Wiedemeier, and Gilles on HBS₂.³ This strongly suggested that HBS was the main component (apart from hydrogen) of the gas from the furnace. Fragment ions from the HBS, which amounted to no more than 5% of the intensity of the parent, were BS⁺ and B⁺. Ions of low abundance at m/e 86, 87, and 88, and 130, 131, and 132, indicated the presence of some H₂B₂S₂ and H₃B₃S₃ respectively.

Thioborine is not stable in the gas phase, decaying on the walls of the containing vessel to H–B–S polymers. Its lifetime seems comparable to that of SiF₄,⁴ *i.e.*, the "half-life" is of the order of a minute at 0.2 mm. pressure in a small flask. At a pressure of 0.2 mm. it passes unchanged through a trap at –130° but it condenses at –150°. This

low condensation temperature shows that HBS is not associated in the gas phase. However, condensation seems irreversible, solid polymers always being formed. Condensation of HBS at -196° gives a yellow solid which changes little on being warmed to room temperature. Heating the polymer above 65° liberates hydrogen. The polymer has strong reducing powers, and it is very readily hydrolysed. It has a B/S ratio of 1.1 to 1.3, and may be similar to the polymer made by Burg and Wagner⁵ from diborane and hydrogen sulphide, although this was richer in sulphur. The infrared spectrum of the HBS polymer condensed as a film on a sodium chloride window at -196° , is rather

diffuse, the main absorption bands being centred at 950, 1400, 2500, and 3000 cm^{-1} .

Gaseous HBS is more stable than HBO which has not been isolated except as its trimer, boroxine.⁶ Attempts by Wiberg and Sturm⁷ to make thio-boroxine (HBS)₃ failed, although they made many substituted thio-boroxines. From our work, thio-boroxine appears to be a minor species in the polymerisation of HBS compared with complex solid polymers.

Porter and Wason⁸ observed the formation of borine carbonyl from carbon monoxide and boroxine, but condensation of HBS in the presence of CO gives no volatile products.

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¹ See J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, 1924, Vol. V.

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