The Synthesis of Thioborine, HBS

By R. W. KIRK and P. L. TIMMS

(*Department of Chemistry, University of California, Berkeley, California*)

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, HBS_2, and boron sulphide, B_2S_3.

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.

$$H_2S + B = HBS + \tfrac{1}{2}H_2$$

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 spectrometer. The dominant ions in the mass spectrum, both at 50 ev and 15 ev, were at *m/e* 43 and 44, corresponding to $H^{10}BS^+$ and $H^{11}BS^+$ respectively. These ions were only minor species in the work of Edwards, Wiedemeier, and Gilles on HBS_2.[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 $H_2B_2S_2$ and $H_3B_3S_3$ 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 SiF_2,[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 Wagner[5] 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 Sturm[7] to make thioboroxine $(HBS)_3$ failed, although they made many substituted thioboroxines. From our work, thioboroxine appears to be a minor species in the polymerisation of HBS compared with complex solid polymers.

Porter and Wason[8] 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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