Chemical Reactions of Boron Atoms

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SEVERAL reports have appeared over the last three years of preparative-scale reactions of unstable gaseous species formed at high temperatures, with other compounds at low temperatures.[1,2] Many new compounds have been synthesised by these atom–molecule or molecule–molecule co-condensation reactions.

This work is concerned with the reactions of boron atoms. A boron rod was heated by electron bombardment to 2500—2800° at a pressure of 10^{-6} mm. The boron vapour, believed to be very largely B_1 in a ^2P electronic state, was condensed on the liquid-nitrogen-cooled walls of the vacuum chamber. Other volatile compounds could be sprayed into the chamber and co-condensed with the boron atoms on the cold walls.

Co-condensation of boron vapour with BF_3, BCl_3, PCl_3, HCl, HBr, NH_3, C_6H_6, and CO_2, resulted in each case in complete reaction of the boron and the formation of volatile or polymeric products. When boron and boron trifluoride were deposited at $-196°$ in alternate layers, rather than simultaneously, no reaction was detected. Co-condensation is thus an essential condition for obtaining reactions with boron atoms.

For each of the hydrogen-containing molecules HCl, HBr, NH_3, and C_6H_6, the initial product of condensation with boron atoms at $-196°$, evolved gaseous hydrogen on warming to between $-170°$ and $-100°$. With HCl and HBr, the other volatile products were BX_3 and HBX_2 (where X = Cl or Br), some free halogen, and tiny amounts of B_2Cl_4 from HCl and B_2H_5Br from HBr. The stoicheiometry can be represented very approximately as

$$20B + 50HX \rightarrow 8BX_3 + 2HBX_2 + 0{\cdot}5X_2 + 18HX + 15H_2 + (BX)_n‡$$

The nature of the products suggests a series of free-radical reactions, perhaps started by the interaction of a boron atom with a hydrogen halide molecule to give $H\dot{B}X$.

Apart from hydrogen the only product from boron atoms and ammonia was a white polymer. This polymer liberated hydrogen but no volatile borane amines or borazine on heating to 200°. A golden coloured polymer, sensitive to air, was obtained from boron and benzene, which had the approximate composition $C_6H_3B_4$. This also yielded only hydrogen on heating to 300°.

The main products of the reaction of BF_3 and BCl_3 with boron were solid BF or BCl polymers, although about 15% of the boron atoms were recovered as B_2F_4 or B_2Cl_4. The BF_3–B reaction gave no B_3F_5 or higher volatile liquid boron fluorides, products which are characteristic of the reaction of BF and BF_3.[2] Phosphorus trichloride and boron atoms gave some BCl_3 and P_2Cl_4, but mainly a solid polymer containing phosphorus,

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‡ Not measured.

boron, and chlorine, which reacted with water to give phosphine.

The condensate formed from CO_2 and B at $-196°$ evolved CO with emission of yellow light at about $-150°$. A fine dust was carried by the mixture of CO and CO_2 pumped out of the vacuum chamber. This dust was shown by chemical analysis and *X*-ray studies to be a mixture of boric oxide, boron carbide, and a BO polymer. The simplest reaction of boron and CO_2 would be $CO_2 + B \rightarrow CO + BO$. Some further reduction of CO must also occur to give boron carbide.

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[2] P. L. Timms, *J. Amer. Chem. Soc.*, 1967, **89**, 1629.