

Chemical Reactions of Boron Atoms

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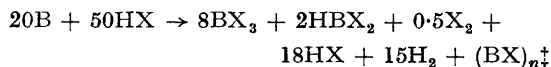
SEVERAL reports have appeared over the last three years of preparative-scale reactions of unstable gaseous species formed at high temperatures, with other compounds at low temperatures.^{1,2} Many new compounds have been synthesised by these atom-molecule or molecule-molecule co-condensation reactions.

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 B₁ 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 BF₃, BCl₃, PCl₃, HCl, HBr, NH₃, C₆H₆, and CO₂, 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, NH₃, and C₆H₆, 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 BX₃ and HBX₂ (where X = Cl or Br), some free halogen, and tiny amounts of B₂Cl₄ from HCl and B₂H₅Br from HBr. The stoichiometry can be represented very approximately as



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 HBX.

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 C₆H₃B₄. This also yielded only hydrogen on heating to 300°.

The main products of the reaction of BF₃ and BCl₃ with boron were solid BF or BCl polymers, although about 15% of the boron atoms were recovered as B₂F₄ or B₂Cl₄. The BF₃-B reaction gave no B₃F₅ or higher volatile liquid boron fluorides, products which are characteristic of the reaction of BF and BF₃.² Phosphorus trichloride and boron atoms gave some BCl₃ and P₂Cl₄, 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 $\text{CO}_2 + \text{B} \rightarrow \text{CO} + \text{BO}$. Some further reduction of CO must also occur to give boron carbide.

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¹ P. S. Skell, L. D. Westcott, J. P. Golstein, and R. R. Engle, *J. Amer. Chem. Soc.*, 1965, **87**, 2829; P. S. Skell and P. W. Owen, *ibid.*, 1967, **89**, 3933; P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *ibid.*, 1965, **87**, 2823.

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