The Preparation of Difluoro(trifluorosilyl)borane

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Summary The reaction of SiF_4 with solid silicon or silicon carbide at 1200°—1850° forms gaseous species which, on condensation with BF_3 at −196°, yield SiF_3BF_2 in addition to known silicon boron fluorides.

WE report the synthesis and characterization of difluoro(trifluorosilyl)borane, the simplest and previously the most elusive of the silicon boron fluorides.[1-3]

Silicon tetrafluoride was passed at the rate of 1·4 mmol min^{-1} downward through a column of granular silicon or silicon carbide contained in a graphite tube heated inductively to 1200°—1850°. The gases emerged from the bottom of the tube into a high vacuum ($<10^{-4}$ Torr) and were immediately condensed on the liquid nitrogen cooled walls of the vacuum chamber. Boron trifluoride was condensed on the walls simultaneously at the rate of 3·0 mmol min^{-1}. After 30 min, unchanged reactants and volatile products were pumped off the walls and fractionated.

The most volatile product was shown to be difluoro(trifluorosilyl)borane by its n.m.r. spectrum [^{19}F (CCl_3F) δ 40·9 and 128·0 p.p.m., ^{11}B (BF_3OEt_2) δ −28·0 p.p.m.], its i.r. spectrum (bands with rotational structure centred at 1375, 1265, 987, and 867 cm^{-1}), its mass spectrum (*m/e* 114—117, $SiBF_4^+$), and from its vapour density and chemical analysis. The gaseous compound (b.p. −19°, m.p. −59°) was stable at 25° in the absence of air. About 1·5 mmols were formed from each run.

The other products of the reaction were identified as the known compounds $SiF_3SiF_2BF_2$ and $SiF_3(SiF_2)_2BF_2$, with a small amount of Si_2F_6. These compounds have been made by reacting SiF_2 with BF_3 at −196° but no SiF_3BF_2 was then formed.[1,3]

Our results suggest that the reaction of SiF_4 with silicon or silicon carbide at 1200°—1850° yields a short-lived species in addition to longer-lived ground state SiF_2 previously reported.[3,4] The former is responsible for the formation of SiF_3BF_2 from BF_3 in this work. Conditions used in earlier work would have allowed decay of a short-lived species before condensation with BF_3. Replacement of the inductively heated graphite tube with a resistance heated quartz tube containing silicon, did not affect the production of SiF_3BF_2. The mol ratio of the products SiF_3BF_2: [$SiF_3SiF_2BF_2$ + $SiF_3(SiF_2)_2BF_2$] varied from 1:3 using silicon heated to 1250°, to 2:1 using silicon carbide heated to 1850°. It seems likely that the short-lived species is an electronically excited form of SiF_2.

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[1] P. L. Timms, T. C. Ehlert, J. L. Margrave, F. E. Brinckman, T. C. Farrar, and T. D. Coyle, *J. Amer. Chem. Soc.*, 1965, **87**, 3819.
[2] R. W. Kirk and P. L. Timms, *J. Amer. Chem. Soc.*, 1969, **91**, 6315.
[3] J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, 1971, **4**, 145.
[4] V. M. Rao, R. F. Curl, P. L. Timms, and J. L. Margrave, *J. Chem. Phys.*, 1965, **43**, 2557.