New Derivatives of Tetrahydroborate(1−), $BH_3SiF_3^-$ and $BH_2(SiF_3)_2^-$

By SYDNEY BROWNSTEIN

(*Division of Chemistry, National Research Council, Ottawa, Ontario* K1A OR9, *Canada*)

Summary Silicon tetrafluoride and tetrabutylammonium (TBA) tetrahydroborate react in methylene chloride solution to produce [TBA][BH_3SiF_3] and [TBA][$BH_2(SiF_3)_2$].

BORON TRIFLUORIDE is reported to react with the tetrahydroborate ion to yield BF_4^- and boranes.[1] The reaction of SiF_4 and BH_4^- has been mentioned but no details given.[1] The species SiF_4, BH_4^-, BF_4^-, $BH_4SiF_4^-$, $BH_3SiF_3^-$, and $BH_2(SiF_3)_2^-$ are now proposed to explain the features of the ^1H, ^{19}F, and ^{11}B n.m.r. spectra of solutions with a ratio of BH_4^- to SiF_4 of 2:1, 1:1, and 1:2. Their n.m.r. parameters are listed in the Table. Some closely related hydrogen analogues are $BH_3GeH_3^-$ [2] and $(BH_3)_2PH_2^-$.[3]

TABLE. Magnetic resonance parameters of some silicon and boron species.

Species	δH^a	δF_{Si}	δF_B	δB	J_{B-H}	J_{F-H}	J_{B-Si-F}
BH_4^-	−0·16			34·8	82		
BF_4^-			−151·1	−2·2			
SiF_4		−156·8					
$BH_4SiF_4^-$	−0·34	−137·7					
$BH_3SiF_3^-$	−0·52	−112·0		46·9	86	6·7	20·9
$BH_2(SiF_3)_2^-$	−0·75	−112·7		55·6	85	5·3	24·3

[a] Chemical shifts are in p.p.m to low field from Me_4Si, $CFCl_3$, and BF_3OEt_2. Spin couplings are in Hz.

A freshly prepared methylene chloride solution with 2 equiv. of [TBA][BH_4] (TBA = tetrabutylammonium) for each SiF_4 has only a single sharp ^{19}F n.m.r. line at −137·7 p.p.m. and a broad line at −0·34 in the ^1H n.m.r. spectrum. Upon standing at room temperature, hydrogen is evolved and a set of four, overlapping ^{19}F quartets is observed at −112·0 p.p.m., a set of four ^1H quartets at −0·52, and a quartet of quartets at 46·9 p.p.m. in the ^{11}B resonance spectrum. These results unambiguously identify the formation of $BH_3SiF_3^-$ in the solution. Since SiF_4 is well known to form complexes with anions,[4] it is assumed that the initial transient species is $BH_4SiF_4^-$ but lack of fine structure from measurable spin coupling, perhaps because of rapid exchange, prevents a definite assignment.

After six months at room temperature for the 2:1 solution and two weeks for a 1:1 solution, in addition to the lines of BF_4^- and $BH_3SiF_3^-$ in the ^{19}F spectrum there is a set of four triplets at −112·7 p.p.m. There is a corresponding set of four apparent ^1H quintets at −0·75 and a triplet of ^{11}B septets at 55·6 p.p.m. These unambiguously identify the species $BH_2(SiF_3)_2^-$ in solution. As an example the ^{11}B n.m.r. spectrum of $BH_3SiF_3^-$ and $BH_2(SiF_3)_2^-$ is shown in the Figure. The reactions can be described by equations (1) and (2) although this is not meant to specify anything about the mechanism of the reaction.

$$BH_4^- + 4BH_4SiF_4^- \rightarrow 4BH_3SiF_3^- + BF_4^- + 4H_2 \qquad (1)$$

$$2BH_3SiF_3^- \rightarrow BH_2(SiF_3)_2^- + BH_4^- \qquad (2)$$

These reactions appear unique to SiF_4 with CH_2Cl_2 as solvent. Rapid decomposition of BH_4^- occurs in CCl_4 and $CHCl_3$ and a very slow reaction with CH_2Cl_2. [TBA][BH_4]

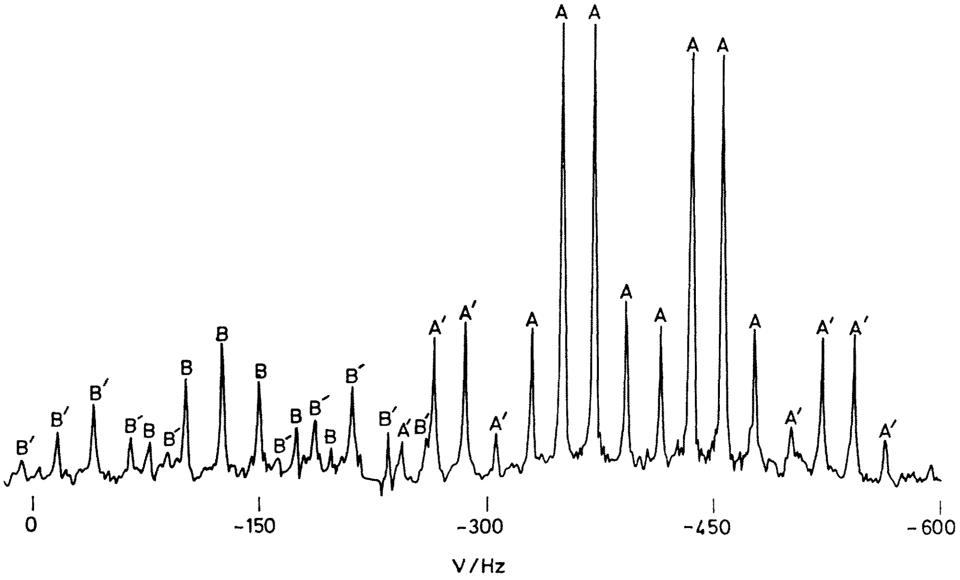

FIGURE. ^{11}B N.m.r. spectrum of some B–H species: (A) [TBA][BH_3SiF_3]; (B) [TBA][$BH_2(SiF_3)_2$].

is insoluble in diethyl ether and reacts differently with SiF_4 when tetrahydrofuran is used as solvent. The reaction of GeF_4 with BH_4^- in methylene chloride solution gives BF_4^-, identified by its ^{19}F n.m.r. spectrum, and a pale yellow solid, identified as orthorhombic germanium difluoride from its *X*-ray powder pattern. No hydrogen-containing species were found with PF_3, PF_5, AsF_3, and WF_6.

$[TBA][BH_3SiF_3]$ and $[TBA][BF_4]$ were isolated as solids by evaporation of all readily volatile materials after a short time from the reaction of $[TBA][BH_4]$ with an excess of SiF_4 in methylene chloride solution. The i.r. spectrum has peaks at 2330 (B–H stretch) and 820 cm^{-1} Si–F stretch). We did not succeed in the separation of $[TBA][BF_4]$ and $[TBA][BH_3SiF_3]$, but an elemental analysis of the solid product for boron, silicon, and fluorine agrees with a ratio of five $[TBA][BH_3SiF_3]$ to one $[TBA][BF_4]$.

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