Boron–Fluorine Chemistry. I.
Boron Monofluoride and Some Derivatives

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Abstract: High yields of gaseous boron monofluoride, BF, have been obtained by passing BF_3 over crystalline boron at 2000° under 1 mm pressure. The short-lived BF gas condenses to a green polymer at −196°, from which small amounts of volatile boron fluorides containing up to 14 boron atoms are released on warming. Cocondensation of BF and B_2F_4 gives B_3F_5, triboron pentafluoride, an unstable, very reactive compound. Condensation of BF in the presence of CO or PF_3 gives $(BF_2)_3BCO$ or $(BF_2)_3BPF_3$, respectively, which are stable crystalline compounds.

Boron monofluoride has been known to spectroscopists for a number of years.[1,2] More recently its thermodynamic properties have been reported by Hildenbrand[3] using mass spectrometry, and by Blauer[4] from a transpiration study.

Hildenbrand proved that BF and BF_3 are the only two major species in the boron–fluorine system at high temperatures. Blauer's transpiration experiments showed that appreciable amounts of boron could be transported as BF when boron trifluoride was passed over boron even at temperatures as low as 1500°. The experiments gave no indication of the possible lifetime of the BF. Nevertheless, on the basis of this work, it seemed worthwhile to attempt to prepare BF gas from boron and boron trifluoride at high temperatures and low pressures, under conditions which would allow its chemistry to be studied.

As Skell[5] demonstrated with the species C_3, under sufficiently low pressures of permanent gases, a gaseous high-temperature species can be very rapidly transferred from a hot source to a liquid-nitrogen-cooled surface in "preparative" amounts. On the cold surface the species may briefly exhibit most of the reactivity expected of it as a gaseous monomer, although reactions with other compounds can only be effected by cocondensation. This technique has been applied in the study of BF.

Experimental Section

The boron monofluoride was prepared by passing boron trifluoride (Matheson, nominally 99.5%) through a 1-in. diameter cylindrical graphite container packed with granules of boron (nominally 99.8%). The apparatus is shown in Figure 1. The graphite container was insulated by 0.5 in. of graphite felt and was heated by a 30-kc induction heater to 1900–2000°. The work coil of the induction heater was external to a water-cooled Pyrex jacket around the graphite container. A mixture of boron monofluoride and unchanged boron trifluoride emerged from the bottom of the graphite container through a $^1/_8$ in. hole. A fast pumping system kept the pressure of permanent gas within the Pyrex envelope below 10^{-6} mm, so that the BF and BF_3 could be condensed quickly and efficiently in a liquid-nitrogen-cooled flask immediately below the graphite container.

In a typical run, the system was first carefully outgassed at the operating temperature. The BF_3, freed from all traces of permanent gases by repeated condensation and evaporation, was passed through the graphite container at the rate of 25 ml/min (measured at STP) for 30–40 min. The run was normally terminated by partial blocking of the outlet from the graphite container by a crystalline boron deposit.

Other vapors could be sprayed into the cooled flask through the side arm located below the graphite container and cocondensed with the BF. Only trace amounts of permanent gases could be introduced through the side arm without increasing the pressure in the flask to the level at which most of the BF polymerized on the walls of the flask above the liquid nitrogen.

At the end of a run, the graphite was allowed to cool and the cold flask was warmed to room temperature. Any volatiles liberated from the condensate in the flask were pumped continuously into a U-trap during warm-up. These were subsequently fractionated using standard vacuum techniques in a vacuum line employing only greaseless O-ring stopcocks (West-Glass Corp.).

A Bendix time-of-flight mass spectrometer was used to take mass spectra. A special all-glass inlet system was built to overcome the ready decomposition of some of the higher boron fluorides on stainless steel surfaces. Infrared spectra were obtained on a Perkin-Elmer 211 spectrophotometer or an Infracord, the latter being especially convenient for unstable compounds because of its relatively rapid scan rate. Silver chloride windows were found more satisfactory than either sodium chloride or potassium bromide for gas-phase spectra of boron fluorides. A Varian HR-60 machine was used for ^{19}F nmr spectra.

Results

The Yield and Lifetime of BF. The action of boron trifluoride on boron forms boron monofluoride according to the equation

$$BF_3 + 2B = 3BF$$

In this work, with the boron heated to 1950–2000°, and an approximate total gas pressure ($BF + BF_3$) of 1 mm over the boron, the conversion of boron trifluoride to boron monofluoride was estimated to be about 85%. This was based on the observed recovery of approximately 15% of the added boron trifluoride from the products trapped at liquid nitrogen temperature, partly as BF_3 and partly as B_2F_4 and B_3F_5. All other products formed, both volatile and involatile, had a B:F ratio very close to unity. The lifetime of boron monofluoride is very much less than that of silicon difluoride,[6] as appreciable amounts of BF polymers were deposited on the walls of the system between the furnace and the cooled flask although the path was straight and the time of travel of the molecules would only have been a few milliseconds under prevailing

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[1] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1950.

[2] R. Onaka, *J. Chem. Phys.*, **27**, 374 (1957).

[3] D. L. Hildenbrand and E. Murad, *ibid.*, **43**, 1400 (1965).

[4] J. Blauer, M. A. Greenbaum, and M. Farber, *J. Phys. Chem.*, **68**, 2332 (1964).

[5] P. S. Skell, L. D. Westcott, J. P. Goldstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965).

[6] P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *ibid.*, **87**, 2824 (1965).

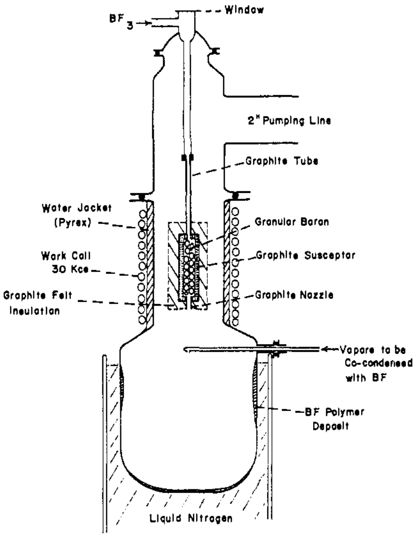


Figure 1. Apparatus used for preparing boron monofluoride.

conditions. Raising the pressure of permanent gas in the system to 5×10^{-5} mm greatly increased this loss of BF on the walls.

Products Formed in the Condensation of BF at −196°. Condensation of the boron monofluoride, as shown in Figure 1, gave a greenish solid at −196°. On warming this to room temperature three main volatile fractions were evolved apart from boron trifluoride. These were respectively diboron tetrafluoride, a compound believed, from evidence presented below, to be triboron pentafluoride, B_3F_5, and a complex mixture of higher boron fluorides.

The Formation of Diboron Tetrafluoride. The amount of B_2F_4 which was formed was very dependent on the amount of BF_3 condensed along with the BF. If BF_3 was introduced through the side arm shown in Figure 1 below the heated crucible and cocondensed with the BF in a roughly 1:1 mole ratio, up to 25% of the BF was recovered as B_2F_4. The remainder of the BF formed a white polymer and small amounts of higher volatile boron fluorides. The low pressure in the flask would have prevented the reaction $BF + BF_3 = B_2F_4$ from occurring in the gas phase to any extent, and so it must have occurred in the condensed phase on the walls of the flask.

Good yields of B_2F_4 could also be obtained if BF_3 was passed so rapidly (100 ml/min at STP) through the heated boron that equilibrium was not reached. Then a mixture of BF and BF_3, rich in BF_3, was sprayed from the graphite crucible.

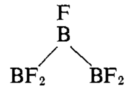
The Characterization of Triboron Pentafluoride. A small amount of a solid was obtained in a −78 to −92° trap in the vacuum fractionation of the volatiles liberated from the BF polymer. The mass spectrum of this material (Table I) indicated that it was B_3F_5, triboron pentafluoride. The ions of *m/e* 125, 126, 127, 128 corresponding to $B_3F_5^+$ with two boron isotopes, had the lowest appearance potential but were much less abundant than $B_3F_4^+$ at 50 ev. The B:F mole ratio of the compound was measured as 3:4.92 by thermal decomposition to boron and BF_3.

Table I. Infrared and Mass Spectrum of Triboron Pentafluoride

Infrared spectrum,[a] cm^{-1}		Mass spectrum			
				Rel abundance	
B_2F_4[b]	B_3F_5	*m/e*	Ion	50 ev	17 ev
1384 s	1400 sh	49	BF_2^+	Large	25
1332 s	1315 vs, br	60	$B_2F_2^+$	760	580
1155 s	1220 sh	79	$B_2F_3^+$	1100	350
1138 s	1170 s, br	90	$B_3F_3^+$	2	...
646 w	1140 w	109	$B_3F_4^+$	460	6
537 m	1120 w	128	$B_3F_5^+$	100	100
	1015 w				
	900 m				
	880 s				
	795 w				
	735 w				

[a] Solid film. [b] After Gayles and Self.[7]

The structure of the compound was suggested by its infrared spectrum. Since it was too unstable to take a gas-phase spectrum, a solid film, sprayed onto a sodium chloride window at −196°, was used. The observed frequencies in this solid phase spectrum are given in Table I. The spectrum was quite similar to that observed by Gayles and Self[7] for B_2F_4 in the solid state, but it contained the rather strong absorption at 880 cm^{-1} which is absent in the B_2F_4 spectrum. Becher[8] found a strong absorption in the spectrum of $(CH_3)_2BF$ at 1152 cm^{-1}, which he assigned to the asymmetric BC_2 stretch. On this basis it seemed probable that the absorption at 880 cm^{-1} was due to the asymmetric $B(B)_2$ stretch, as would occur in the structure



This structure was also indicated by the ^{19}F nmr spectrum taken at −60° in dilute solution in B_8F_{12} (see below) with CCl_3F as external reference. The spectrum showed two resonances, one at −26.2 ppm, the other at +61.0 ppm relative to CCl_3F. The high-field resonance is only a little above that of B_2F_4 in B_8F_{12} (at 55.7 ppm) and is in a typical position for fluorine atoms bonded in $-BF_2$ groups.[9] The work of Coyle and Stone[10] with BF_2X and BFX_2 compounds indicates that a −BF− group could be expected to have a fluorine resonance 50–90 ppm lower than a corresponding $-BF_2$ group. This makes the assignment of the -26.2-ppm resonance to a −BF− group very probable. The area ratio of the high- to low-field resonance was measured as 3.5 : 1, although quadrupole relaxation broadening effects make this area ratio of dubious worth at such a low temperature.

Triboron pentafluoride is thus a homolog of B_2F_4 and is believed to be the first compound to be reported containing a simple chain of three boron atoms. It melts with decomposition at −55 to −50° (compare B_2F_4, mp −55°). The compound decomposes completely in a few hours at −50° and very rapidly above −30°. The decomposition products are mainly B_2F_4 and a yellow, oily, volatile liquid of molecular formula B_8F_{12}. Traces of BF_3 are also formed, probably mainly by the decomposition of B_8F_{12}. The decomposition of B_3F_5 is represented approximately by the equation

$$4B_3F_5 = B_8F_{12} + 2B_2F_4$$

The structure of B_8F_{12} is still being investigated.

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(7) J. N. Gayles and J. Self, *J. Chem. Phys.*, **40**, 3530 (1964).

(8) H. J. Becher, *Z. Anorg. Allgem. Chem.*, **291**, 151 (1957).

(9) P. L. Timms, T. C. Ehlert, J. L. Margrave, F. E. Brickmann, T. C. Farrar, and T. D. Coyle, *J. Am. Chem. Soc.*, **87**, 3819 (1965).

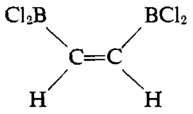
(10) T. D. Coyle and F. G. A. Stone, *J. Chem. Phys.*, **32**, 1892 (1960).

Reactions of Triboron Pentafluoride. Triboron pentafluoride, in common with all the compounds containing B–B bonds made in this work, was found to react explosively with air and water. It reacted rapidly with gaseous hydrogen at $-70°$ or above to form HBF_2, B_2F_4, B_2H_6, and a small amount of an involatile BF polymer. The difluoroborane was identified by its mass spectrum and known infrared spectrum.[11]

This reaction is similar to that between diboron tetrachloride and hydrogen,[12] which also gives some diborane at 0°. Diboron tetrafluoride does not react readily with hydrogen.

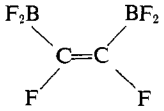
The action of gaseous carbon monoxide on B_3F_5 at $-70°$ produced B_4F_6CO, a compound discussed below. The other product of the reaction was B_2F_4 which forms no stable carbonyl.

With liquid tetrafluoroethylene at $-100°$, B_3F_5 reacted quickly and smoothly to give fair yields of a stable crystalline compound. The mass spectrum of the compound indicated a formula $C_2B_2F_6$, and the vapor density was measured as 163 (required for $C_2B_2F_6$, 164). The compound had an absorption in its gas phase infrared spectrum at 1615 cm^{-1}, in a very similar position to that observed by Schlesinger[13] for the C=C stretch in



the reaction product of acetylene and B_2Cl_4.

The ^{19}F nmr spectrum showed two resonances, one at 80.6 ppm and the other at 158 ppm on the high-field side of CCl_3F. Coyle, Stafford, and Stone[14] reported the ^{19}F resonance of the $-BF_2$ groups in perfluorovinylboron difluoride to be at 86.7 ppm. On this basis, the resonance at 80.6 ppm is assigned to the $-BF_2$ groups and the resonance at 158 ppm to the C–F groups in the structure



The area ratio of the two resonances was close to 2:1.

No trace of perfluorovinylboron difluoride was detected in the reaction of B_3F_5 and C_2F_4. At temperatures only slightly above $-100°$, C_2F_4 was explosively polymerized by the B_3F_5.

Reactions of other organic compounds with B_3F_5 are under investigation. No reaction has been observed between B_3F_5 and hexafluorobenzene, and the pentafluoride decomposes smoothly to B_8F_{12} above $-30°$ in hexafluorobenzene solution.

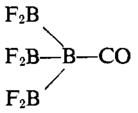
The Higher Boron Fluorides. A maximum of about 5% of the BF condensed at $-196°$ was recovered as a complex mixture of slightly volatile, white or yellow, higher boron fluorides. Analysis of the mixture gave a B:F ratio of unity. There were at least four components of the mixture, two solid and two liquid, but it has not been possible to isolate any of them in a pure state. The mass spectrum of the mixture at 50 ev showed very many of the possible B–F combination ions, with B:F ratios ranging from 1:1 to 2:3. The ion-abundance distribution was amazingly uniform, and the progression of ions ended cleanly at $B_{14}F_{13}^+$. At low electron voltages, ions containing 12, 13, and 14 boron atoms were most abundant. These higher boron fluorides all seem rather unstable at room temperature, slowly evolving BF_3 and forming white, involatile solids.

The Formation of CO and PF_3 Adducts. During fractionation of volatiles liberated on warming a BF condensate to room temperature, a small amount of a beautifully crystalline solid was always obtained in a -35 to $-55°$ trap. The gas-phase infrared spectrum of this material showed a complex series of absorptions in the B–F stretch region (Table II) but a very strong absorption at 2162 cm^{-1}, very close to the carbonyl stretch in borine carbonyl (2165 cm^{-1}). The heaviest ions in the mass spectrum were at *m/e* 116–118, 136–139, and 164–167, corresponding in mass to $B_3F_3CO^+$, $B_4F_5^+$, and $B_4F_5CO^+$, respectively. At low electron voltages, $B_3F_3CO^+$ was the most abundant ion. Chemical analysis gave a B:F ratio of 4:5.95, and the vapor density was measured as 184 (required for B_4F_6CO, 185.2). From this the molecular formula was assigned as B_4F_6CO.

Table II. Infrared Spectrum (cm^{-1}) of B_4F_6CO and $B_4F_6PF_3$

B_4F_6CO	$B_4F_6PF_3$	
2162 vs		
1390 s	1390 s	B–F stretch
1361 vs	1360 vs	
1300 m	1300 m	
1238 s	1238 s	
1221 vs	1222 vs	
1205 vs	1206 vs	
1150 m	1145 m	
983 w	995 s	P–F stretch
855 w	974 vs	
592 w	890 w	PF_3 bands
477 w	872 w	
	852 w	
	830 w	

The ^{19}F nmr spectrum of the solid dissolved in CCl_3F showed only one resonance at $+38.4$ ppm. This indicated there was only one type of fluorine atom in the molecule, which was probably combined in $-BF_2$ groups. The combined infrared and nmr data strongly suggested the structure



The formation of this compound in the condensation of BF may have been due to traces of sulfur dioxide in the BF_3 which was passed over the boron. The sulfur dioxide would have been reduced by the graphite container to carbon monoxide, and this could interact with BF, presumably on the cold surface, to give B_4F_6CO. Attempts to prove the existence of a gaseous BFCO, which would explain the rather efficient conversion of

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(11) T. D. Coyle, J. J. Ritter, and T. C. Farrar, *Proc. Chem. Soc.*, 25 (1964).

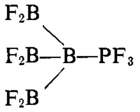
(12) G. Urry, T. Wartik, and H. I. Schlesinger, *J. Am. Chem. Soc.*, 74, 5809 (1952).

(13) P. Ceron, A. Finch, J. Frey, T. Parsons, G. Urry, and H. I. Schlesinger, *ibid.*, 81, 6368 (1959).

(14) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *Spectrochim. Acta*, 17, 968 (1961).

noncondensable CO to B_4F_6CO, have not been successful. Slightly larger amounts of the carbonyl were made when CO was deliberately added to the high-temperature system, but then the pressure of CO as a permanent gas reduced the efficiency of transfer of BF from the graphite container to the cold surface.

The action of CO on the yellow B_8F_{12} at $-50°$ was found to give almost quantitative yields of B_4F_6CO. The analogous phosphorus trifluoride adduct was made very simply in high yield by cocondensation of PF_3 and BF in a roughly 1:4 mole ratio. It was collected as a white crystalline solid in a -35 to $-55°$ trap. The infrared spectrum of the vapor was identical with that of B_4F_6CO in the B–F stretch region (Table II). There were very strong absorptions at 995 and 974 cm^{-1}. These are close to the P–F stretch absorption in BH_3PF_3 at 994 and 958 cm^{-1}, reported by Taylor and Bissot.[15] The B:P:F ratio was determined analytically to be 3.97:1:8.92, and the vapor density was determined as 244, indicating the molecular formula B_4PF_9 or $B_4F_6PF_3$. The ion of lowest appearance potential in the mass spectrum was $B_3PF_6^+$, formed, as with B_4F_6CO, by loss of BF_3 from the parent molecule. The ^{19}F nmr spectrum showed a broad singlet at $+37.4$ ppm relative to CCl_3F, partly overlapped by one sharp resonance of a doublet centered at 53.9 ppm, assigned to fluorine atoms of a $-PF_3$ group with $J_{P-F} = 1350$ Hz. The structure of $B_4F_6PF_3$ was thus indicated as



The two compounds B_4F_6CO and $B_4F_6PF_3$ are analogs of BH_3CO and BH_3PH_3 with $-BF_2$ replacing hydrogen. They are rather more stable than the hydrogen compounds. The carbonyl melts at 40° and has a vapor pressure of 760 mm at 82°. The PF_3 adduct melts at 55° and has a vapor pressure of 760 mm at 74°. Only slight irreversible decomposition occurs with pure samples of both compounds at temperatures up to 100°, but it is thought that some reversible dissociation may be occurring as the Trouton constants of the CO and PF_3 adducts are both near 27 eu.

Discussion

There is no doubt from the observed formation of B_2F_4 and B_3F_5 by cocondensation of BF with BF_3 and B_2F_4, respectively, that boron monofluoride will insert efficiently into B–F bonds forming B–BF_2. However, there is little evidence yet to suggest that boron monofluoride will react on cocondensation with compounds not containing B–F bonds. When C_2F_4 was cocondensed with BF, no more $C_2B_2F_6$ was formed than could be accounted for by consumption of all the B_3F_5 also formed during condensation. Even with silicon tetrafluoride, in which the Si–F bond is of similar character to the B–F bond, preliminary experiments have indicated only traces of reaction with BF, SiF_3-BF_2 being the product.

This indicates that the use of boron monofluoride as a synthetic reagent may be restricted to the formation of the new compound B_3F_5 and of the higher boron fluorides not readily accessible *via* B_3F_5. Advances in synthetic chemistry in this area will most likely be obtained from reactions of B_3F_5.

It is expected that more compounds in which BF_2–B replaces H–B, as observed already in $(BF_2)_3BCO$, will be found. In particular derivatives of the simpler boron hydrides like diborane and tetraborane, with partial replacement of hydrogen by $-BF_2$, may well be capable of isolation.

Acknowledgment. This work was in part supported by the U. S. Army Research Office, Durham.

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(15) R. C. Taylor and T. C. Bissot, *J. Chem. Phys.*, **25**, 780 (1956).