Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, BORON TRIFLUORIDE

Boron trifluoride [7637-07-2] (trifluoroborane), BF_3, was first reported in 1809 by Gay-Lussac and Thenard (1) who prepared it by the reaction of boric acid and fluorspar at dull red heat. It is a colorless gas when dry, but fumes in the presence of moisture yielding a dense white smoke of irritating, pungent odor. It is widely used as an acid catalyst (2) for many types of organic reactions, especially for the production of polymer and petroleum (qv) products. The gas was first produced commercially in 1936 by the Harshaw Chemical Co. (see also Boron compounds).

The boron atom in boron trifluoride is hybridized to the sp^2 planar configuration and consequently is coordinatively unsaturated, ie, a Lewis acid. Its chemistry centers around satisfying this unsaturation by the formation with Lewis bases of adducts that are nearly tetrahedral (sp^3). The electrophilic properties (acid strengths) of the trihaloboranes have been found to increase in the order $BF_3 < BCl_3 < BBr_3 < BI_3$ (3, 4).

1. Physical Properties

The physical properties are listed in Table 1. The molecule has a trigonal planar structure in which the F—B—F angle is 120° and the B—F bond distance is 0.1307 ± 0.0002 nm (13).

Nuclear magnetic resonance ^{11}B spectral studies of BF_3 have given a value of 9.4 ± 1.0 ppm for the chemical shift relative to $BF_3{\cdot}O(C_2H_5)_2$ as the zero reference (14). Using methylcyclohexane as a solvent at 33.5°C and $BF_3{\cdot}O(CH_2CH_3)_2$ as the internal standard, a value of 10.0 ± 0.1 ppm was obtained for the chemical shift (15). A value for the ^{19}F chemical shift of BF_3 in CCl_3F relative to CCl_3F is reported to be 127 ppm (16). The coupling constant $J_{^{11}B-^{19}F}$ is reported to be 15 ± 2 Hz for BF_3 (17). Additional constants are available (3, 18). See Table 2 for solubilities.

Aqueous mineral acids react with BF_3 to yield the hydrates of BF_3 or the hydroxyfluoroboric acids, fluoroboric acid, or boric acid. Solution in aqueous alkali gives the soluble salts of the hydroxyfluoroboric acids, fluoroboric acids, or boric acid. Boron trifluoride, slightly soluble in many organic solvents including saturated hydrocarbons (qv), halogenated hydrocarbons, and aromatic compounds, easily polymerizes unsaturated compounds such as butylenes (qv), styrene (qv), or vinyl esters, as well as easily cleaved cyclic molecules such as tetrahydrofuran (see Furan derivatives). Other molecules containing electron-donating atoms such as O, S, N, P, etc, eg, alcohols, acids, amines, phosphines, and ethers, may dissolve BF_3 to produce soluble adducts.

2. Chemical Properties

In addition to the reactions listed in Table 3, boron trifluoride reacts with alkali or alkaline-earth metal oxides, as well as other inorganic alkaline materials, at 450°C to yield the trimer trifluoroboroxine [13703-95-2], $(BOF)_3$, MBF_4, and MF (29) where M is a univalent metal ion. The trimer is stable below -135°C but

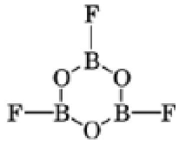
Table 1. Physical Properties of Boron Trifluoride

Property	Value	Reference
molecular weight	67.8062	5
melting point, °C	−128.37	6
boiling point, °C	−99.9	6
vapor pressure of liquid, kPa[a]		
at 145 K	8.43	
at 170 K	80.19	
at 220 K	1156	
at 260 K	4842	7
triple point at 8.34 kPa,[a] K	144.78	5
critical temperature, T_c, °C	-12.25 ± 0.03	7
critical pressure, P_c, kPa[a]	4984	7
density		
critical, d_c, g/cm^3	ca 0.591	8
gas at STP, g/L	3.07666	9
gas limiting, L_N, g/L	3.02662	9
liquid, for 148.9 to 170.8 K, g/cm^3	$1.699 - 0.00445\,(t + 125.0)$	10
enthalpy of fusion, $\Delta H_{144.45}$, kJ/mol[b]	4.2417	11
enthalpy of vaporization, $\Delta H_{154.5}$, kJ/mol[b]	18.46	12
entropy, $S_{298.15}$, J/(mol·K)[b]	254.3	
Gibbs free energy of formation, $\Delta G_{f298.15}$, kJ/mol[b]	−1119.0	13
enthalpy of formation, $\Delta H_{f298.15}$, kJ/mol[b]	−1135.6	13
infrared absorption frequencies, cm^{-1}		
v_1	888	
v_2	696.7	
v_3	1463.3	
v_4	480.7	

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

disproportionates to B_2O_3 and BF_3 at higher temperatures (30).



The reaction of metal hydrides and BF_3 depends on the stoichiometry as well as the nature of the metal hydride. For example, LiH and $BF_3{\cdot}O(C_2H_5)_2$ may form diborane (6) or lithium borohydride (31, 32):

$$6\ \mathrm{LiH} + 8\ \mathrm{BF_3{\cdot}O(C_2H_5)_2} \longrightarrow \mathrm{B_2H_6} + 6\ \mathrm{LiBF_4} + 8\ \mathrm{(C_2H_5)_2O}$$

$$4\ \mathrm{LiH} + 4\ \mathrm{BF_3{\cdot}O(C_2H_5)_2} \longrightarrow \mathrm{LiBH_4} + 3\ \mathrm{LiBF_4} + 4\ \mathrm{(C_2H_5)_2O}$$

The first method is commonly used for preparing diborane.

Table 2. Solubilities of Boron Trifluoride

BF_3, g	Solvent, g	Temperature,°C	Product	CAS Registry Number	Reference
369.4	water,[a] 100[b]	6	$BF_3{\cdot}H_2O$	[15799-89-0]	
			$HBF_3(OH)$	[16903-52-9]	19
2.06	sulfuric acid, conc, 100%	25			20
	nitric acid[a]	20	$HNO_3{\cdot}2BF_3$	[20660-63-3]	21
	orthophosphoric acid[a]	25	$H_3PO_4{\cdot}BF_3$	[13699-76-6]	22
2.18	hydrofluoric acid,[c]	4.4			24
	hydrochloric acid, anhydrous (l)	24	miscible		25

[a] Dissolves with reaction to form complexes and other species.

[b] A higher dilution results in a mixture of $H[BF_2(OH)_2]$, HBF_4, and H_3BO_3.

[c] Equations for the solubility of BF_3 in liquid HF at 24, 49, and 90°C and up to 6.8 kPa (51 mm Hg) may be found in Reference 23.

Table 3. Reactions of Boron Trifluoride

Reactant	Temperature,°C	Products	Formula	Reference
sodium[a]		boron, amorphous, sodium fluoride	NaF	26
magnesium, molten alloys	no reaction			
calcium	1600	calcium hexaboride	CaB_6	
aluminum	1200	aluminum boride (1:12), tetragonal boron	AlB_{12}	
	1650[b]	β-rhombohedral boron		
titanium	1600	titanium boride	TiB_2	27
copper, mercury, chromium, iron	RT or below	no reaction[c]		
sodium nitrate, sodium nitrite	180	sodium fluoroborate, boric oxide	$NaBF_4$	28

[a] With incandescence.

[b] Further reaction.

[c] Even when subjected to pressure for a considerable length of time; also no reaction with red-hot iron.

Metal halides react with BF_3 (33) when heated to form BX_3 and the metal fluoride. For example,

$$AlBr_3 + BF_3 \longrightarrow BBr_3 + AlF_3$$

The reaction of BF_3 with alkali halides yields the respective alkali fluoroborates (34):

$$3\,KCl + 4\,BF_3 \longrightarrow 3\,KBF_4 + BCl_3$$

Alkyl and arylboranes are obtained (35) from BF_3 using the appropriate Grignard reagent, alkylaluminum halide, or zinc alkyl, using diethyl ether as the solvent:

$$BF_3 + 3\,RMgX \longrightarrow BR_3 + 3\,MgXF$$

Tetraorganylborate complexes may be produced when tetrahydrofuran is the solvent (36).

Alkylfluoroboranes result from the reaction of the appropriate alkylborane and BF_3 under suitable conditions (37):

$$BR_3 + 2\,(C_2H_5)_2\,O{\cdot}BF_3 \longrightarrow 3\,RBF_2 + 2\,(C_2H_5)_2\,O$$

Table 4. Boron Trifluoride Adducts with Oxygen-Containing Compounds

Donor	Adduct name	CAS Registry Number	Molecular formula
alcohols	ethanol trifluoroborane	[353-41-3]	$C_2H_5OH{\cdot}BF_3$
	bis(ethanol) trifluoroborane	[373-59-1]	$2C_2H_5OH{\cdot}BF_3$
	bis(2-chloroethanol) trifluoroborane	[72985-81-0]	$2ClCH_2CH_2OH{\cdot}BF_3$
	benzyl alcohol trifluoroborane	[456-31-5]	$C_6H_5CH_2OH{\cdot}BF_3$
acids	acetic acid trifluoroborane	[753-53-7]	$CH_3COOH{\cdot}BF_3$
	bis(acetic acid) trifluoroborane	[373-61-5]	$2CH_3COOH{\cdot}BF_3$
	stearic acid trifluoroborane	[60274-92-2]	$CH_3(CH_2)_{16}COOH{\cdot}BF_3$
	bis(phenol) trifluoroborane	[462-05-5]	$2C_6H_5OH{\cdot}BF_3$
ethers	diethyl ether trifluoroborane	[109-63-7]	$(C_2H_5)_2O{\cdot}BF_3$
	tetrahydrofuran trifluoroborane	[462-34-0]	$(CH_2)_4O{\cdot}BF_3$
	anisole trifluoroborane	[456-31-5]	$CH_3OC_6H_5{\cdot}BF_3$
acid anhydride	acetic anhydride trifluoroborane	[591-00-4]	$(CH_3CO)_2O{\cdot}BF_3$
esters	ethyl formate trifluoroborane	[462-33-9]	$HCOOC_2H_5{\cdot}BF_3$
	phenyl acetate trifluoroborane	[30884-81-6]	$CH_3COOC_6H_5{\cdot}BF_3$
ketones	acetone trifluoroborane	[661-27-8]	$(CH_3)_2CO{\cdot}BF_3$
	benzophenone trifluoroborane	[322-21-4]	$(C_6H_5)_2CO{\cdot}BF_3$
	acetphenone trifluoroborane	[329-25-9]	$C_6H_5COCH_3{\cdot}BF_3$
aldehydes	acetaldehyde trifluoroborane	[306-73-0]	$CH_3CHO{\cdot}BF_3$
	neopentanal trifluoroborane	[306-78-5]	$(CH_3)_3CCHO{\cdot}BF_3$
	benzaldehyde trifluoroborane	[456-30-4]	$C_6H_5CHO{\cdot}BF_3$

Adducts of BF_3 and some organic compounds having labile hydrogen atoms in the vicinity of the atom bonding to the boron atom of BF_3 may form a derivative of BF_3 by splitting out HF. For example, β-diketones such as acetylacetone or benzoylacetone react with BF_3 in benzene (38):

$$BF_3 + CH_3COCH_2COCH_3 \longrightarrow CH_3COCH{=}C\,(CH_3)\,OBF_2 + HF$$

In Group 14 (IV), carbon serves as a Lewis base in a few of its compounds. In general, saturated aliphatic and aromatic hydrocarbons are stable in the presence of BF_3, whereas unsaturated aliphatic hydrocarbons, such as propylene or acetylene, are polymerized. However, some hydrocarbons and their derivatives have been reported to form adducts with BF_3. Typical examples of adducts with unsaturated hydrocarbons are 1:1 adducts with tetracene and 3,4-benzopyrene (39), and 1:2 BF_3 adducts with α-carotene and lycopene (40).

In Group 15 (V), nitrogen compounds readily form molecular compounds with BF_3. Phosphorus compounds also form adducts with BF_3. Inorganic or organic compounds containing oxygen form many adducts with boron trifluoride, whereas sulfur and selenium have been reported to form only a few (41–43).

Boron trifluoride forms two hydrates, $BF_3{\cdot}H_2O$ and boron trifluoride dihydrate [13319-75-0], $BF_3{\cdot}2H_2O$, (also $BF_3{\cdot}D_2O$ [33598-66-2] and $BF_3{\cdot}2D_2O$ [33598-66-2]). According to reported nmr data (43, 44), the dihydrate is ionic, $H_3O^+F_3BOH^-$;. The trihydrate has also been reported (45). Acidities of BF_3–water systems have been determined (46). Equilibrium and hydrolysis of BF_3 in water have been studied (47–49).

Most of the coordination compounds formed by trifluoroborane are with oxygen-containing organic compounds (Table 4). Although the other boron halides frequently react to split out hydrogen halide, boron trifluoride usually forms stable molecular compounds. The reason is attributed to the back coordination of electrons from fluorine to boron forming a strong B—F bond which is 28% ionic (50).

It has been reported (51) that some adducts of alkyl ethers and/or alcohols are unstable and decompose at $-80^\circ C$ to yield BF_3, H_2O, and the polyalkene. Adducts of BF_3 have been reported with hydrogen sulfide, sulfur dioxide, thionyl fluoride, and the sulfur analogues of many of the kind of oxygen-containing organic

Table 5. Boron Trifluoride Adducts with Compounds Containing Chlorine and Fluorine

Name	CAS Registry Number	Molecular formula
potassium tetrafluoroborate	[14075-53-7]	KBF_4
hexaamminenickel(II) tetrafluoroborate	[13877-20-8]	$[Ni(NH_3)_6](BF_4)_2$
nitrosyl tetrafluoroborate	[14635-75-7]	$NOBF_4$
acetylium tetrafluoroborate	[2261-02-1]	CH_3COBF_4
tetramethylammonium tetrafluoroborate	[661-36-9]	$(CH_3)_4NBF_4$
difluorobromine tetrafluoroborate	[14282-83-8]	BrF_2BF_4
anilinium tetrafluoroborate	[15603-97-1]	$C_6H_5NH_2HBF_4$

molecules cited in Table 4. The carbonyl oxygen or the carbonyl sulfur is the donor to BF_3 in 1:1 adducts such as $CH_3COOCH_3 \cdot BF_3$ [7611-14-5], $CH_3COSCH_3 \cdot BF_3$ [52913-04-9], and $CH_3CSOCH_3 \cdot BF_3$ [52912-98-8] (52).

Compounds containing fluorine and chlorine are also donors to BF_3. Aqueous fluoroboric acid and the tetrafluoroborates of metals, nonmetals, and organic radicals represent a large class of compounds in which the fluoride ion is coordinating with trifluoroborane. Representative examples of these compounds are given in Table 5. Coordination compounds of boron trifluoride with the chlorides of sodium, aluminum, iron, copper, zinc, tin, and lead have been indicated (53); they are probably chlorotrifluoroborates.

Trifluoroborane may form adducts with some of the transition elements. See Reference 54 for a detailed discussion of complexes of trifluoroborane with various Group 6–10 (VI, VII, and VIII) species.

3. Manufacture

Boron trifluoride is prepared by the reaction of a boron-containing material and a fluorine-containing substance in the presence of an acid. The traditional method used borax, fluorspar, and sulfuric acid.

In another process fluorosulfonic acid is treated with boric acid:

$$3\,HSO_3F + H_3BO_3 \longrightarrow BF_3 + 3\,H_2SO_4$$

Numerous other reactions are available for the preparation of small quantities of boron trifluoride, some of which are of high purity (55).

4. Shipment and Handling

The gas is nonflammable and is shipped in DOT 3A and 3AA steel cylinders at a pressure of approximately 12,410 kPa (1800 psi). Boron trifluoride is classified as a poison gas, both domestically and internationally. Cylinders must have a poison gas diamond and an inhalation hazard warning label. Tube trailers carry both a poison gas placard and an inhalation hazard warning. Cylinders containing 27.2 kg and tube trailers containing 4.5–10 metric tons are available. If boron trifluoride is compressed using oil as a compressor lubricant, it must not be used with oxygen under pressure nor with gauges, valves, or lines that are to be used with oxygen.

Inasmuch as the gas hydrolyzes readily, all equipment should be purged repeatedly using inert dry gas before admitting boron trifluoride. Under anhydrous conditions, carbon steel equipment is satisfactory. Stainless steel and aluminum silicon bronze may also be used. Stainless steel tubing is recommended for both temporary and permanent connections.

In the presence of moisture, boron trifluoride may be handled in polytetrafluoroethylene (PTFE), polyethylene, Pyrex glass (limit to atmospheric pressure), or Hastelloy C containers. At 600°C, stainless steel (304 L) and Hastelloy N are attacked by BF_3; Hastelloy C is more resistant (56). Kel F and PTFE serve as satisfactory gasket and packing materials, whereas rubber, fiber, polymerizable materials, or organic oxygen- and nitrogen-containing compounds must be avoided. Because boron trifluoride is soluble in, and reacts with, many liquids, the gas must not be introduced into any liquid unless a vacuum break or similar safety device is employed.

5. Economic Aspects, Standards, and Analyses

The sole United States producer of boron trifluoride is AlliedSignal, Inc. The 1992 price of boron trifluoride was $9.59–12.46/kg, depending on purity and the quantity purchased.

Commercial boron trifluoride is usually approximately 99.5% pure. The common impurities are air, silicon tetrafluoride, and sulfur dioxide. An excellent procedure for sampling and making a complete analysis of gaseous boron trifluoride has been developed (57).

6. Health and Safety Factors

Boron trifluoride is primarily a pulmonary irritant. The toxicity of the gas to humans has not been reported (58), but laboratory tests on animals gave results ranging from an increased pneumonitis to death. The TLV is 1 ppm (59, 60). Inhalation toxicity studies in rats have shown that exposure to BF_3 at 17 mg/m^3 resulted in renal toxicity, whereas exposure at 6 mg/m^3 did not result in a toxic response (61). Prolonged inhalation produced dental fluorosis (62). High concentrations burn the skin similarly to acids such as HBF_4 and, if the skin is subject to prolonged exposure, the treatment should be the same as for fluoride exposure and hypocalcemia. No chronic effects have been observed in workers exposed to small quantities of the gas at frequent intervals over a period of years.

7. Uses

Boron trifluoride is an excellent Lewis acid catalyst for numerous types of organic reactions. Its advantages are ease of handling as a gas and the absence of undesirable tarry by-products. As an electrophilic molecule, it is an excellent catalyst for Friedel-Crafts and many other types of reactions (63–65) (see Friedel-crafts reactions).

$BF_3 \cdot HF$ compositions have been reported to act as super acids in catalyzing condensation reactions (66). BF_3-catalyzed preparation of 1- or 2-naphthol is reported to be regioselective (67). Dehydration reactions may also be regioselective (68). Selected fluorinations may be catalyzed by BF_3 using HF as the fluoride source (69). BF_3 is widely used for the preparation of hydrocarbon resins (70), tall oil (qv) resins (71), and tackifier resins (72). Alpha olefin-based synthetic lubricants are commonly made using BF_3-based catalysts (73–75). BF_3 is widely used as a polymerization catalyst (76–78). A developing use for BF_3 is as an ion implant medium for semiconductor materials (79). BF_3 may be used as a chemical reagent for the manufacture of fluoroboro complexes (80), boron nitride [10043-11-5] (81), and boron trichloride [10294-34-5] (82). Carboxylic acids and esters may be prepared by reacting CO with olefins in the presence of BF_3-containing catalysts (83).

In addition, boron trifluoride and some of its adducts have widespread application as curing agents for epoxy resins (qv), and in preparing alcohol-soluble phenolic resins (qv) (41).

Boron trifluoride catalyst is used under a great variety of conditions either alone in the gas phase or in the presence of many types of promoters. Many boron trifluoride coordination compounds are also used.

Boron trifluoride catalyst may be recovered by distillation, chemical reactions, or a combination of these methods. Ammonia or amines are frequently added to the spent catalyst to form stable coordination compounds that can be separated from the reaction products. Subsequent treatment with sulfuric acid releases boron trifluoride. An organic compound may be added that forms an adduct more stable than that formed by the desired product and boron trifluoride. In another procedure, a fluoride is added to the reaction products to precipitate the boron trifluoride which is then released by heating. Selective solvents may also be employed in recovery procedures (see Catalysts, regeneration).

Boron trifluoride is also employed in nuclear technology by utilizing several nuclear characteristics of the boron atom. Of the two isotopes, ^{10}B and ^{11}B, only ^{10}B has a significant absorption cross section for thermal neutrons. It is used in $^{10}BF_3$ as a neutron-absorbing medium in proportional neutron counters and for controlling nuclear reactors (qv). Some of the complexes of trifluoroborane have been used for the separation of the boron isotopes and the enrichment of ^{10}B as $^{10}BF_3$ (84).

Boron trifluoride is used for the preparation of boranes (see Boron compounds). Diborane is obtained from reaction with alkali metal hydrides; organoboranes are obtained with a suitable Grignard reagent.

Boron trifluoride has been used in mixtures to prepare boride surfaces on steel (qv) and other metals, and as a lubricantfor casting steel (see Lubrication and lubricants).

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FRANCIS EVANS
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