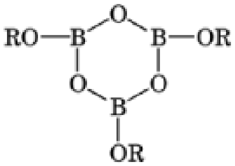
Kirk-Othmer Encyclopedia of Chemical Technology.

BORIC ACID ESTERS

In 1846 the first boric acid esters were prepared by reacting aliphatic alcohols and boron trichloride (1). The chemistry and properties of boric acid esters from that first paper through 1961 have been extensively reviewed (2). Short reviews were published in 1964, 1978, and two in 1980 (3, 4).

The general formula for boric acid esters is $B(OR)_3$. The lower molecular weight esters such as methyl, ethyl, and phenyl are most commonly referred to as methyl borate [121-43-7], ethyl borate [150-46-9], and phenyl borate [1095-03-0], respectively. Some of the most common boric acid esters used in industrial applications are listed in Table 1. The nomenclature in the boric acid ester series can be confusing. The IUPAC committee on boron chemistry has suggested using trialkoxy- and triaryloxyboranes (5) for compounds usually referred to as boric acid esters, trialkyl (or aryl) borates, trialkyl (or aryl) orthoborates, alkyl (or aryl) borates, alkyl (or aryl) orthoborates, and in the older literature as boron alkoxides and aryloxides. Cyclic boric acid esters, which are trimeric derivatives of metaboric acid (HBO_2), are known as boroxines (**1**).



(**1**)

1. Physical Properties

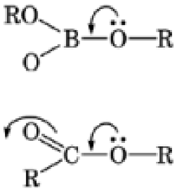
Most reported boric acid esters are trialkoxy or triaryloxy boranes. The esters range from colorless low boiling liquids to solids that possess high melting points. Boric acid esters usually have an odor similar to the hydroxy compound from which they are derived. A more complete description of the physical properties of the compounds, given in Table 1, has been published (2). The density and viscosity (6), surface tension (7), vapor pressure, and other thermodynamic data (8, 9) of a number of common boric acid esters have been summarized. In addition, information on the dipole moments of boric acid esters has been published (10).

The trialkoxy(aryloxy)boranes are typically monomeric, soluble in most organic solvents, and dissolve in water with hydrolysis to form boric acid and the corresponding alcohol and phenol. Although the rate of hydrolysis is usually very fast, it is dependent on the bulk of the alkyl or aryl substituent groups bonded to the boron atom. Secondary and tertiary alkyl esters are generally more stable than the primary alkyl esters. The boron atom in these compounds is in a trigonal coplanar state with sp^2 bond hybridization. A vacant p orbital exists along the threefold axis perpendicular to the BO_3 plane. This vacant p orbital readily accepts adjacent unshared electrons, electronically acting in a manner similar to the carbonyl group of an organic ester.

Table 1. Properties of Boric Acid Ester Derivatives

Compound name	CAS Registry Number	Molecular formula	Mp, °C	Bp, °C[a]	d_4^t	n_D[b]
trimethyl borate	[121-43-7]	$B(OCH_3)_3$	−29	68.0–68.5	0.920^{20}	1.3548
trimethyl borate azeotrope		$B(OCH_3)_3 \cdot CH_3OH$		54.3	0.8804^{25}	1.3472
triethyl borate	[150-46-9]	$B(OCH_2CH_3)_3$	84.8	117–119	0.859^{26}	1.3723
triethyl borate azeotrope		$B(OCH_2CH_3)_3 \cdot 7.75CH_3CH_2OH$		76.6		
tri-*n*-propyl borate	[688-71-1]	$B(OCH_2CH_2CH_3)_3$		176–179	0.356^{24}	1.3933
triisopropyl borate	[5419-55-6]	$B[OCH(CH_3)_2]_3$		139–140	0.815^{23}	1.3750
tri-*n*-butyl borate	[688-74-4]	$B(OCH_2CH_2CH_2CH_3)_3$		227	0.856^{25}	1.4077
triphenyl borate	[1095-03-0]	$B(OC_6H_5)_3$	80–90[c]	360–370 224–230[d]		
tricresyl borate[e]	[26248-41-9]	$B(OC_6H_4CH_3)_3$		185–200[f]		
trimethoxyboroxine (**1**, R = CH_3)	[102-24-9]	$C_3H_9B_3O_6$		dec	1.2286^{25}	
triisopropoxyboroxine (**1**, R = i–CH_73)	[10298-87-0]	$C_9H_{21}B_3O_6$	52–54	235–239 dec		
2,2′-oxybis[4,4,6-trimethyl-1,3,2-dioxaborinane] (**2**)	[1497-50-8]			114–115[f]	1.013^{24}	1.4308
2,2′-[1-methyl-1,3-propanediyl]bis(oxy)-bis[4-methyl-1,3,2-dioxaborinane] (**3**)	[2665-13-6]	$C_{12}H_{24}B_2O_6$		207–213[d]	1.071^{25}	1.4464[g]
2,2′-[1,1,3-trimethyltrimethylene-dioxy]bis[4,4,6-trimethyl-1,3,2-dioxaborinane] (**4**)	[26545-48-2]	$C_{18}H_{40}B_2O_8$		274–276 170–172[h]	0.932^{21}	1.4381
triethanolamineborate	[283-56-7]	$B(OCH_2CH_2)_3N$	235–239			

[a] At 101.3 kPa (760 mm Hg) unless otherwise indicated.
[b] At 25°C unless otherwise indicated.
[c] Triphenyl borate has been reported to melt at temperatures from 38 to 146°C. Most values are in the range of 80–90°C.
[d] At 2.3 kPa (17 mm Hg).
[e] Mixture of the m- and p-isomers.
[f] At 0.27 kPa (2 mm Hg).
[g] At 17°C.
[h] At 2.7 kPa (20 mm Hg).



This comparison is further demonstrated by observing that the chemistry of both trigonal boron and carbonyl carbon are strongly influenced by the ready acceptance of attacking nucleophiles.

$$H_3BO_3 + 3\,ROH \rightleftharpoons (RO)_3B + 3\,H_2O \qquad (1)$$

$$R'COOH + ROH \rightleftharpoons R'COOR + H_2O \qquad (2)$$

2. Chemical Properties

Alkyl boric acid esters derived from straight-chain alcohols and aryl boric acid esters are stable to relatively high temperatures. Methyl borate is stable to 470°C (11). Trialkoxyboranes from branched-chain alcohols are much less stable, and boranes from tertiary alcohols can even decompose at 100°C (12). Decomposition of branched-chain esters leads to mixtures of olefins, alcohols, and other derivatives.

Boric acid esters are very susceptible to hydrolysis in the presence of water, or in some cases atmospheric moisture. Partially hydrolyzed derivatives such as $(RO)_2BOH$ have not been isolated except in special cases involving large substituent groups. The comparative hydrolysis rates for a number of borate esters has been reported (13). When borate esters are hydrolyzed, the boron atom is transformed from an sp^2 trigonal coplanar configuration in the ester to an sp^3 hybridization in a tetrahedral intermediate. Therefore, the most obvious rate-determining factors in the transformation are the steric requirements of the tetrahedral species. Tri-*n*-propanolamine borate is somewhat stable, presumably because of the compactness of the transannular form that completely precludes the inversion to the necessary tetrahedral configuration on entry of water. Most hydrolytically stable derivatives contain bulky alcohol or phenolic groups dispersed both above and below the BO_3 plane. Some particularly stable examples are tri-*t*-amyl borate [22238-22-8], $C_{15}H_{33}BO_3$, tri-2-cyclohexylcyclohexyl borate [5440-19-7], $C_{36}H_{63}BO_3$, and the general class of hindered phenolic borates. Borate esters, in which the boron atom is coordinated through its vacant orbital with an internal nitrogen atom containing a free electron pair, also exhibit good hydrolytic stability. Two examples are triethanolamine borate and triisopropylamine borate [101-00-8], $C_9H_{18}BNO_3$. Nuclear magnetic resonance (nmr) (14) and infra red (ir) spectroscopy (15, 16), as well as mass spectrometry (16, 17) have been used to help elucidate the structures of various borate esters.

3. Preparative Methods

There are a number of methods used for the preparation of borate esters.

3.1. From Boric Acid

The most common method for the preparation of trialkoxy- and triaryloxyboranes is the esterification of boric acid using three moles of an alcohol or phenol.

$$B(OH)_3 + 3\ ROH \rightleftharpoons B(OR)_3 + 3\ H_2O \qquad (3)$$

The equilibrium shown in equation 3 normally lies far to the left. Usually the water formed is removed by azeotropic distillation with excess alcohol or a suitable azeotroping solvent such as benzene, toluene, or various petroleum distillate fractions. The procedure used depends on the specific ester desired. Preparation of methyl borate and ethyl borate is complicated by the formation of low boiling azeotropes (Table 1) which are the lowest boiling constituents in these systems. Consequently, the ester–alcohol azeotrope must be prepared and then separated in another step. Some of the methods that have been used to separate methyl borate from the azeotrope are extraction with sulfuric acid and distillation of the enriched phase (18), treatment with calcium chloride or lithium chloride (19, 20), washing with a hydrocarbon and distillation (21), fractional distillation at 709 kPa (7 atmospheres) (22), and addition of a third component that will form a low boiling methanol azeotrope (23).

3.2. From Boric Oxide and Alcohol

To avoid removing water, boric oxide, B_2O_3, can be used in place of boric acid. The water of reaction (eq. 4) is consumed by the oxide (eq. 5). Because boric acid reacts with borates at high temperatures, it is necessary to filter the reaction mixture prior to distillation of the product. Only 50% of the boron can be converted to ester by this method. In cases where this loss can be tolerated, the boric oxide method is convenient. This is particularly true for methyl borate and ethyl borate preparation because formation of the undesirable azeotrope is avoided.

$$\frac{1}{2}\,B_2O_3 + 3\,ROH \longrightarrow B(OR)_3 + \frac{3}{2}\,H_2O \qquad (4)$$

$$\frac{1}{2}\,B_2O_3 + 3\,H_2O \longrightarrow 2\,B(OH)_3 \qquad (5)$$

The esterification of boric oxide does not require the removal of water. However, if high yields based on boron are desired, six or more moles of alcohol must be used and the water must be removed.

$$B_2O_3 + 6\,ROH \longrightarrow 2\,B(OR)_3 + 3\,H_2O \qquad (6)$$

The rate of ester production is dependent on the removal of water (or ester) from the reaction, and consequently on the azeotroping agent used. The rate of ester production is greater using boric oxide than using boric acid and a given azeotroping agent.

3.3. Transesterification

Transesterification is another method that does not require the removal of water. If a borate of lower molecular weight is available, higher molecular weight esters may be prepared by reaction of the appropriate higher molecular weight alcohol.

$$B(OR)_3 + 3\,R'OH \rightleftharpoons B\left(OR'\right)_3 + 3\,ROH \qquad (7)$$

The liberated alcohol must be lower boiling than any other species present so that it may be distilled at a convenient rate and drive the reaction to completion. It is possible to prepare esters of lower molecular weight from a higher member by using a large excess of alcohol and rapid inefficient distillation, but the method is generally not practical.

Steric factors are important in transesterification reactions. With a given alcohol, primary alkyl borates react at a rate too fast to measure, secondary alkyl borates react at measurable rates, and *tert*-butyl borate reacts very slowly.

A continuous process has been developed for preparing borate esters using transesterification (24). Another modification of this method has been reported where use of molecular sieves (qv) to absorb the low boiling alcohol is used rather than distillation (25).

3.4. From Boron Halides

Using boron halides is not economically desirable because boron halides are made from boric acid. However, this method does provide a convenient laboratory synthesis of boric acid esters. The esterification of boron halides with alcohol is analogous to the classical conversion of carboxylic acid halides to carboxylic esters. Simple mixing of the reactants at room temperature or below in a solvent such as methylene chloride, chloroform, pentane, etc, yields hydrogen halide and the borate in high yield.

$$BCl_3 + 3\ ROH \longrightarrow (RO)_3\,B + 3\ HCl \qquad (8)$$

The reaction is irreversible and can be used to synthesize aliphatic and aromatic esters. In addition, there are no complications involving water removal or azeotrope formation. Boron tribromide can be used in place of boron trichloride, but the bromide has a stronger tendency to halogenate the alkyl group of the alcohol (26). Boron trifluoride does not give the ester, but gives either a complex or dehydrated product.

3.5. Miscellaneous Methods

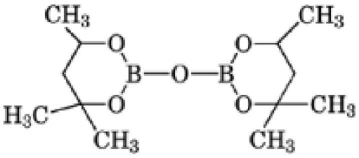
Other methods for preparing borate esters have also been described (2, 3). These include alcoholysis of borax or other alkali metal borates in either neutral or acidic media, disproportionation, decomposition or reaction of alkoxyhaloboranes, and disproportionation of trialkoxyboroxines. A simple and convenient method for synthesizing trialkoxyboranes and trialkoxyboroxines using calcium hydride as a drying agent has been published (27). It is claimed that a variety of borate esters containing sterically hindered alcohols can be prepared by using this procedure.

4. Manufacture and Economic Aspects

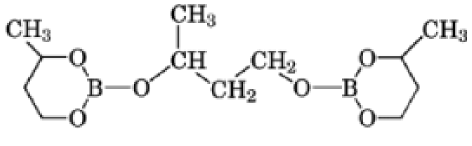
There are relatively few producers of boric acid esters in the United States. Eight domestic producers of these compounds (28) are: Anderson Development Co., Akzo America, Inc., E. I. du Pont de Nemours & Co., Inc., Eagle-Picher Industries, Inc., The Gas Flux Co., Morton International, Callery Chemical Co., and U.S. Borax & Chemical Corp. In addition, Rhone-Poulenc Chemicals, Manchester, UK, produces commercial quantities of selected boric acid esters.

Methyl borate is believed to be the boric acid ester produced in the largest quantity, approximately 8600 metric tons per year (28). Most methyl borate is produced by Morton International and used captively to manufacture sodium borohydride [16940-66-2]. Methyl borate production was studied in detail during the 1950s and 1960s when this compound was proposed as a key intermediate for production of high energy fuels. Methyl borate is sold as either the pure compound or as the methanol azeotrope that consists of approximately a 1:1 molar ratio of methanol to methyl borate.

A combination of the two dioxaborinanes, (**2**) and (**3**), is marketed as a fuel microbiocide by Hammonds Fuel Additives, Inc., Houston, Texas, under the trademark BIOBOR JF. Annual U.S. production and consumption is estimated at 140–230 metric tons (28).

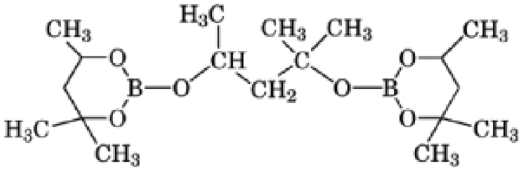


(**2**)



(3)

U.S. Borax Research Corp., Anaheim, California, markets several borate esters under the trademark BORESTER. These include triethanolamine borate (BORESTER 20), tricresyl borate (m- and p-isomers) (BORESTER 8), and the biborate (**4**) (BORESTER 7). Whereas the chemical name for (**4**) is given in Table 1, it is commonly referred to as trihexylene glycol biborate [26545-48-2] and is prepared by the reaction of two moles of boric acid and three moles of hexylene glycol.



(4)

Processes to produce boric acid esters are based on the azeotropic removal of water from a mixture of the appropriate alcohol, phenol, or glycol, and boric acid. A suitable hydrocarbon azeotroping agent is used to help remove the water. The water is removed continuously by using a condenser that allows continuous return of the solvent to the reaction vessel. For some borate esters, such as the glycol borates, distillation can result in decomposition. As a result the undistilled bottoms product is often used commercially. If further purification is necessary, these products can be vacuum distilled.

Prices for borate esters vary depending on the ester and the quantity. Whereas prices are usually between \$3 and 9/kg, some esters are priced as high as \$30–40/kg (28, 29). U.S. imports and exports of the various boric acid esters is negligible (28).

5. Handling and Shipping

Procedures for shipping boric acid esters depend on the particular compound. Aryl borates produce phenols when in contact with water and are therefore subject to shipping regulations governing such materials and must carry a Corrosive Chemical label. Lower alkyl borates are flammable, flash points of methyl, ethyl, and butyl borates are 0, 32, and 94°C, respectively, and must be stored in approved areas. Other compounds are not hazardous, and may be shipped or stored in any convenient manner. Because borate esters are susceptible to hydrolysis, the more sensitive compounds should be stored and transferred in an inert atmosphere, such as nitrogen.

The usual containers for shipping are glass for small quantities, and steel cans, drums, or tank cars for bulk items. Over a period of time, moisture passes through the walls of some plastic containers. If this occurs, the more hydrolytically unstable borate esters may hydrolyze. Thus caution should be used when storing borate esters in plastic. In addition, shipping in metal cans or drums is not acceptable where hydrolysis can lead to a corrosive product, such as a halogenated alcohol.

6. Analytical and Test Methods

For the most part boric acid esters are quantitated by hydrolysis in hot water followed by determination of the amount of boron by the mannitol titration (see Boron compounds, boric oxide, boric acid and borates). Separation of and measuring mixtures of borate esters can be difficult. Any water present causes hydrolysis and in mixtures, as a result of transesterification, it is possible to have a number of borate esters present. For some borate esters, such as triethanolamine borate, hydrolysis is sufficiently slow that quantitation by hydrolysis and titration cannot be done. In these cases, a sodium carbonate fusion is necessary.

7. Health and Safety

The toxicity of a few boric acid esters has been summarized (30). In general the toxicities are directly related to the toxicity of the alcohol or phenol produced on hydrolysis. Methyl borate has an oral rat LD_{50} of 6.14 mL/kg in a range finding test (31) and the percutaneous LD_{50} for the rabbit of 1.98 mL/kg. In earlier work (32), the oral LD_{50} for the rat was 2.82 mL/kg; the intraperitoneal LD_{50} was 3.2 mL/kg. It has been shown that the mouse is more susceptible to these compounds than the rat. Methyl borate was found to be moderately irritating in an ocular toxicity test using rabbits (31, 32) but only mildly irritating to skin (31).

8. Uses

8.1. Production of Sodium Borohydride

In the pulp and paper industry, sodium borohydride is used to generate sodium hydrosulfite (sodium dithionite), a bleaching agent, from sodium bisulfite. Methyl borate is used as an intermediate in the production of sodium borohydride (33).

$$(CH_3O)_3\,B + 4\,NaH \longrightarrow NaBH_4 + 3\,NaOCH_3 \qquad (9)$$

8.2. Gas Fluxing

The methyl borate azeotrope is used as a gaseous flux for welding and brazing. The Gas Flux Co., Elyria, Ohio, manufactures the methyl borate azeotrope for their own use. The azeotrope acts as a volatile source of boric oxide and is introduced directly into the gas stream as a flux for the surfaces to be joined in the welding process. The European automobile industry is the primary user of this process, though there may be some usage for this purpose in the United States.

8.3. Polymer Additives

The addition of borate esters to polymers has been thoroughly investigated. Though the patent literature in this field has expanded, the actual usage of borate esters for this application is believed to be small. Studies have been done indicating that borate esters can be used as curing agents or hardeners in epoxy systems (see Epoxy resins). However, there is no indication that borate esters are being used in large quantities for this application. Some patents describing this application are given (34–39).

Borate esters have been used as antioxidants (qv) (40). Because of commercial inaccessibility and high cost their commercial use has not been extensive, although interest in this use does exist (41, 42).

8.4. Hydraulic Fluids and Lubricants

The use of borate esters in hydraulic fluids (qv) and lubricants (see Lubrication and lubricants) has been described in numerous patents (40, 43, 44). A variety of borate esters have been described that can be used as multifunctional lubricant additives having antiwear and antifriction properties (45).

8.5. Biocides

Many boric acid esters have been tested against microorganisms. BIOBOR JF is effective against microorganisms that contaminate hydrocarbon fuel. This product, which contains glycol borates (**2**) and (**3**), has been used successfully in jet fuels, heating oils, and various diesel applications. A variety of boric acid esters of various alcohols have been screened for antimicrobial activity in spent coolants of water-based cutting fluids. Some of the compounds tested showed good antimicrobial activity (46).

8.6. Hydrocarbon Oxidation

The oxidation of hydrocarbons (qv) and hydrocarbon derivatives can be significantly altered by boron compounds. Several large-scale commercial processes, such as the oxidation of cyclohexane to a cyclohexanol–cyclohexanone mixture in nylon manufacture, are based on boron compounds (see Cylcohexanol and cyclohexanone; Fibers, polyamide). A number of patents have been issued on the use of borate esters and boroxines in hydrocarbon oxidation reactions, but commercial processes apparently use boric acid as the preferred boron source. The literature in this field has been covered through 1967 (47). Since that time the literature consists of foreign patents, but no significant applications have been reported for borate esters.

8.7. Miscellaneous Uses

Research has demonstrated that fabrics could be treated with vaporous trimethyl borate (70% azeotrope) resulting in textiles (qv) that are smoulder resistant (48).

Borates can be used as wood preservatives. Technology is being developed to treat wood (qv) with trimethyl borate in a vapor-treating process similar to that used for textiles (qv) (49). This method is based on impregnation using a preservative vapor. Gaseous trimethyl borate reacts with moisture in wood or wood products to form solid boric acid. The boric acid formed acts as a wood preservative preventing damage from wood-destroying fungi and insects. Shaped rods, pellets, or tablets composed of inorganic borates have also been used as wood preservatives. Borate esters have also been proposed for this use (50).

Isopropyl borate is used primarily in the production of catalysts for polyolefins and as an antiscratch agent for glass containers. *N*-Butyl borate is used as an adhesion promoter and had been used in fire retardant compositions.

Various borate esters are chemosterilantsfor house flies (51). Tributyl borate, available from Eagle-Picher, Miami, Oklahoma, which is isotopically enriched in boron-10, is being used as a chemical precursor in the synthesis of pharmacologically active boron compounds suitable for boron neutron capture therapy.

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