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BORON HYDRIDES, HETEROBORANES, AND THEIR METALLA DERIVATIVES (COMMERCIAL ASPECTS)

Boranes, B–H-containing compounds, having proven commercial value are the tetrahydroborates, several borane complexes, and some hetereoboranes.

1. Tetrahydroborates

Sodium tetrahydroborate [16940-66-2], $NaBH_4$, more commonly called sodium borohydride, is the most widely used commercial boron hydride. The largest manufacturer is Morton International Specialty Chemicals Group, which has two plants in the United States and one in Europe (1). Oy Nokia Ab Chemicals (FN) (2) also produces commercial quantities. Smaller producers include Farbenfabrik Bayer A.G. and Chemetall Gmbh in Germany (2).

Sodium borohydride is available as a 12% solution in caustic soda and in solid form either as powder or pellets (3). The predominant form produced is the solution, the DOT shipping classification for which is corrosive liquid. Forms of packaging are 18.9-L pails, 208.2-L drums, and either tank truck or tank car for bulk shipments. 1991 pricing for the solution form was $40.34/kg of borohydride contained. Solid sodium borohydride, a white powder packaged in polyethylene bags in metal containers, was priced at $48.39/kg.

Solid sodium borohydride does not ignite upon contact with moisture and is not shock sensitive. These characteristics allow it to be handled safely in air. Because it does liberate hydrogen upon contact with water it should be handled with care.

The predominant use for sodium borohydride is in wood pulp (qv) bleaching (4–7). The next largest commercial use is as a reducing agent of functional groups in organic synthesis (3). Examples are the reduction of aldehydes (qv) and ketones (qv) to the corresponding alcohols. A significant application in pharmaceutical synthesis is the stereospecific and selective reduction in steroid production (8). Other commercial applications include control of odors in alcohols (9), decolorization of ketones (10) and polyols (11), and electroless plating (qv) of nickel (12), gold (13, 14), and other metals for electronic and aerospace applications. An important application is the removal of toxic or heavy metals from process waste streams and spent plating solutions (15–17).

Sodium borohydride reacts with Lewis acids in nonprotic solvents to yield diborane [19287-45-7], B_2H_6 (18), which can then be used to generate other useful organoboranes such as amine boranes, alkyl boranes, and boron hydride clusters.

Other tetrahydroborates of less commercial importance are lithium borohydride [16949-15-8], $LiBH_4$, and potassium borohydride [13762-51-1], KBH_4.

2. Borane Complexes

Borane complexes are the most widely used commercial boron compounds, after sodium borohydride. Examples used in organic synthesis are amine borane complexes and borane complexes of tetrahydrofuran and dimethyl sulfide.

Dimethylamine borane [74-94-2], $C_2H_7N{\cdot}BH_3$, *t*-butylamine borane [7337-45-3], $C_4H_{11}N{\cdot}BH_3$, and pyridine borane [110-51-0], $C_5H_5N{\cdot}BH_3$, are the most common amine borane complexes. The stability, ease of handling, solubility in a variety of protic and aprotic solvents, and ability to chemo- and stereoselectively reduce aldehydes and ketones (19–21) of these complexes has lead to their use as reducing agents in organic synthesis. Other applications include the development of photographic film and electroless plating (22–24) of metals such as Cu, Ni, and Au.

Tetrahydrofuran borane [14044-65-6], $C_4H_8O{\cdot}BH_3$,and dimethyl sulfide borane [13292-87-0], $C_2H_6S{\cdot}BH_3$, have found use in organic synthesis as reducing agents and hydroborating agents (25, 26). Diisopinocampheylchloroborane [85116-37-6], $C_{20}H_{34}BCl$ (27) and oxazaborolidines, C_2H_4BNORR' (28) are important reagents for chiral synthesis.

2.1. Potential Uses of $B_{12}H_{11}SH^{2-}$

Although not commercial as yet, an interesting potential use of borane compounds as therapeutic agents for the treatment of inoperable cancerous tumors is being developed (see Chemotherapeutics, anticancer). Boron neutron capture therapy (bnct) involves the uptake of boron compounds enriched with the boron-10 [14798-12-0], ^{10}B, isotope, selectively accumulating in cancerous tumors (29). Low energy thermal or epithermal neutrons penetrate healthy tissue, reacting with ^{10}B in the tumor releasing an alpha particle. This high energy alpha particle selectively destroys the tumor cells. One particular borane, disodium mercaptoundecahydrododecaborate [12448-24-7], $Na_2B_{12}H_{11}SH$, can across the blood–brain barrier and is taken up by Grade IV glioblastomas (brain tumors). This borane has been used in Japan (30) to treat tumors clinically. Other tumors, such as malignant melanoma (31), are being treated with borono-phenylalanine [74923-16-3], $(OH)_2{}^{10}BC_6H_4CH_2CHNH_2COOH$, a boron containing amino acid. There is also research into using boron containing macromolecules such as borated monoclonal antibodies or borated porphrins for treatment of other tumors (32).

3. Heteroboranes

Heteroboranes, compounds where one or more of the cage borons are replaced by a main group element (33), are not themselves commercially available. However, carborane siloxanes containing *m*-carborane [16986-21-6], $C_2H_{12}B_{10}$, are available under the trade name of Dexsil for the stationary phase in gas–liquid chromotography (qv) (34). The carborane, 1,7-dicarba-*closo*-dodecaborane(10) (35), contributes enhanced chemical and thermal stability to the siloxane polymer.

Potential areas of application for carboranes include adhesives, gaskets, and O-rings (27). Research has been reported on improving the oxidation resistance and strength of carbon materials by coating with a carborane siloxane polymer (36).

Two alkyl derivatives of the $C_2B_{10}H_{12}$ carboranes were developed for propellant additives: *n*-hexyl carborane (*n*HC) [20740-05-0], $C_2B_{10}H_{11}C_6H_{13}$ (37–39) and carboranyl methyl propionate (CMP) [62906-37-0], $C_2B_{10}H_{11}CH_2O_2CCH_2CH_3$ (40). These two carboranes can be synthesized from decaborane(14), $B_{10}H_{14}$. Decaborane(14) [17702-41-9], $B_{10}H_{14}$, has been synthesized from diborane (9), pentaborane[19624-22-7], B_5H_9 (41–43) and sodium borohydride (44). At the manufacturing level, a pyrolitic process to produce decaborane from diborane has been reported (45). A production plant having the capacity to produce ton qualities of *n*HC from decaborane(14) was operated in the 1980s for the U.S. Army. The production of CMP and other derivatives of decaborane(14) are also feasible in this plant which is inactive as of this writing.

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