

Review of Chemical Processes for the Synthesis of Sodium Borohydride

Millennium Cell Inc.

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Introduction

Sodium borohydride (NaBH_4) is a versatile reducing agent used in a number of industrial processes. Major applications include organic and pharmaceutical synthesis, wastewater treatment, and paper pulp bleaching. Additionally, NaBH_4 can be used to store and generate hydrogen gas via a hydrolysis reaction.

It is estimated that in order for sodium borohydride to be widely utilized as an energy storage medium in a hydrogen economy, the cost must be reduced by at least an order of magnitude from its present price. The manufacturing process of NaBH_4 has largely remained the same since it became commercial in the 1950s and is based on synthetic pathways developed by Brown and Schlesinger.¹

In addition to the Brown-Schlesinger process, there are several alternatives that may become economically viable. However, uncertainties in market demand and raw material supply make it unclear which, if any, of the possible options could lead to the greatest cost reduction. It has been many years since any significant research has been actively pursued in many of these methods. A reinvestigation of some of these synthetic routes could lead to modifications that will result in a substantial cost reduction.

This paper is intended to provide a brief review of the sodium borohydride synthesis processes that have been either reported in the literature or studied in some detail at Millennium Cell Inc.. The reactions examined are grouped into six sections, each of which covers a different approach. Section 1 considers synthetic processes that are or have been in operation on an industrial scale. Section 2 looks at potential routes to sodium borohydride based on direct use of carbon, hydrocarbon, or hydrogen reducing agents. Section 3 describes several multi-step thermo-chemical reaction pathways that were developed to address the inadequacies of the direct reactions discussed in Section 2. This family of reactions takes advantage of the characteristic disproportionation chemistry of boron compounds. Section 4 discusses reaction pathways that utilize metals as reducing agents, while Section 5 covers the use of alternative energy sources such as microwaves and nuclear radiation. Finally, in Section 6, electrochemical methods are briefly discussed.

Section 1: Commercially Practiced Sodium Borohydride Synthesis Process

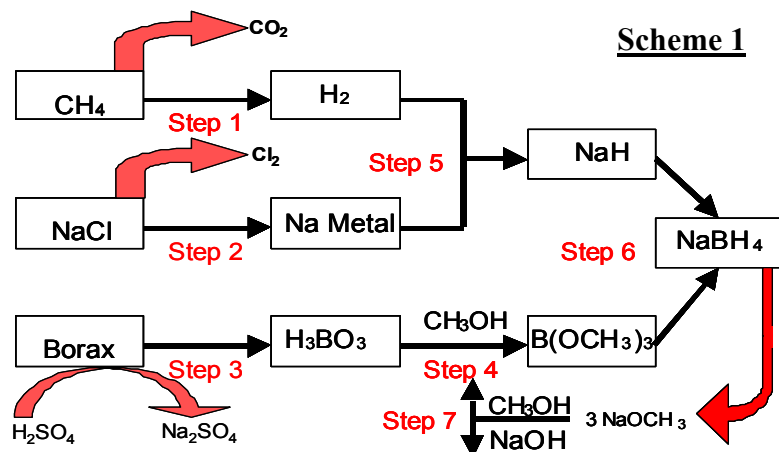
The Brown-Schlesinger Process

The Brown-Schlesinger process¹ is the process in use today for making sodium borohydride.² The key step of the process is the reaction between sodium hydride (NaH) and trimethylborate (B(OCH₃)₃, TMB). When taking into account the steps of raw materials production, the overall NaBH₄ process consists of seven steps:

1. Steam Reforming of Methane to Make Hydrogen
2. Electrolysis of Sodium Chloride to Make Sodium Metal
3. Refining of Borax to Make Boric Acid
4. Converting Boric Acid to Trimethylborate with Methanol
5. Reaction of Sodium Metal and Hydrogen to Make Sodium Hydride
6. Combining Sodium Hydride and Trimethylborate to Make Sodium Borohydride
7. Recycling Sodium Methoxide By-Product to Methanol



Steam reformation of methane is a mature technology practiced at large scale in many industries for many purposes. At this level of development, only small incremental improvements may be expected and such improvements are unlikely to have a significant impact on cost reduction and improved energy efficiency in the manufacture of sodium borohydride. Presently, the reformation process is performed on the site of sodium borohydride manufacturing plant.



Electrolysis of sodium chloride is also a mature technology, but there is room for improvement. Since the majority of the energy input in the Brown-Schlesinger Process occurs at

this step (Step 2), any improvements could substantially impact the cost of manufacturing sodium borohydride. First, more energy is required to electrolyze sodium chloride to produce sodium metal than the electrolysis of a number of other sodium salts. Further, the electrolysis of sodium chloride is presently not integrated with the production of sodium borohydride, and sodium metal is instead purchased from an outside manufacturer. Due to the reactive nature of metallic sodium, there is a significant cost associated with the transportation of the sodium raw material to the borohydride production site. In-house sodium manufacture will provide benefits such as significant shipping cost savings, efficient process integration, and safety.

The refining of borax to boric acid is a straightforward procedure, but another with some room for improvement. The mineral borax is treated with sulfuric acid and the boron precipitates from the reaction and is collected as boric acid.³ Moving the procedure in-house will eliminate some cost and allow for the choice of a more desirable acid, which may result in a more industrially useful by-product than sodium sulfate. Millennium Cell has developed one alternative solution, wherein borax is treated with carbon dioxide and methanol to directly obtain trimethylborate.⁴ This combines Steps 3 and 4, and eliminates sodium sulfate as a side product in favor of sodium carbonate, which is a more industrially valuable chemical.

While Step 4 is straightforward, combining it with Step 3 would save on process costs. A difficulty with the production of trimethylborate is that the borate and methanol distill off together as an azeotrope, and a further separation step is required to isolate trimethylborate.⁵ The separation, however, is not listed as a distinct step of the Brown-Schlesinger process.

Step 5 is the direct reaction of hydrogen gas with sodium metal in a mineral oil dispersion. This is followed by Step 6 where sodium hydride reacts with trimethylborate to make sodium borohydride and sodium methoxide. This reaction likely occurs through a disproportionation, wherein the simple acid-base adduct sodium trimethoxyborohydride ($\text{Na}[\text{HB}(\text{OCH}_3)_3]$) forms initially and then disproportionates into sodium borohydride and sodium tetramethylborate ($\text{NaB}(\text{OCH}_3)_4$). Sodium tetramethylborate is a simple acid-base adduct of sodium methoxide and trimethyl borate. In the presence of excess sodium hydride, the sodium tetramethyl borate will continue to exchange with sodium hydride until all of the borate has been converted to borohydride. Detailed mechanistic elucidation of this reaction was presented by Schlesinger in his 1953 paper.¹

Step 6, the borohydride-generating reaction, takes place with 94% yield. The fact that this key step takes place in high yield with relatively low loss of free energy (167 kJ/mol NaBH₄) suggests that the synthesis of sodium borohydride by the Brown-Schlesinger route is not intrinsically poor with respect to energy, and may yet form the basis of an efficient route to sodium borohydride if the predecessor steps are improved.

Step 7 is the quenching of Step 6 reaction products with water. Sodium borohydride and sodium methoxide are insoluble in mineral oil and are easily separated from the oil by dissolving them in water. Sodium methoxide reacts with water to make sodium hydroxide and methanol. The latter is recovered by distillation and recycled back into Step 4. The sodium hydroxide is either sold along with the borohydride in an aqueous mixture, or extracted in the production of pure solid sodium borohydride and sold as a by-product caustic.

Much of the cost inefficiency associated with the Brown-Schlesinger Process results from the use of raw materials that are themselves products of costly or inefficient processes, carried out separately by a number of producers. It can thus be deduced that integration of the process steps from start to finish will impact the bottom line cost. The energy inefficiency of the Brown-Schlesinger Process derives almost entirely from the sodium metal manufacture in which greater than 50% of the electrical energy input is lost as heat. A more efficient sodium process could eliminate much of this wasted energy. Generation of sodium hydride from the elements is exothermic showing some additional energy loss, as does the borohydride-manufacturing step. These inefficiencies cannot be eliminated unless the underlying chemistry is changed, but are small compared to the energy penalty of the sodium-manufacturing step.

The Bayer Process

A second process that has been employed on a commercial scale to make sodium borohydride is a process referred to as the Bayer Process.^{6,7} The Bayer Corporation employed this process at one time to supply the internal sodium borohydride needs of that company and is not known to have sold sodium borohydride externally. The Bayer Process is a one-pot synthesis combining borax, metallic sodium, and hydrogen in the presence of silica to produce sodium borohydride.



The reaction takes place at about 700 °C. Borax, Na₂B₄O₇, melts at about 740 °C, and sodium metal is a liquid at the reaction temperature, therefore it is likely that reaction (2a) takes place in a liquid phase. It is rather surprising that this synthesis works at all, as the decomposition temperature of sodium borohydride is listed in literature sources as 400 °C, with rapid decomposition taking place above 500 °C. From the perspective of a one-pot reaction, this is a rather attractive process. It would appear that if the cost of sodium were low enough, borohydride could be produced very cheaply, since all of the other feed stocks are inexpensive materials.

There are flaws in using the Bayer Process, however, particularly in large quantity production. First is the build-up of sodium silicate, a mineral for which there is little demand. If borohydride were produced in the quantities needed for transportation markets, sodium silicates disposal issues need to be seriously considered. More importantly, the Bayer reaction presents some explosion risks, perhaps because it operates above the decomposition temperature of sodium borohydride. Finally, this process operates in a batch-wise mode in which raw materials are added to a reactor, processed into products and then sent on for separations. More preferable would be a continuous flow wherein raw materials are continuously fed into a reactor and products are continuously removed from the reactor. The higher production rates associated with continuous flow processes are often an important contributor to reducing the final product cost.

There is currently an effort to modify the Bayer Process by employing the less expensive reducing metal magnesium (Mg) in place of sodium. The work is largely conducted in Japan by Toyota,⁸⁻¹⁰ and by an academic research group.¹¹⁻¹⁵ Reactions such as:



and



are promising modifications to the Bayer Process, but have not been developed far enough to exhibit both high yield and fast reaction rates. Formation of magnesium hydride (MgH₂) from the metal is a challenging chemical activation problem whose solution involves finely dividing the metal into micro-scale particles before the reducing step. Finely divided NaBO₂ is also required for good reaction yield at a reasonable rate.

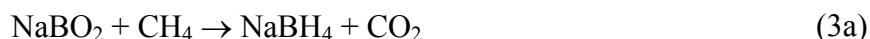
Regarding the explosion risk associated with the original Bayer Process, these new processes appear to operate at reduced temperatures compared to the original, or even at room temperature. The reaction is driven by mechanical milling of the solids rather than operating in a molten phase. The ultimate energy efficiency of a mechanical milling process remains open for discussion.

Despite these early difficulties, with the reasonably low cost of magnesium, it may be possible that a modified Bayer Process might prove to be a cost effective route to sodium borohydride. Whether a disproportionation takes place in the original Bayer Process is hard to say, but in the low temperature milling processes it almost certainly does, as a boron species with a mixture of hydrogen and oxygen bonds is a likely first step of the reaction mechanism.

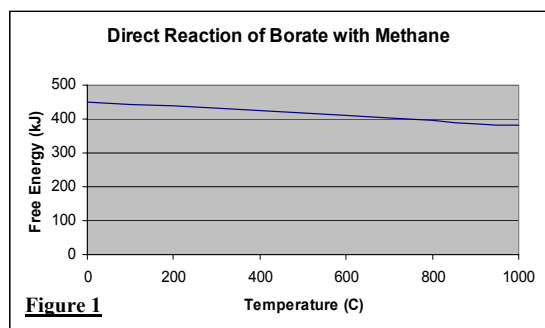
Section 2: Direct Thermal Reductions

Methane (or Natural Gas) as Reducing Agent

While modifications of the Brown-Schlesinger and Bayer processes are the most logical starting point for examination of sodium borohydride manufacture, a different approach might be to first consider what the most desirable reactions are, and then examine their plausibility in terms of thermodynamics. Two critical problems with the Brown-Schlesinger Process that lead to a high-cost product are (1) the multiple steps, and (2) the use of an expensive reducing agent. A more desirable reaction would therefore be a one step reaction of sodium borate with an inexpensive reducing agent such as methane, shown in reaction (3a).



This reaction would have the advantage of being a one step process, a direct conversion of borate raw material. Plus, it would employ an exceptionally inexpensive reducing agent: methane. However, a plot of reaction free energy versus temperature (Figure 1) shows that change in free energy (ΔG) for the reaction remains significantly



positive at all temperatures between zero and 1000 °C.¹⁶ There is no anticipation that the ΔG will become negative at any reasonable temperature. With the same number of moles of gas on

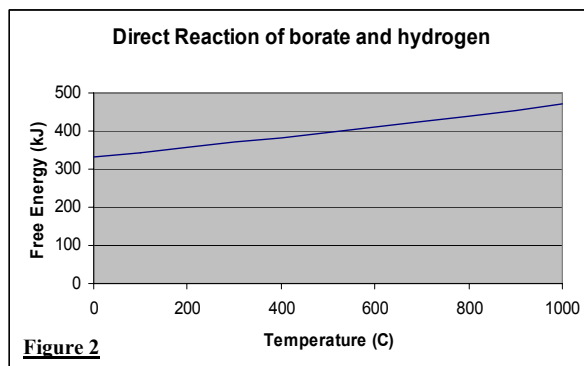
both sides of reaction (3a), increasing the pressure of methane is not expected to help either. Reaction (3a) is therefore ruled out as a possible synthesis of sodium borohydride. Since reaction (3a) is dependent on methane, it would also inevitably produce CO₂.

Hydrogen Gas as Reducing Agent

A related, and only slightly less direct, method than reaction (3a) would be the reaction of sodium metaborate with hydrogen gas. This reaction is less direct because hydrogen gas itself needs to be synthesized by some method, but not necessarily from methane and therefore the reaction is energy source neutral.

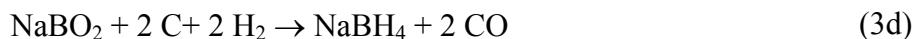
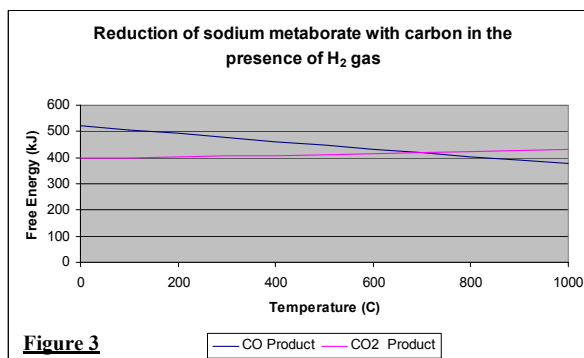


An analysis of the free energy of reaction for (3b), similar to that shown for reaction (3a), eliminates reaction (3b) on the same basis.¹⁶ In Figure 2, there is no serious expectation that the free energy will ever become negative, and it will never be close enough to zero to take advantage of equilibrium effects.



Carbon as Reducing Agent

Continued analysis shows that reactions using carbon as a reducing agent, for example coking boron oxide or sodium metaborate in the presence of hydrogen gas, yields results similar (Figure 3) to those above.¹⁶ There is no expectation that carbon reducing agents will prove any more effective than methane.



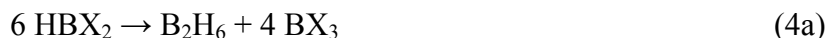
Section 3: Multi-Step Thermal Reductions

In developing an all-thermal synthetic process for sodium borohydride,¹⁷⁻²⁰ Millennium Cell Inc. proposed a family of processes, which can be modified in various ways to optimize the trade-offs among energy efficiency, cost, and greenhouse gas emissions. A discussion of all of the possible permutations of the reaction schemes is beyond the scope of this review, but three examples are shown here to illustrate the nature and intent of the methodology.

We derive much of our insight from an excellent review of the work on boron chemistry in the 1950's and 1960's: "Production of the Boranes and Related Research" by Hughes, Smith, and Lawless (edited by Holzmann).²¹ A number of reaction schemes are described in this book that might have led to new processes for borohydride synthesis had research continued along these lines. An early objective of Millennium Cell's borohydride synthesis effort was aimed at learning what could be achieved with chemistry that had already been proven in the laboratory, if not yet proposed as a complete process for making sodium borohydride.

Disproportionation Reactions

An important insight derived from the Hughes Review is the disproportionation reactions of boron compounds. Disproportionation is a prevalent characteristic of boron chemistry and is therefore extremely important when discussing possible synthetic methodologies. It occurs because three- and four-coordinate boron species do not favor mixed ligands. Moieties like HBX_2 and HBX_3^- tend to react with themselves, undergoing ligand exchange to reach the preferred fully oxidized and fully reduced states. The general equations are presented below:

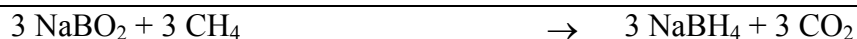
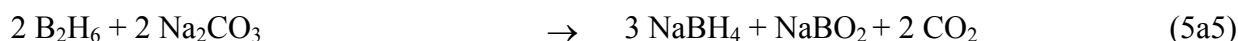
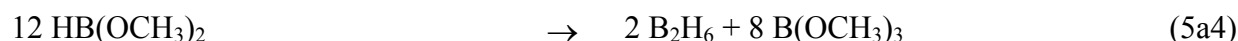
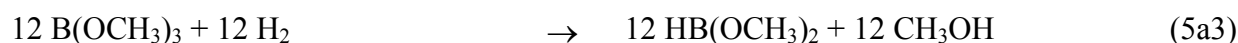
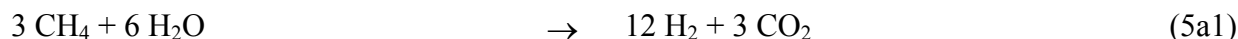


Because of thermodynamics, after the first reduction of the boron center, the disproportionation reaction then generates the fully reduced product and fully oxidized starting material. Due to this phenomenon, only one hydride needs to be added to the boron center in order to generate the fully reduced species. Therefore in calculating the energy input needed to form the fully reduced product, only the initial step of adding the first hydride needs to be taken into account. However,

there must also be a recycling loop associated with any boron-hydride synthetic methodology to handle the regeneration of the fully oxidized species.

For the boron disproportionation approach, a few specific reactions were selected and combined with the necessary transformations to yield an energetically efficient scheme for making sodium borohydride. A sample process is shown below:

Process (5a) Reaction Steps

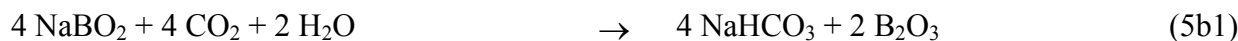


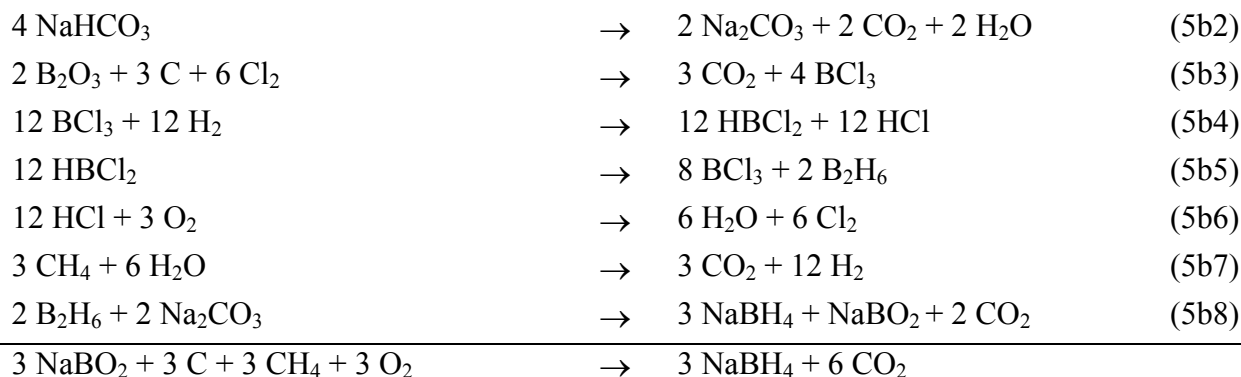
Process (5a) appears plausible. An estimation of the free energies of reaction and the process heat required suggests that this synthesis would be quite efficient from a chemical potential or free energy perspective. The overall reaction is the same as reaction (3a), which was defined as the most desirable of synthesis reactions. It should be noted that reaction (5a5) has not been specifically described in older literature. Employing sodium carbonate as a disproportionation agent to convert diborane into sodium borohydride and sodium metaborate is a recent development of Millennium Cell.¹⁸⁻²⁰

In practice, however, process (5a) is not ideal because equation (5a3) is difficult to carry out. The free energy of reaction for (5a3) becomes negative only at temperatures above 850 °C (at 1 atm), which is above the pyrolysis temperature of B(OCH₃)₃. As a result, the reaction yield of (5a3) is very low, and essentially precludes process (5a) from being practical.

Reaction (5a3) may be circumvented by using B(OR)₃ to produce more reactive boron intermediates, which will then be converted to B-H species. The Hughes review gives examples of other tri-coordinate boron species, and boron trihalides are prime examples. Consequently, the following reaction sequence may be written:

Process (5b) Reaction Steps

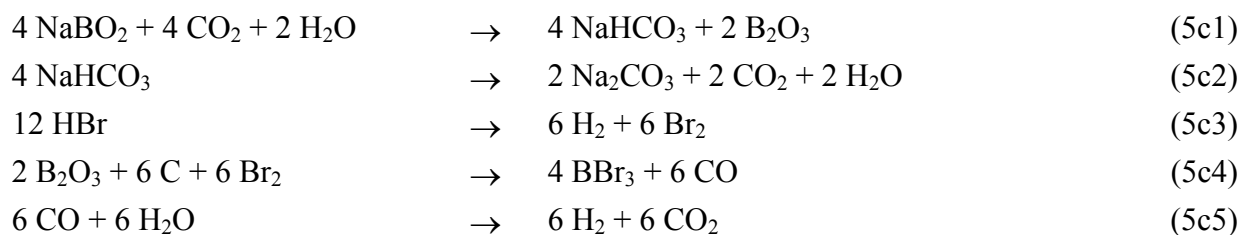


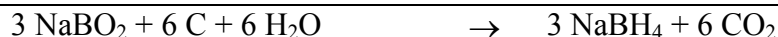
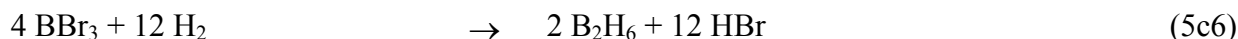


Although more complicated than the previous example, the direct hydrogenation of trimethylborate has been eliminated. The key elements of this scheme are reactions (5b4) and (5b5). Similar to reaction (5a3), the calculated ΔG of reaction (5b4) is positive in moderate temperature ranges and only becomes negative at temperatures above approximately 1200 °C. However, it has been shown that this reaction can be driven at temperatures as low as 700°C, by continuous removal of the product HBCl₂, which is accomplished by allowing the equilibrium concentration of HBCl₂ to disproportionate to diborane in a cooler zone of the reactor. Detailed mechanistic study and reactor development to make B₂H₆ from BCl₃ was the subject of the Air Force Project HEF (High Energy Fuels Project) dated back to 1959-1962. Once the diborane product has been formed, back reaction of diborane with hydrochloric acid does not appear to occur according to the Holzmann review,²¹ presumably due to sluggish kinetics at low temperatures.

A third sample process is outlined below, where steam methane reforming has been eliminated, and less expensive coke is used as the reducing agent. Carbon monoxide is the product of the reduction (5c4), and it can be shifted to CO₂ and hydrogen gas (5c5). The stoichiometry of the reaction scheme is such that all of the necessary hydrogen can be obtained from the shift reaction.

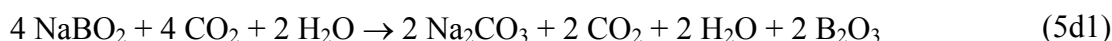
Process 5c Reaction Steps





The net reaction of this scheme is the reduction of sodium borate using coke and water, as opposed to the previous routes that utilize methane as the hydrogen source. Although the overall reaction of (5c) is similar to reaction (3c), the individual steps constituting (5c) are feasible by taking advantage of high temperature equilibrium effects of the various reactive intermediates. The calculated ΔG for the overall reaction reflects the free energy change when each constituent reaction step is carried out at the same temperature and pressure conditions. However, if these individual reaction steps are carried out at their respective optimal conditions, it renders the desired overall transformation possible. The net result is to drive an otherwise thermodynamically unfavorable reaction with thermal energy inputs.

In this version, sodium bicarbonate is partially dehydratively decarboxylated to sodium carbonate (5c1). It is possible that sodium bicarbonate is converted to sodium carbonate *in situ* in the first reaction shown above where the optimal conditions were found to be experimentally between 175 and 200 °C. The combined reaction of (5c1) and (5c2) is shown below in two forms (5d1) and (5d2), where boric oxide can be separated from the solid sodium carbonate by extraction with an organic alcohol (e.g., methanol or ethanol); the other products are in the gas phase.



or



The preparation of BBr_3 from the reaction of B_2O_3 with carbon and Br_2 (5c4) is a known reaction, as is the preparation of BCl_3 (5b3) in the previous scheme.²²⁻²⁵ By generating carbon monoxide in the presence of excess carbon (5c4) an appropriate amount of hydrogen gas can be generated by the water-gas shift reaction (5c5).

For decomposition of HBr into its elements, a gas stream of HBr can be passed over a catalyst such as platinum metal or platinized silica gel at temperatures ranging from 100 to 500 °C.²⁶ The reaction can be driven to completion by condensing bromine from the product gas stream at temperatures between 0 and 60 °C. For 100% conversion of HBr to bromine and

hydrogen, it may be necessary to recycle the product gas stream over the catalyst to completely consume HBr.

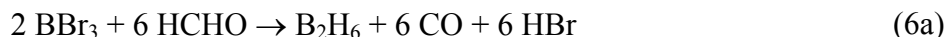
Although all three of the processes described above have not been demonstrated in their entirety to show overall process feasibility, significant insight has been gained. To make diborane, a single hydride is added to a three coordinate boron species to make a monohydridic borane with two X ligands. This species is allowed to disproportionate into diborane and the starting three-coordinate boron species. Diborane itself is disproportionated by sodium carbonate to yield borohydride and borate. The importance of this disproportionation chemistry to the synthesis of boron hydrides is demonstrated by these reactions that are capable of reaching fully hydrided boron species.

The chemical feasibility of making diborane from boron halides were undoubtedly shown, however incorporating these reactions in a multi-step process to produce sodium borohydride has serious drawbacks. Taking the BCl_3 route as an example, the feasibility of diborane production by these reactions relies on the rapid cooling of HBCl_2 to give liquid phase HBCl_2 which then disproportionates. This requires a temperature drop from approximately 700°C to approximately 70°C in a few seconds. From an engineering perspective, this cooling process will require large amounts of energy and sophisticated reactor design that is likely to result in large capital requirements. When all these factors are taken into account, it is difficult to envision that an energy efficient and cost effective process will emerge from this reaction route.

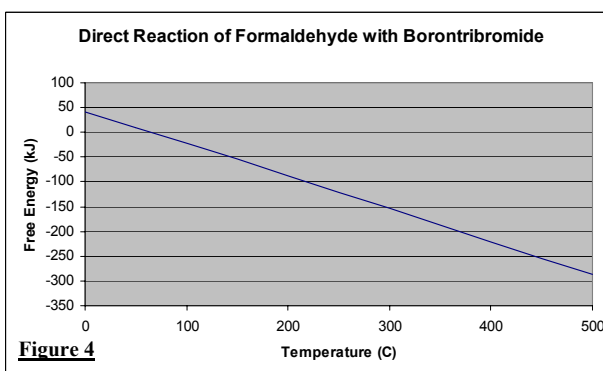
Unfortunately, there are as many or more process steps in these all-thermal routes as in the original Brown-Schlesinger scheme. The substantial cost reduction needed for sodium borohydride to become a low cost fuel for the transportation market is unlikely by implementing these or similar processes, simply because of the complexity of the processes. Each step will require its own separations, drying, recycling, and other sub-processes to make each of the reactions proceed efficiently and in good yield. When all of the necessary support structure is considered, the concept of reducing cost by cutting process steps and complexity is lost even if efficiency is gained in chemical potential of selected intermediates.

Formaldehyde Reductions

Another proposed carbon-based reduction method is to reduce boron compounds using formaldehyde as a reducing agent.²⁷ Formaldehyde is a more active reducing agent than methane or coke, not requiring high temperatures to activate. It is also inexpensive, ultimately being generated from methane via a methanol intermediate. An example reduction employing formaldehyde would be:

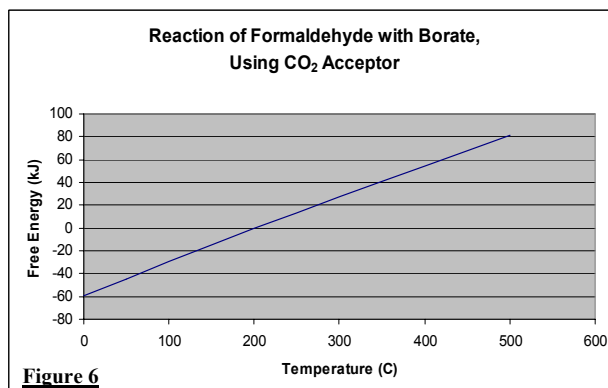
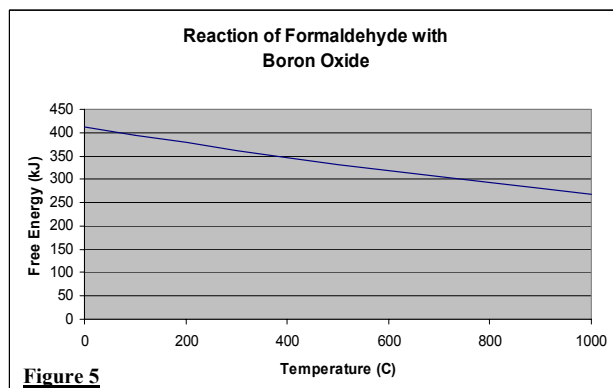


This process also precedes using boron trichloride. Unlike the methane and hydrogen based direct reductions, this reaction has a negative free energy of reaction at 100 °C,¹⁶ as shown in Figure 4. Experimentally, this reaction is performed at 400 °C over a copper catalyst.²⁷ This reaction could be incorporated



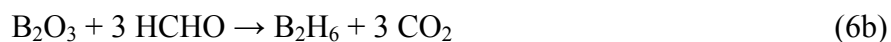
into a process not unlike those described above, in which coke is the reducing agent, possibly with fewer steps. The reaction of BBr_3 with a hydride donor occurs through a disproportionation process, which is described in greater detail in section 5.

The formaldehyde process appears promising but it is not without flaws. A side product of the reaction when boron trichloride is employed is phosgene (COCl_2), a chemical that requires extreme safety measures in handling. To further complicate things, the vapor pressure curves of BCl_3 and COCl_2 are very similar, rendering traditional separation methods (e.g. distillation) inadequate. The bromine equivalent is found when boron tribromide is employed. Furthermore, the low molar yield of B_2H_6 results in a very dilute concentration of the desired product in the



reaction mixture, resulting in further challenges in separation. Carbon monoxide also coordinates to diborane, which gives a chemical product that must be separated. In this all gas phase reaction, the separation issues are worse than for most other processes considered.

Formaldehyde reactions have also been suggested using boron oxide starting reagents like boric oxide and sodium metaborate. The simplest reaction (6b) has a positive ΔG under standard conditions (Figure 5),¹⁶ but the ΔG could be made negative by including another oxide, which will accept carbon dioxide (Figure 6).¹⁶ For example, (6c) has a negative ΔG of reaction. Unfortunately, reaction (6c) has not been demonstrated in high yield. Though not proven, it is probable that the activation energy remains too high for the reaction to initiate. Even with the formation of lower energy calcium carbonate as the thermodynamic driving force, the formaldehyde must still react with sodium metaborate, a reaction known to be energetically disfavored.



The “Steel-Making” Process

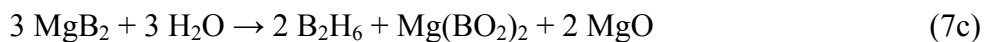
Another approach is to consider industrial processes used to manufacture other high-energy compounds, and determine whether they can be adapted to making sodium borohydride. One compound that is made very cheaply by thermal processes is steel. When making steel, iron oxide is reduced with coke or carbon monoxide as follows:



The “steel-making” process can be adapted for use with boron. An example reaction might be:



Metal borides can be hydrolyzed to metal oxides and boron hydrides as shown:



Boron hydrides can be converted into borohydrides by reacting with certain bases. It is already known that coking boron oxide in the presence of a metal or metal oxide can make refractory metal borides,^{28,29} so this process for making borohydride cannot be ruled out by thermodynamic considerations. King and Russell claim the preparation of borohydrides by the hydrolysis of magnesium diboride (MgB_2) with bases.^{29,30} For example, potassium hydroxide yields potassium borohydride and sodium hydroxide yields sodium borohydride through disproportionation reactions. The preparation of diborane by reaction of metal borides with metal sulfide and hydrogen to give diborane has also been claimed.^{31,32}

Coke is a very cheap reducing agent, but the main concern with employing it to make borohydride is cleanliness. This method of making borohydride will produce more carbon dioxide than burning hydrocarbons directly as fuel. The ease with which the reaction product magnesium borate can be recycled back into the process is also open to discussion. Magnesium borate must be recycled to magnesium oxide and boric oxide to be employed in reaction (7b), however this step could prove too energy intensive.

Section 4: Metallic Reducing Agents

A number of metallic reducing agents can also be employed to reduce boron centers and give B-H species. Many metals also form hydrides with which boron compounds will exchange ligands. The alkali metals are well known examples of this, and the Brown-Schlesinger Process is based on exchange between sodium hydride and trimethylborate. Boron ends up with hydride ligands, and the alkoxide is transferred to the sodium. There are other metals with which boron will exchange, and a boron-hydride making process might be based on these. Magnesium, aluminum, and silicon all exchange favorably with boron.³³⁻³⁷ Magnesium and aluminum are metals made much the same way as sodium, but are less expensive. The question about these other metals is activation, which is often challenging in both magnesium and aluminum reactions. In addition to hydrides, metal alkyls may also be employed in a ligand exchange reaction with boron compounds, forming alkyl substituted boron that are more easily converted to boron hydrides such as B_2H_6 .

One possible way to put hydride ligands onto boron using a metal like aluminum is to employ trialkyl aluminum or alane, which are liquid or gas phase monomers or dimers that need no activation. Pyrophoricity is a concern, however, when dealing with alkyl aluminum

compounds. In a recent study at Millennium Cell, zinc alkyl compounds were also found to exchange ligands with alkyl borates.

The reduction of BX_3 species to diborane can be achieved by direct hydrogenation or by transfer hydrogenation conditions such as the reaction with aldehydes²⁷ (see reaction (6a)). Alternative transfer hydrogenation conditions included reaction with the hydrides of silicon, germanium, lead, and tin (preferably silicon or tin) of the general formula R_3MH ($M = Si, Ge, Pb, Sn$; $R =$ branched and linear C1 to C6 alkanes, phenyl [C_6H_5], halides and H, where the three groups do not have to be the same), as sources of hydrogen. The preferable reagents are the silicon hydrides (a class collectively referred to as silanes).



Reaction conditions are controlled such that the gas streams of BCl_3 and silane are mixed and maintained at temperatures between 0 and 170 °C under an inert atmosphere.³⁸ At these temperatures diborane is produced as a gas and the silicon tetrachloride can be separated by cooling the gas stream down to between 20 and 55 °C. Alternatively, BCl_3 and silane can be stirred in an organic ether (such as diglyme, tetraglyme, tetrahydrofuran) solution under the conditions given above. Reaction (8a) can form the basis of a process like reaction schemes (5a-c), in which sodium borohydride is made. Unfortunately, the use of silanes is unlikely to prove less expensive than producing the boron hydride more directly, and may also contain more process steps.

At present, none appear sufficiently simple to lower the cost of borohydride manufacture below its current level, and thus using metallic reducing agents and their hydride or alkyl derivatives suffer from the same weakness as the all-thermal reductions described above.

Section 5: Alternative Energy Sources

Microwave Processes

A different approach to reducing borates was published in the early 1980's.^{39,40} The reaction does not proceed readily via thermal methods, but microwave excitation can allow the reaction to proceed. This reaction is of interest in the synthesis of borohydride because the classic chemistry of boron compounds, disproportionation, transforms the dimethoxyborane

(HB(OCH₃)₂) product to diborane and trimethylborate. Diborane can be converted to sodium (or another alkaline earth metal) borohydride by further disproportionation with basic reagents.



With carefully controlled microwaves, a reported 54% of the B(OCH₃)₃ was converted to HB(OCH₃)₂, with the majority of the unreacted starting material reclaimed. What was not reported is the efficiency of the microwave absorption. To date there are no industrial syntheses that employ microwave irradiation as an energy source, and ultimately very little is known about the economic efficacy of this method.

Nuclear Processes

A newer idea for making sodium borohydride is being pioneered at the Idaho National Engineering and Environmental Laboratory (INEEL). Waste nuclear energy might be usable to make sodium borohydride.^{41,42} Preliminary results from INEEL show that gamma-irradiated aqueous solutions of sodium metaborate can be converted to sodium borohydride. The mechanism is not understood at this point. One possibility is that the gamma ray, which is a very high-energy photon, can be absorbed by the solution and radiate energy through a pathway that involves the generation of a shower of electrons. Once electrons are in the metaborate solution there is some probability that they will form hydride species that will react with borate to make boron hydrogen bonded intermediates. Another possibility is that the electrons form reduced boron species that accept hydrogen to make boron hydrogen bonded intermediates. Boron and hydrogen species that are unsaturated with hydride favorably disproportionate into fully saturated hydrides (borohydride) and fully oxidized borates.

Much study remains to resolve the mechanisms of borohydride formation, verify the efficacy of the reaction, and study the economic potential.

Section 6: Electrochemical Methods

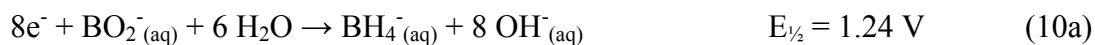
Finally there are electrochemical processes to consider. In essence, the Brown-Schlesinger and Bayer processes are both electrochemical in nature, given that the majority of

the energy needed to make sodium borohydride is introduced into the system in the form of electricity used to make sodium metal.

As in the thermal reactions, it makes sense to envision the most desirable electrochemical reaction for making sodium borohydride, and then examine its feasibility. From a practical standpoint, it would be best if sodium borohydride could be made by electrolysis of aqueous borate. Liquid fuels are desirable from a number of viewpoints, and separation of sodium borohydride from an aqueous solution can be achieved by established procedures, as in the final extraction step of the Brown-Schlesinger Process.

Cooper, Sherifian, and Hale⁴³⁻⁴⁵ have reported the electrochemical conversion of borate to borohydride in an aqueous medium, and a Chinese patent application published in 2003 by Sun⁴⁶ *et. al.* claimed electro-reduction of metaborate in aqueous solution with >30% current efficiency. However, a publication by Gyenge,⁴⁷ *et. al.* reported their systematic attempt to reproduce the results by Cooper, Sherifian, and Hale, but failed to verify that any borohydride was synthesized in these aqueous electrochemical systems.

Sodium borohydride does not react quickly with water in alkaline medium at low to moderate temperatures, suggesting that an aqueous phase synthesis might be possible. Unfortunately, even though borohydride is an inert ion in basic aqueous solutions, the inactivity is due to kinetics. A thermodynamic analysis indicates that water is not likely to be a good medium for the electrolytic production of sodium borohydride.



It takes less energy to split water into hydrogen at the cathode and oxygen at the anode than it does to make borohydride at the cathode and oxygen at the anode, as evidenced by the voltage of the cathodic half-reactions. The anodic reactions are the same in both cases with hydroxide ions being oxidized to oxygen gas and water. High overpotential materials can be employed at the cathode to inhibit the hydrogen evolution reaction, but experimental results suggest that the same materials that have high hydrogen overpotentials are also poor choices for transferring electrons and hydrogen to a boron center. It is reasonably clear that water should be avoided, at least for

the direct electrochemical generation of borohydride. Rigorously dried molten hydroxide systems are an area of present study at Millennium Cell, wherein it is hoped that the electro-reduction of the boron species will take place before the electro-reduction of the molten salt cations, which are usually light alkali metals. Also being studied are aprotic organic media, where borohydride is known to be stable and borate species are known to be soluble. Thermodynamically, the area of concern is the energy it requires to reduce a boron species compared to the energy required to reduce either the solvent or the supporting electrolyte.

Another area of research is in electro-catalysis. It may be possible to electrolytically generate a hydride species with sufficient reducing power to take a borate to a boron with both boron-hydrogen and boron-oxygen bonds. A mixed ligand species will disproportionate into a fully reduced boron hydride and borate. The search for such a hydride species has begun and several candidates have been identified. This approach circumvents potential problems associated with the electro-activity of borates, which can be poor.

Considering the Brown-Schlesinger Process outline earlier, Steps 1, 5, 6, and 7 are reasonably efficient. If Step 2 can be improved, the process might prove economically and environmentally viable. Outside of the Brown-Schlesinger reaction scheme, an organic or molten salt medium might provide an electrochemical window where the easiest thing to reduce is the boron center, rather than a solvent molecule. If this is the case, generation of borohydride may yet prove straightforward, simply requiring a clever choice of reaction medium. This may be the highest hope for finding a simple, cost effective way for manufacturing sodium borohydride. Transfer of energy in the form of electricity rather than heat can often prove far more efficient, and has the added benefit of being source neutral, such that any renewable energy source that leads to electricity can in turn lead to a renewable method of generating sodium borohydride.

Conclusion

The reaction schemes included in this review certainly do not cover all of the possible methodologies to synthesize sodium borohydride, but rather provide a broad overview of past research. This attempt to categorize the field will hopefully make it easier for those who are interested in the subject to reference past work. It is important to become familiar with the classic papers by Brown and Schlesinger on their original work to develop the borohydride

synthesis process. In addition to the exhaustive review by Holzmann,²¹ there is another very thorough review on boron chemistry by Adams,⁴⁸ which provides a comprehensive description of reactive boron chemistry. Since most of the research effort to synthesize sodium borohydride took place more than forty years ago, renewed endeavors in this field with recently developed synthetic chemistry tools may provide answers that were not available then.

Another objective of this review was to demonstrate and reiterate the benefit of a disproportionation approach. Taking advantage of and utilizing this classic characteristic of boron compounds greatly simplifies the problem of making fully reduced boron hydride species. Thus, it is only necessary to form the first boron-hydrogen bond; disproportionation, which is thermodynamically favorable, takes care of the rest by generating the desired fully hydrogenated and reduced species. Therefore, by generating the first boron-hydrogen bond in a more efficient and cost-effective manner, the complete conversion to sodium borohydride will subsequently be more efficient and cost-effective as well. Cost reduction of sodium borohydride production will lead to broader applications of hydrogen storage systems based on sodium borohydride and related chemicals.

Based on the analyses above, we anticipate that the most likely route to achieving the low-cost production of sodium borohydride lies with the electrochemical methods. Electrochemical methods can be much more efficient and cost-effective with respect to the corresponding thermochemical methods, as demonstrated in electrochemical aluminum production versus its thermal counterpart. The field of electrochemical synthesis for borohydride has not been as thoroughly explored; a lot of work is needed in order to fully understand how this technique can be utilized in the syntheses of sodium borohydride.

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