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An improved synthesis of unsolvated NaB₃H₈ and its application in preparing Na₂B₁₂H₁₂

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Abstract
Octahydrotriborates are potential hydrogen storage materials and chemical vapor deposition precursors to boride films. Their syntheses have been quite challenging, however. In this paper, an improved facile route for the preparation of unsolvated sodium octahydrotriborate (NaB₃H₈), which is an important precursor to other octahydrotriborates and derivatives, is reported. The key steps in the synthesis involve dispersing Na finely in inert media and preparing fresh tetrahydrofuran (THF)·BH₃ at room temperature. High purity unsolvated NaB₃H₈ can be obtained in tens of grams or more in one batch, depending on the reactor size. Using NaB₃H₈ as the precursor, sodium dodecaborate (Na₂B₁₂H₁₂) has been successfully synthesized. Both octahydrotriborates and dodecaborates have been observed as intermediates during the thermal dehydrogenation of borohydrides, and their facile syntheses would facilitate mechanistic studies on the hydrogen storage of borohydrides, among other potential applications.

Introduction
Various compounds with high hydrogen content have recently attracted intense attention for hydrogen storage.[1-5] Metal octahydrotriborates (M(B₃H₈)ₙ), sometimes known as metal triboranes, have therefore aroused attention.[6-8] Mg(B₃H₈)₂, an intermediate during the thermal decomposition of Mg(BH₄)₂, has shown a cycling capacity of 2.5 wt %.[8] They have been observed during the thermal decomposition of borohydrides.[9, 10] Metal dodecaborates (M(B₁₂H₁₂)ₙ) have also been observed as intermediates among others during the thermal decomposition of borohydrides.[8, 11] Their high thermal stability makes complete dehydrogenation of borohydrides difficult, so it may be desirable to change the reaction pathway to avoid their formation. The availability of metal octahydrotriborates and metal dodecaborates is important for in-depth investigations of the borohydrides’ hydrogen storage mechanism.[11, 12]

Both metal octahydrotriborates and metal dodecaborates could be used in other fields. For instance, metal octahydrotriborates have been studied as chemical vapor deposition (CVD) precursors for metal boride thin films.[13, 14] NaB₃H₈ is a potential anodic fuel for direct liquid fuel cell.[15] Owing to its good solubility in ethyl ether, NaB₃H₈ can be used as a precursor for the further synthesis of other octahydrotriborates.[13, 16] Na₂B₁₂H₁₂ has recently attracted great interest as solid electrolyte for solid battery applications due to its outstanding ionic conductivity.[17-19] A dual-cation dodecaborate, LiNaB₁₂H₁₂, possesses ion conductivity approximately 8 and 11 times higher than Na₂B₁₂H₁₂ and Li₂B₁₂H₁₂, respectively.[20] Additionally, dodecaborates have long...
been studied as effective drug delivery vehicles for neutron capture therapy, which is one of the minimally invasive cancer therapies.[21, 22]

Unsolvated NaB\textsubscript{3}H\textsubscript{8} was first synthesized from the direct reaction between B\textsubscript{2}H\textsubscript{6} and Na[23-25] or Na/Hg amalgam,[26, 27] but the high toxicity and high flammability of B\textsubscript{2}H\textsubscript{6} make these methods hard to repeat. Reacting sodium borohydride with oxidation reagents such as I\textsubscript{2}, metal halides or dichloromethane, can also yield NaB\textsubscript{3}H\textsubscript{8} but with a small amount of impurities.[28-30] Furthermore, in most cases, it is hard to remove the solvents due to the strong coordination between the solvents and the Na\textsuperscript{+} ions.[9, 28, 30-35] Sodium borohydride or sodium hydride would react with B\textsubscript{4}H\textsubscript{10} leading to NaB\textsubscript{3}H\textsubscript{8}.[36] B\textsubscript{4}H\textsubscript{10}, however, is highly toxic and unstable, and not commercially available. Based upon an early report on the reactions between alkali metal and THF-BH\textsubscript{3}, solvent-free NaB\textsubscript{3}H\textsubscript{8} was recently obtained by the reacting Na/Hg amalgam with tetrahydrofuran (THF)-BH\textsubscript{3}.[37] Subsequently, an innovative modification was made to replace Na/Hg amalgam with Na dispersed on silica gel through heating.[38] These demonstrate that a good dispersion of Na is the key to improve the synthesis.

Na\textsubscript{2}B\textsubscript{12}H\textsubscript{12} is commercially available but with a very high price. MgB\textsubscript{12}H\textsubscript{12} can be directly synthesized via a gas-solid reaction between Mg(BH\textsubscript{4})\textsubscript{2} and B\textsubscript{2}H\textsubscript{6}.[39] MgB\textsubscript{12}H\textsubscript{12} is also known to form during the dehydrogenation of Mg(B\textsubscript{3}H\textsubscript{8})\textsubscript{2}, but only as a small fraction of the products and never in an isolated form.[8, 11] One pot synthesis of metal B\textsubscript{12}H\textsubscript{12}\textsuperscript{2-} from metal borohydrides and alkyl or aryl halides were reported but further purification process were needed to obtain pure and unsolvated metal B\textsubscript{12}H\textsubscript{12}\textsuperscript{2-} salts.[40] Solid-state reaction between metal borohydrides and B\textsubscript{10}H\textsubscript{14} leads to solvent-free metal B\textsubscript{12}H\textsubscript{12}.[12, 41], but B\textsubscript{10}H\textsubscript{14} is a rarely available. Small scale [NEt\textsubscript{3}]\textsubscript{2}B\textsubscript{12}H\textsubscript{12} was prepared through the decomposition of corresponding B\textsubscript{4}H\textsubscript{10} salt and further be used as precursor for preparing metal B\textsubscript{12}Cl\textsubscript{12}\textsuperscript{2-} salts.[42] Therefore, a convenient and high purity synthetic method for Na\textsubscript{2}B\textsubscript{12}H\textsubscript{12} is worth to be investigated.

In this paper, we report an improved synthesis method for unsolvated NaB\textsubscript{3}H\textsubscript{8}, which involves an improved method to disperse Na and a refined procedure to produce fresh THF-BH\textsubscript{3}. The procedure avoids toxic reagents such as Hg and B\textsubscript{2}H\textsubscript{6}, employs simple setup, and thus facilitates large-scale production of NaB\textsubscript{3}H\textsubscript{8}. Using NaB\textsubscript{3}H\textsubscript{8} as the precursor, we have successfully synthesized Na\textsubscript{2}B\textsubscript{12}H\textsubscript{12} by isolating it from the decomposition residue of NaB\textsubscript{3}H\textsubscript{8}.

**Experimental**

**Reagents**

Sodium borohydride (NaBH\textsubscript{4}) (≥ 97%), sodium fluoride (NaF) (≥ 99.5%), sodium chloride (NaCl) (≥ 99.5%), sodium bromide (NaBr) (≥ 99.5%), sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}) (≥ 99.5%), dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) (≥ 99.5%), and diethyl ether ((C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O) (≥ 99.5%) were purchased from Kermel. NaF, NaCl, NaBr, and Na\textsubscript{2}SO\textsubscript{4} were dried at 400 °C for 4 h under flowing argon before they were used. Sodium (Na) (≥ 99.7%), silicon powder (Si) (99.9%, 1 μm), and cuprous chloride (CuCl) (≥ 97%) were purchased from Aladdin and used as received. Bismuth fluoride (BiF\textsubscript{3}) (99%), bismuth chloride (BiCl\textsubscript{3}) (99.9%), chromium chloride (CrCl\textsubscript{3}) (99%), tin chloride (SnCl\textsubscript{2}) (99%), lead fluoride (PbF\textsubscript{2}) (99%), and lead chloride (PbCl\textsubscript{2}) (99%) were purchased from Alfa Aesar and used as received. Tetrahydrofuran was purchased from Merck (≥ 99.9%). All the organic solvents were dried over 5 Å molecule sieves before use. All the manipulations were carried out under argon protection to avoid air contamination.
**Instruments and characterization**

Solvent nuclear magnetic resonance spectroscopy (NMR) was performed on a Bruker Avance 500 MHz spectrometer equipped with a liquid detector. Solution $^{11}$B NMR was externally referenced to BF$_3$·Et$_2$O. Ball milling was performed on a Retsch planetary ball-mill (PM400) machine. Powder X-ray diffraction (XRD) characterization was performed on a PANalytical X'Pert diffractometer (Cu Kα, 40 kV, 40 mA) with a home-made sample holder that protects the samples from exposure to air. The closed system for the synthesis of Na$_2$B$_{12}$H$_{12}$ consists of a sealed reactor coupled with a pressure detector. All the manipulations were carried out in an air-free environment.

**Results and Discussions**

**Synthesis of unsolvated NaB$_3$H$_8$**

1. Preparation of THF·BH$_3$ and well-dispersed Na

Commercial THF·BH$_3$ is expensive and tends to decompose over time. Additives are therefore normally introduced to stabilize the solution. THF·BH$_3$ is synthesized from the reaction between boron tri-halides (BF$_3$ or BCl$_3$) and NaBH$_4$, or from the oxidation of NaBH$_4$ by certain oxidants such as I$_2$.[28, 32, 43] These methods are not cost effective and/or require special care when dealing with these highly reactive/corrosive reagents. Inspired by a previous report,[30] we have thus developed an economical and efficient way to produce fresh THF·BH$_3$ without additives according to the equation shown below:

$$\text{NaBH}_4 + \text{MX} \rightarrow \text{M} + \text{NaX} + \text{THF·BH}_3 + n\text{H}_2 \quad \text{Eq. (1)}$$

($M = \text{Bi}^{3+}, \text{Cr}^{3+}, \text{Sn}^{2+}, \text{Pb}^{2+}$, and $\text{Cu}^+$, $X =$ Halides)

The choice of metal halides depends on their oxidation capability, which should be neither too weak so to form metal borohydrides, nor too strong so to remove all the hydrogens on B. For example, stirring NaBH$_4$ (0.3 mol) and CuCl (0.36 mol, 20% excess) in THF at 40 ºC for 4 h leads to high purity THF·BH$_3$ (Fig. 1). Low-pressure evaporation and condensation (liquid nitrogen cold trap) were employed to isolate the product. 500 mL of 1 M THF·BH$_3$ can be produced in one batch. High purity THF·BH$_3$ was also obtained after reacting other halides respectively with NaBH$_4$ for 4 h (Fig. 1).

For the synthesis of unsolvated NaB$_3$H$_8$, Na/Hg amalgam or Na on silica gel was used to maximize the reaction surface of Na and consequently to improve the reaction rate and final yield.[37, 38] Na on silica gel is a better way to disperse Na, since Hg is expensive and environmentally unfriendly, but the high temperature (160 ºC) used could be a concern when dealing with highly reactive melted Na. Ball milling at room temperature is well known as an effective way to reduce the particle size and create highly reactive surfaces. Na is a soft material, however, and unsuitable to be ball milled alone. We found that if Na is ball milled together with a chemically inert medium (towards Na), for instance NaCl, it will be mixed homogenously with NaCl as extremely fine particles (Fig. 2a). The inert media that we have tried include Si, NaF, NaCl, NaBr, and Na$_2$SO$_4$. Since ball milling is simple and efficient, large amounts of Na/NaCl powder can be acquired in one batch, which will help with scaling up. In all cases, the weight ratio between Na and the dispersion medium is about 1:10 and the milling speed is 150-200 rpm.
(Caution! Freshly dispersed Na powders are highly reactive in air and may catch fire and be explosive. They must be handled under inert atmosphere.)

Fig. 1 A representative solution $^{11}$B NMR spectrum of THF·BH$_3$ prepared by reacting NaBH$_4$ with metal halides, including BiF$_3$, BiCl$_3$, CrCl$_3$, SnCl$_2$, PbF$_2$, PbCl$_2$, and CuCl. (Inset is a digital photograph of a 500 mL bottle filled with 1 M THF·BH$_3$ that was synthesized in one batch.)

2. Synthesis and characterization of unsolvated NaB$_3$H$_8$

Well-dispersed fine Na/NaCl (28.5 g, 50% excess) powder (Fig. 2a) was mixed with 0.1 M fresh THF·BH$_3$ (300 ml) and stirred at room temperature for 12 h. The following reaction (Eq 2) occurs according to the literature.[37, 44]

$$\text{Na} + 4\text{THF} \cdot \text{BH}_3 \rightarrow \text{NaB}_3\text{H}_8 + \text{NaBH}_4 + \text{THF} \quad (2)$$

The detailed isolation procedure can be found in our previous report.[37] Briefly, filtration (to remove NaCl and other insoluble residue) and rotary evaporation (to remove THF) were carried out first. After introducing diethyl ether, filtration (to remove NaBH$_4$) and rotary evaporation (to remove diethyl ether) were conducted again. Upon adding dry CH$_2$Cl$_2$ to the oily products, white unsolvated NaB$_3$H$_8$ powder precipitates out. The yield was determined to be 67.3% based on THF·BH$_3$. $^{11}$B NMR and $^1$H NMR spectra (Fig. 2b, c) and the XRD pattern (Fig. 2d) are in good agreement with the previous reports,[37, 38] attesting to the high quality of the as-prepared NaB$_3$H$_8$. Depending on the volume of the reactor, this process can be scaled up to obtain tens of grams or a larger quantity.

Fig. 2 (a) Digital photographs of ball-milled fine powders of Na/Si, Na/NaF, Na/NaCl, Na/NaBr, and Na/Na$_2$SO$_4$ (from left to right). Solution $^{11}$B (b) and $^1$H NMR (c) spectra of the as-prepared NaB$_3$H$_8$ in
CD3CN. (d) Powder XRD pattern of the as-prepared NaB3H8. The 1H NMR resonances at 2.2 ppm and 1.9 ppm are associated with water and CH3CN residue, respectively.

Compared with NaBH4 for hydrogen storage via hydrolysis, unsolvated NaB3H8 has higher solubility and much improved stability in water.[7] In addition, the higher Na to B ratio (1:3) in NaB3H8 compared with NaBH4 (1:1) also affords highly soluble hydrolytic products. These merits have made NaB3H8 an interesting liquid-phase hydrogen carrier.[45] We have also found that the unsolvated form is not flammable in air.

**Synthesis of Na2B12H12**

NaB3H8 (5 g) was placed in a tubular furnace with an argon flow of 10 mL/min. The temperature was elevated to 150 °C and the sample was held at this temperature for 24 h. The temperature was then raised to 500 °C, and held for 1 h. Solid samples were collected and characterized by 11B NMR. The results indicate that the thermal decomposition of NaB3H8 at 150 °C produces NaBH4, Na2B12H12, Na2B10H10, and other minor impurities (Fig. 3a). Heat treatment at 500 °C for 1 h eliminates Na2B10H10. When higher temperatures were chosen, Na2B10H10 will decompose completely. Lower temperatures will also eliminate Na2B10H10 but with extended time (Fig. 4). Since Na2B10H10 and Na2B12H12 are both soluble in diethyl ether and NaBH4 is not, once Na2B10H10 consumed, Na2B12H12 can be isolated from NaBH4 by ethyl ether. Therefore, 500 °C was chosen. Diethyl ether was employed to extract Na2B12H12 from the solid products. After removing the diethyl ether, Na2B12H12 was obtained as a white powder, as clearly evidenced by 11B NMR (Fig. 3b).

Previously reported results showed that H2, B2H6, B6H10, and B3H6 could be detected as the gaseous products in the heat treatment.[46] It is reported that B2H6 could react with BH4− to produce B12H122−.[39, 47] We also found that the back pressure of the reacting system affects the yield of Na2B12H12. In a closed system, the yield of Na2B12H12 is improved (~10%, based upon NaB3H8), which indicates a more efficient reaction between the volatile boranes and the solid products forming Na2B12H12. Although the yield is relatively low, the starting material, NaB3H8, could be efficiently synthesized in a large quantity according to the method developed above. Therefore, this method could be a facile way to prepare Na2B12H12 for laboratory usage. Further optimizations are still necessary to increase the yield. This would include the adjustment of the back pressure using high-pressure system and introduction of extra boranes (B2H6, B6H10, and B3H6).

**Fig. 3** Solution 11B NMR spectra of a) the thermal decomposition products of NaB3H8 at 150 °C dissolved in CH3CN, and b) the isolated Na2B12H12 in CH3CN.
Conclusion

In this paper we report a scalable synthetic method for unsolvated NaB\textsubscript{3}H\textsubscript{8}, which is based upon the reaction between well-dispersed Na in a chemically inert medium (towards Na) and freshly prepared THF·BH\textsubscript{3}. Additionally, no highly toxic regents were employed in this procedure. Unsolvated NaB\textsubscript{3}H\textsubscript{8} has been the key precursor to many other octahydrotriborates.[13, 16, 48-50] Its improved synthesis would enable the preparation of new octahydrotriborates. Benefiting from the facile synthesis of unsolvated NaB\textsubscript{3}H\textsubscript{8}, a simple method to obtain Na\textsubscript{2}B\textsubscript{12}H\textsubscript{12} was developed. Na\textsubscript{2}B\textsubscript{12}H\textsubscript{12} can be used to prepare other dodecaborates, which could contribute to further studies in relevant fields.

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An improved synthesis of unsolvated NaB$_3$H$_8$ and its applications in preparing Na$_2$B$_{12}$H$_{12}$

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High purity unsolvated NaB$_3$H$_8$ can be obtained in tens of grams or more in one batch by reactions between well dispersed Na and freshly prepared THF·BH$_3$ at room temperature. Benefit from the large quantity of NaB$_3$H$_8$, sodium dodecaborates (Na$_2$B$_{12}$H$_{12}$) has been successfully prepared by directly heat treatment of NaB$_3$H$_8$. No high toxic reagent is involved in the whole process.