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Synthesis of lithium octahydrotriborate and investigation on its thermal decomposition

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ABSTRACT

Octahydrotriborates are found to be key intermediates in the dehydrogenation of many borohydrides. In this work, $\text{LiB}_3\text{H}_8 \cdot 1.5\text{THF}$ is synthesized via the reaction between lithium amalgam and $\text{BH}_3 \cdot \text{THF}$. The structure is confirmed by ^{11}B NMR and FT-IR spectrometry. The synthetic reaction of $\text{LiB}_3\text{H}_8 \cdot 1.5\text{THF}$ is monitored by using ^{11}B NMR. Some boron hydrides, LiB_2H_7 and LiB_4H_9 , are found to be possible intermediates in this reaction. Thermal dehydrogenation analyses including TPD/MS and TG suggest 6 successive decomposition steps upon heating to 500 °C. The compound emits THF, diborane, pentaborane(9) and hydrogen simultaneously below 170 °C and emits almost pure hydrogen at elevated temperature. LiBH_4 is formed at 170 °C as one of the products and disappears at 400 °C. At least two kinds of other intermediates are found in the decomposition reaction, with one of them suspected to be $\text{Li}_2\text{B}_{12}\text{H}_{12}$.

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Introduction

Hydrogen is believed to be one of the most promising alternative energy sources due to its rich abundance, cleanliness and high energy density [1–3]. However, the extensive use of hydrogen, especially in on-board applications, is restricted by the lack of suitable hydrogen carriers [4–7]. Such a hydrogen carrier should meet a target gravimetric hydrogen capacity of more than 5.5% (DOE target, based on system weight) as well as other limits in thermodynamics, kinetics and cost. These limits determine that the materials are mostly made up of light-weight metals and/or hydrides of second-row p-block

elements. Many of these materials are intensively studied, including amides, borohydrides, alanates, ammonia borane based compounds and their combination [8–17].

Among them, tetrahydroborates ($\text{M}(\text{BH}_4)_n$, where n is the valence of metal cation M^{n+}), are regarded as one of the most promising candidate for hydrogen storage in on-board applications [18–21]. This is because that (i) tetrahydroborates have high gravimetric hydrogen capacity (e.g. LiBH_4 18.3%, $\text{Mg}(\text{BH}_4)_2$ 14.9%, $\text{Ca}(\text{BH}_4)_2$ 11.5%, etc.) and (ii) the decomposition reactions of most stable tetrahydroborates are endothermic, which is a thermodynamically favorable property for reversibility under hydrogen pressure [18,22–24] and (iii) the heat of formation of tetrahydroborates are linearly related to the

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Pauling electronegativity of the metal, indicating that the stability of these compounds could be well-predicted [11,25]. However, these compounds also suffer from a series of problems such as (i) $M(\text{BH}_4)_n$ with low $\chi_{\text{p,M}}$ (i.e. high stability) can only release hydrogen at temperature above 200 °C, which exceeds the operation temperature of general fuel cells and (ii) $M(\text{BH}_4)_n$ with high $\chi_{\text{p,M}}$ (i.e. low stability) are likely to release hydrogen at lower temperature but accompanied by borane emission, which is harmful to the fuel cells and the environment [11,22,26].

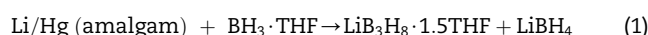
In the studies of tetrahydroborates, researchers realize that dehydrogenation of tetrahydroborates involves many polyborane anions as the intermediates [27–33]. These species include both *closo*-boranes such as $\text{B}_{12}\text{H}_{12}^{2-}$, $\text{B}_{10}\text{H}_{10}^{2-}$, $\text{B}_6\text{H}_6^{2-}$ and *arachno*-boranes such as B_3H_8^- , which exhibit diverse thermal stability and decomposition behavior. Understanding these intermediates could help not only in tuning thermodynamic properties but also in improving the kinetic performance. However, it is difficult to synthesize or isolate these M-B-H intermediates, especially the meta-stable ones for fundamental study. Therefore, a more profound investigation on these polyborane anions is not only of interest for the fundamental boron chemistry, but will also assist the development of high capacity hydrogen storage materials based on the metal-B-H system.

Among them, octahydrotriborates are particularly interesting because they can be treated as a potential hydrogen storage material because of its moderate stability. Furthermore, these compounds receive special concern because they are found to be important intermediates in the decomposition of some tetrahydroborates [32,34–36]. For example, $\text{Mg}(\text{B}_3\text{H}_8)_2$ is found to be the main product in decomposition reaction of $\text{Mg}(\text{BH}_4)_2$ at 200 °C in vacuum. Meanwhile, this compound can take up hydrogen to form $\text{Mg}(\text{BH}_4)_2$ again [37]. In another study, $\text{Y}(\text{B}_3\text{H}_8)_3$, instead of $\text{Y}_2(\text{B}_{12}\text{H}_{12})_3$, is believed to be the key intermediate in the decomposition of $\text{Y}(\text{BH}_4)_3$ [32]. Early synthetic works of octahydrotriborates were done by Titov and co-workers [38–43]. But the investigation of dehydrogenation properties has not been reported yet. Recently, several octahydrotriborates including NaB_3H_8 , $[(\text{NH}_3)_2\text{BH}_2]\text{B}_3\text{H}_8$, $\text{NH}_4\text{B}_3\text{H}_8$, $\text{Mg}(\text{B}_3\text{H}_8)_2$ etc have been synthesized [44–49]. These octahydrotriborates are carefully examined for their hydrogen storage properties in either hydrolysis or pyrolysis way.

However, LiB_3H_8 , which bears the highest gravimetric hydrogen capacity (up to 16.9 wt%), is absent in the hydrogen storage studies. It is only involved in some theoretical studies on the dehydrogenation reaction of LiBH_4 [31]. As it is shown to be a two-electron σ -aromatic system, which helps to stabilize the compound, it may serve as an intermediate in the dehydrogenation process of hybrid systems such as $\text{Mg}(\text{BH}_4)_2\text{--LiH}$ [50,51]. But such study is severely limited by the lack of understanding on the thermal decomposition properties of this compound. Moreover, the synthetic reaction, which contains the information of how BH_3 units convert into the B_3H_8^- polyanion, is of fundamental interest. Therefore, we are motivated to synthesize LiB_3H_8 and to investigate its hydrogen storage properties.

Conventionally, octahydrotriborates are synthesized via a two-step reaction [39,48,52]. The first step is the reaction between Na/Hg amalgam and $\text{BH}_3\cdot\text{THF}$ to form NaB_3H_8 . The

second step is the metathesis reaction between NaB_3H_8 and metal halides. The first synthesis of LiB_3H_8 was reported by Titov and co-workers in 1980 [43]. They obtained this compound as an ethereal solution via a two-step reaction between non-solvated NaB_3H_8 and LiBr. Inspired by the synthesis of NaB_3H_8 , we develop a simple method to synthesize LiB_3H_8 using Li/Hg amalgam and $\text{BH}_3\cdot\text{THF}$ (eq (1)):



Experimental section

Materials

Lithium rods (99%) was purchased from Sinopharm Chemical Reagents Co., Ltd. and $\text{BH}_3\cdot\text{THF}$ (1.0 mol/L) was purchased from J&K Chemicals. They were used as-received without further purification. Tetrahydrofuran (THF) was dehydrated in a 500 mL round-bottom flask with sodium granules for 12 h with benzophenone as an indicator. After the solution turned blue, the solvent was distilled and collected in a 500 mL Schlenk tube. Dichloromethane (DCM) was stirred with anhydrous CaCl_2 for 24 h to remove residual water. It is further distilled prior to use. All the materials mentioned above were stored in an argon-filled glovebox.

Synthesis and purification of $\text{LiB}_3\text{H}_8\cdot 1.5\text{THF}$

Twenty granules of lithium metal (0.010 g per granule) was dissolved in 30 mL of mercury under vacuum to form Li/Hg amalgam. 60 mL of $\text{BH}_3\cdot\text{THF}$ (1.0 mol L⁻¹) was added to the amalgam through a syringe under argon flow. The solution immediately turned into a dark grey suspension. After stirring for 48 h under argon atmosphere at room temperature, the suspension turned into a clear and colourless solution. The solution was filtrated into a round-bottom flask and evacuated to get a light grey, oily crude product. The oily product was dissolved in DCM and turned into a white suspension. The suspension was filtered through a glass funnel and the supernatant was collected. This process was repeated until no precipitate was formed upon adding DCM. The solution was evacuated at room temperature for 24 h to remove volatile components. The final product is a clear oily liquid, which is further confirmed to be the THF adduct of LiB_3H_8 , $\text{LiB}_3\text{H}_8\cdot 1.5\text{THF}$. All manipulations were performed in an argon-filled glovebox or on a Schlenk's line.

Results and discussion

The synthetic reaction of $\text{LiB}_3\text{H}_8\cdot 1.5\text{THF}$

Fig. 1 shows the ¹¹B NMR spectra of the purified product of equation (1) in DMSO-d₆. A set of well-defined symmetrical nonet are found at -29.40 ppm for both crude and purified samples. These results are in accordance with previous studies of B_3H_8^- species [35,47,52]. ICP-AES results give Li/B = 1/3 in molar ratio and molecular weight of 154.2 per Li⁺, which results in a nominal formula of $\text{LiB}_3\text{H}_8\cdot 1.5\text{THF}$. The major hydroborate

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