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Selective Reversible Hydrogenation of $Mg(B_3H_8)_2/MgH_2$ to $Mg(BH_4)_2$: Pathway to Reversible Borane-Based Hydrogen Storage?

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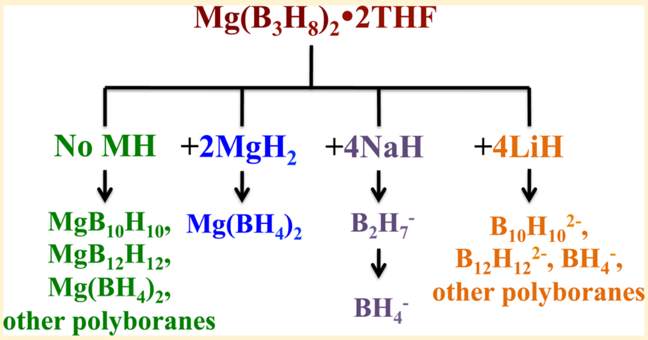

ABSTRACT: $Mg(B_3H_8)_2·2THF$ (THF = tetrahydrofuran) was prepared by the addition of $BH_3·THF$ to Mg/Hg amalgam. Heating a 1:2 molar mixture of $Mg(B_3H_8)_2·2THF$ and MgH_2 to 200 °C under 5 MPa H_2 for 2 h leads to nearly quantitative conversion to $Mg(BH_4)_2$. The differential scanning calorimetry profile of the reaction measured under 5 MPa H_2 shows an initial endothermic feature at ~65 °C for a phase change of the compound followed by a broad exothermic feature that reaches a maximum at 130 °C corresponding to the hydrogenation of $Mg(B_3H_8)_2$ to $Mg(BH_4)_2$. Heating $Mg(B_3H_8)_2·2THF$ to 200 °C under 5 MPa H_2 pressure in the absence of MgH_2 gives predominantly $MgB_{12}H_{12}$ as well as significant amounts of $MgB_{10}H_{10}$ and $Mg(BH_4)_2$. Hydrogenation of a mixture of $Mg(B_3H_8)_2·2THF$ and LiH in a 1:4 molar ratio at 130 °C under 5 MPa H_2 yields $[B_{12}H_{12}]^{2-}$ in addition to $[BH_4]^-$, while a 1:4 molar ratio of $Mg(B_3H_8)_2·2THF$ and NaH yields $[BH_4]^-$ and a new borane, likely $[B_2H_7]^-$. Hydrogenation of the NaH-containing mixture at 130 °C gives primarily the alternative borane, indicating it is an intermediate in the two-step conversion of the triborane to $[BH_4]^-$. The solvent-free triborane $Mg(B_3H_8)_2$, derived from the low-temperature dehydrogenation of $Mg(BH_4)_2$, also produces $Mg(BH_4)_2$, but higher temperature and pressure is required to effect the complete transformation of the $Mg(B_3H_8)_2$. These results show that the reversible transformation of the triborane depends on the stability of the metal hydride. The more stable the metal hydride, that is, LiH > NaH > MgH_2, the lower is the "regeneration" efficiency.

■ INTRODUCTION

Magnesium borohydride, $Mg(BH_4)_2$, has among the highest hydrogen capacity and lowest enthalpy of dehydrogenation of the group I and II borohydrides.[1] Thus, it has been widely explored as a potential hydrogen storage material for onboard applications of polymer electrolyte membrane fuel cells.[2−9] The 11.2 wt % hydrogen that can be cycled through the reversible dehydrogenation of $Mg(BH_4)_2$ to MgB_2 stands as the highest hydrogen storage capacity that has been experimentally demonstrated for any material that can be **directly** hydrogenated.[9] However, cycling to MgB_2 requires extreme reaction conditions (i.e, dehydrogenation >400 °C and rehydrogenation at 400 °C and 900 atm H_2). We found that under moderate conditions (dehydrogenation at 200 °C; rehydrogenation 250 °C, 120 atm H_2), $Mg(BH_4)_2$ undergoes reversible dehydrogenation to $Mg(B_3H_8)_2$ as seen in eq 1.[2]

$$3Mg(BH_4)_2 \Leftrightarrow Mg(B_3H_8)_2 + 2MgH_2 + 2H_2 \qquad (1)$$

At sufficiently low temperatures this process was found to occur without formation of $MgB_{12}H_{12}$. While $MgB_{12}H_{12}$ is a plausible intermediate in the high temperature (>400 °C) decomposition of $Mg(BH_4)_2$ to MgB_2, its stability precludes its participation in low-temperature hydrogen cycling.[6] Although only 2.5 wt % hydrogen can be cycled in the reversible dehydrogenation of $Mg(BH_4)_2$ to MgH_2 and $Mg(B_3H_8)_2$, it does establish that the cycling of magnesium borohydride to magnesium boranes can be accomplished at moderate temperatures. This raises the possibility that alternative pathways might exist for the reversible dehydrogenation of the borohydride to higher polyboranes having one-to-one B/H stoichiometries, thus facilitating higher hydrogen storage capacities.

The development of such systems will benefit from a better mechanistic understanding of the reversible dehydrogenation of $Mg(BH_4)_2$. The dehydrogenation of borohydrides has been widely explored, but there have been few studies focusing on the rehydrogenation of the corresponding products. The studies that have been reported in the literature have required high temperatures and pressures to regenerate $Mg(BH_4)_2$.[6,8,9] Herein we report the first detailed investigation of the hydrogenation of the triborane to regenerate $Mg(BH_4)_2$.

To confirm the direct cycling between $Mg(BH_4)_2$ and $Mg(B_3H_8)_2$, we prepared an authentic sample of the

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tetrahydrofuran (THF) adduct of Mg(B$_3$H$_8$)$_2$, that is, Mg(B$_3$H$_8$)$_2$·2THF, and monitored the hydrogenation reaction by differential scanning calorimetry (DSC) in the presence of MgH$_2$. Attempts to desolvate the Mg(B$_3$H$_8$)$_2$·2THF were unsuccessful, so we proceeded to test our hypothesis that the efficient rehydrogenation of triborane depends on the stability of the metal hydride, with the solvated triborane.

As indicated in eq 1, the hydrogenation of Mg(B$_3$H$_8$)$_2$ to yield Mg(BH$_4$)$_2$ requires the presence of magnesium hydride, MgH$_2$, to satisfy the Mg mass balance. Therefore, we surmise that hydrogenation of Mg(B$_3$H$_8$)$_2$ to Mg(BH$_4$)$_2$ requires rupture of the B−B bond and subsequent hydride transfer from MgH$_2$ to make a new B−H bond. We further infer that the stability of alternative metal hydrides has a significant effect on the reaction pathway and energetic parameters governing the conversion of Mg(B$_3$H$_8$)$_2$ to Mg(BH$_4$)$_2$. To validate these hypotheses, we studied the hydrogenation of Mg(B$_3$H$_8$)$_2$·2THF in the presence of metal hydrides of varied thermodynamic stability by DSC and ^{11}B NMR.

EXPERIMENTAL METHODS

General Experimental Details. All sample preparation was conducted in an argon or nitrogen glovebox or on a Schlenk line. Solvents were purified by an SPS system. Borane THF complex (1 M) and magnesium turnings (98%) were purchased from Sigma-Aldrich and used without further purification.

Hydrogenation trials were conducted in a Suzuki Shokan PCT-2SDWIN Sievert type apparatus on 20−50 mg of sample powder. Precise temperature control was achieved using customized heating mantle sleeves. The differential scanning calorimetric studies of the hydrogenation reactions were conducted under 5 MPa in a Mettler Toledo Inc. DSC827e instrument contained in a helium glovebox using aluminum sample cells. The sample compartment was pressurized to 5 MPa H$_2$ and heated at a rate of 5 K/min with a H$_2$ flow of 200 mL/min. Thermogravimetry and differential thermal analysis were conducted on powders using a Rigaku TG8120 with He flow of 150 mL/min and heating at 5 K/min.

NMR Studies. Solution NMR analyses were performed on a Varian Unity Innova 500 MHz spectrometer with ^{11}B chemical shifts referenced to BF$_3$·OEt$_2$ (δ = 0 ppm) at 20 °C. ^{11}B was measured at 160.4 MHz, and ^{1}H was measured at 500.1 MHz. ^{1}H and ^{11}B NMR characterization of the products of hydrogenation trials were conducted in D$_2$O solution to obtain the narrow line widths that allowed the resolution of resonances that overlap in the solid state, observation of J couplings, and exact determination of chemical shifts, which are required for the identification of the different borane species. All samples were quenched in deuterium oxide and immediately analyzed. While closo-boranes are stable in aqueous solution, arachno and nido-boranes rapidly hydrolyze to form boric acid;[10,11] thus, we interpreted the presence of a boric acid resonance in our spectra as signaling the formation of these more reactive boranes. The mixture of Mg(B$_3$H$_8$)$_2$/MgH$_2$ dissolved completely in solvent, while trace amounts of insoluble materials remained for the Mg(B$_3$H$_8$)$_2$/LiH and Mg(B$_3$H$_8$)$_2$/NaH mixtures.

Solid-state NMR was also used to characterize as-synthesized Mg(B$_3$H$_8$)$_2$·2THF on a Varian Unity Innova 400 MHz with a 32 mm HX CPMAS probe. Sample powders were packed into zirconium oxide rotors and spun at 12 kHz. A spectral frequency of 128.32 MHz was used for ^{11}B magic-angle spinning (MAS) NMR with a 1 M boric acid solution (δ = 0 ppm) as a reference. A resonance at −22 ppm was observed for Mg(B$_3$H$_8$)$_2$·2THF.

Preparation of Mg(B$_3$H$_8$)$_2$·2THF. The preparation is based on the procedure of Shore et al.[12] and later modified by Hoy[13] for the synthesis of alkali and transition metals salts of B$_3$H$_8^-$. Magnesium turnings (0.20 g) were added to purified mercury (7 mL) in a 100 mL Schlenk flask under nitrogen flow. The flask was then heated to 190 °C with vigorous stirring overnight and allowed to cool to room temperature. Borane THF complex (50 mL) was then injected into the flask containing the Mg/Hg amalgam and stirred for 5−7 d, during which a white precipitate formed. The solid was filtered through a Schlenk frit under nitrogen flow and washed with THF to remove any residual Mg(BH$_4$)$_2$. The product was dried under vacuum at 50 °C for several hours and stored in an argon glovebox. The final yield was 0.60 g, 58% yield. ^{1}H NMR (D$_2$O, 500 MHz): δ 3.75(s, 2H, O−C$\mathbf{H}_2$), δ 1.85(s, 2H, C$\mathbf{H}_2$), δ 0.15(m, 9H, B$_3\mathbf{H}_8$). ^{11}B{^{1}H} NMR (D$_2$O, 500 MHz): δ −30.8 (nonet, $\mathbf{B}_3$H$_8$). ^{11}B{^{1}H} NMR (D$_2$O, 500 MHz): δ −30.8 (s, $\mathbf{B}_3$H$_8$).

RESULTS AND DISCUSSION

Mg(B$_3$H$_8$)$_2$·2THF was prepared by the addition of BH$_3$·THF to Mg/Hg amalgam at room temperature (eq 2). Our synthesis follows the general procedure of Shore et al.,[12] which was later

$$2\text{Mg/Hg} + 8\text{BH}_3\cdot\text{THF} \rightarrow \text{Mg(BH}_4)_2 + \text{Mg(B}_3\text{H}_8)_2\cdot 2\text{THF} + \text{Hg} + 6\text{THF} \quad (2)$$

modified by Hoy[13] for the synthesis of alkali and transition metals salts of B$_3$H$_8^-$ through the reaction BH$_3$·THF with the corresponding mercury amalgams. The insoluble Mg(B$_3$H$_8$)$_2$·2THF can be easily separated from the soluble Mg(BH$_4$)$_2$ by filtration. The ^{1}H-coupled ^{11}B NMR spectrum (Figure 1b) shows only the characteristic nonet resonance of [B$_3$H$_8$]$^-$ at −30.8 ppm due to coupling of the boron to the eight time-averaged hydrogens. The ^{1}H NMR spectrum of the product (Figure 2) contained the 10-line signal associated with [B$_3$H$_8$]$^-$ at 0.15 ppm as well as resonances for the THF adducts at δ = 3.75 and 1.85 ppm. On the basis of the integrated signal areas, we formulated the complex as Mg(B$_3$H$_8$)$_2$·2THF. Attempts to remove the THF by heating at 60 °C under vacuum, ball-milling the powder, or by sublimation were unsuccessful.

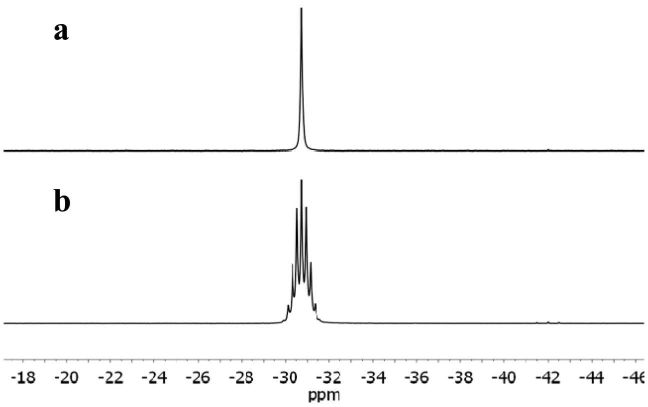

Figure 1. (a) ^{11}B{^{1}H} NMR of as-synthesized Mg(B$_3$H$_8$)$_2$·2THF; (b) ^{11}B NMR for the same material.

We next explored whether a mixture of Mg(B$_3$H$_8$)$_2$·2THF and MgH$_2$ could serve as an entry point for the hydrogen cycling system seen in eq 1. Accordingly, a 1:2 molar ratio of Mg(B$_3$H$_8$)$_2$·2THF and MgH$_2$ was heated to 200 °C under 5 MPa H$_2$ for 2 h. The MAS solid-state ^{11}B NMR spectrum of the product indicated a quantitative conversion to Mg(BH$_4$)$_2$ had occurred as it contained only a single peak at −35 ppm, which is the characteristic chemical shift for Mg(BH$_4$)$_2$ in the solid state. The solution ^{11}B {^{1}H} NMR (Figure 3) spectrum of the completely D$_2$O-soluble product mixture contained only one resonance at the −42 ppm chemical shift that is characteristic for Mg(BH$_4$)$_2$ in D$_2$O solution.

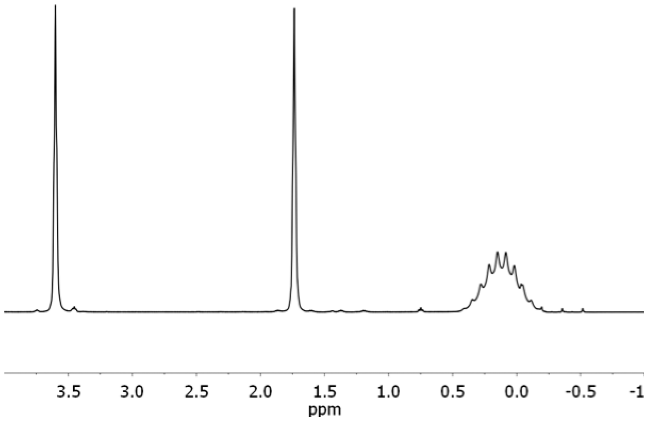

Figure 2. ^{1}H NMR of as-synthesized $Mg(B_3H_8)_2{\cdot}2THF$. A trace signal can be seen for $Mg(BH_4)_2$ centered around 0.25 ppm, which partially overlaps with the 10-line signal for $Mg(B_3H_8)_2$.

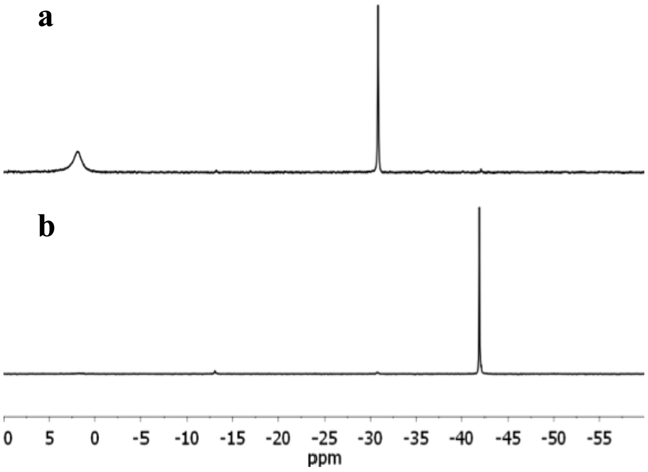

Figure 3. $^{11}B\{^{1}H\}$ NMR (D_2O solution) of (a) $Mg(B_3H_8)_2{\cdot}2THF$ and MgH_2 before hydrogenation; (b) after hydrogenation at 200 °C, 2 h, 5 MPa.

The hydrogenation of a 1:2 mixture of $Mg(B_3H_8)_2{\cdot}2THF$ and MgH_2 was further studied by DSC. The DSC reaction profile (Figure 4) displayed an initial endothermic feature at ~65 °C, which matches the visual observation of the material undergoing a phase change from a free-flowing powder to a gel at this temperature. This was followed by a large exothermic feature that reaches a maximum at 130 °C corresponding to the hydrogenation of $Mg(B_3H_8)_2$ to $Mg(BH_4)_2$.

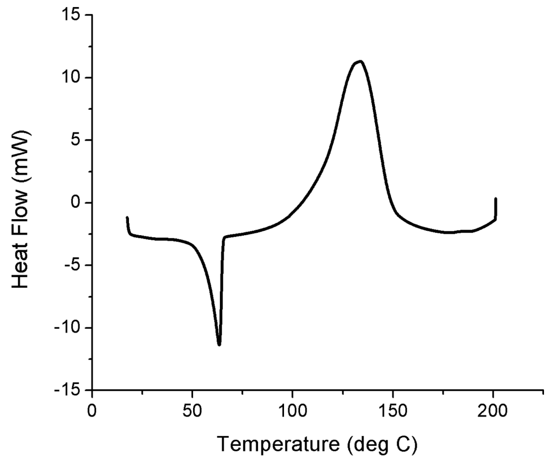

Figure 4. DSC profile of mixture of $Mg(B_3H_8)_2{\cdot}2THF$ and MgH_2 (1:2) under 5 MPa H_2.

To better understand the role of MgH_2 in the hydrogenation reaction, $Mg(B_3H_8)_2{\cdot}2THF$ was heated to 200 °C under 5 MPa H_2 pressure in the absence of MgH_2 and immediately cooled. The ^{11}B $\{^{1}H\}$ NMR spectrum (Figure 5) of the completely D_2O-soluble product mixture was found to consist of $MgB_{12}H_{12}$ (−15 ppm), $MgB_{10}H_{10}$ (−1, −30 ppm), $Mg(BH_4)_2$ (−42 ppm), and several unidentified products. Comparison of the integrated intensities of dodecaborane, decaborane, and borohydride products allows their yields to be roughly estimated as 54, 13, and 9%, respectively (Table 1). These observations are consistent with the results reported by Titov[14] for the thermal decomposition of $Mg(B_3H_8)_2$ solvated with diglyme under vacuum. At temperatures >185 °C they observe the formation of $Mg(BH_4)_2$ and $MgB_{12}H_{12}$ as the main dehydrogenation products. They propose that the initial reaction is the rupture of the two bridging B···H bonds leading to the formation of a transient B_2H_4 species that oligomerizes to form intermediate polyboranes, for example, B_4H_{10} and B_5H_9, which in turn thermally decompose to form $[B_{12}H_{12}]^{2-}$.

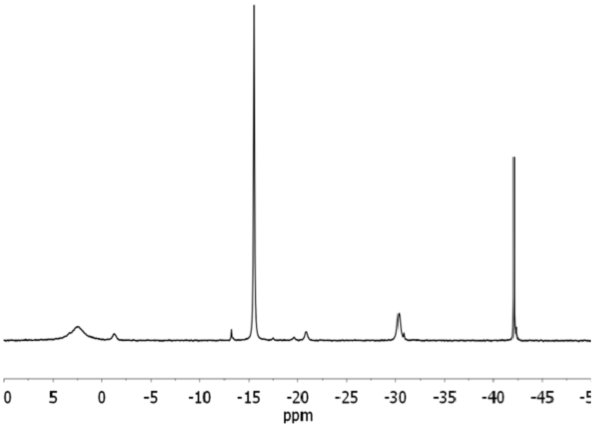

Figure 5. $^{11}B\{^{1}H\}$ NMR (D_2O solution) of $Mg(B_3H_8)_2{\cdot}2THF$ hydrogenated at 200 °C under 5 MPa H_2 pressure followed by immediate cooling.

Table 1. Boron Species (mol %) Determined by NMR Analysis of Hydrogenated $Mg(B_3H_8)_2{\cdot}2THF$

	boric acid	$[B_{10}H_{10}]^{2-}$	$[B_{12}H_{12}]^{2-}$	$[BH_4]^{-}$
δ, ppm	2	−1, −30	−15	−42
mol %	20	13	54	9

We previously proposed that the stability of the metal hydride formed in the dehydrogenation of group I and II borohydrides was the principal factor governing the reversibility of the reaction.[2] The reverse reaction, hydrogenation of the triborane, requires the scission of a B—B bond accompanied by the scission of an M—H bond. If the M—H bond is too strong, that is, the metal hydride is too stable, then the efficiency of the regeneration will be impacted. To test this hypothesis we examined the hydrogenation of mixtures of $Mg(B_3H_8)_2{\cdot}2THF$ and other metal hydrides. A mixture of $Mg(B_3H_8)_2{\cdot}2THF$ and LiH in a 1:4 molar ratio was heated to 200 °C under 5 MPa H_2 pressure for 2 h.

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The solution ^{11}B {^{1}H} NMR (Figure 6) spectrum of the D_2O-soluble product mixture contained large peaks corresponding to $[B_{12}H_{12}]^{2-}$ (−15 ppm) and $[BH_4]^-$ (−42 ppm) as well as minor peaks for unreacted $[B_3H_8]^-$ (−31 ppm) and several other products. The DSC reaction profile of the hydrogenation with LiH (Figure 7) shows the phase change at 65 °C followed by an exothermic signal with a maximum at 140 °C. The higher thermodynamic stability of LiH versus MgH_2 (ΔH_f° = −181.6 vs −74.5 kJ/mol)[15] apparently results in higher activation barrier thus slowing hydrogenation to $[BH_4]^-$ and allowing competition by condensation reactions leading to the formation of $[B_{12}H_{12}]^{2-}$.

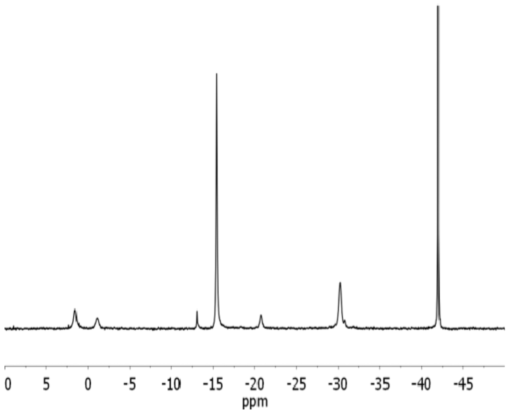

Figure 6. $^{11}B\{^{1}H\}$ NMR of $Mg(B_3H_8)_2{\cdot}2THF$ and LiH (1:4) after hydrogenation at 200 °C, 1 h, 5 MPa H_2.

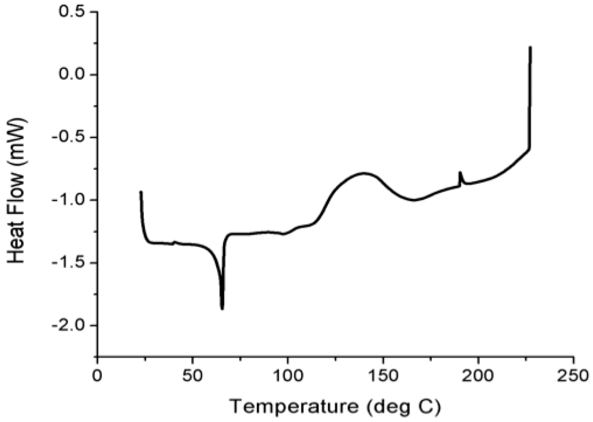

Figure 7. DSC profile of $Mg(B_3H_8)_2{\cdot}2THF$ and LiH (1:4) under 5 MPa H_2.

In a parallel experiment, a 1:4 molar ratio of $Mg(B_3H_8)_2{\cdot}2THF$ and NaH was hydrogenated at 225 °C and allowed to cool immediately for NMR analysis. The ^{11}B NMR analysis of the products exhibited resonances at 2 and −42 ppm, representing a hydrolyzed borane(s) and $[BH_4]^-$ respectively, (Figure 8), with the borohydride signal having approximately twice the intensity of that for the reactive borane(s). The DSC profile for the reaction also displayed two prominent exothermic features between 80 and 150 °C (Figure 9). The same mixture was hydrogenated to 130 °C, a temperature between that of the two exothermic steps observed in the DSC scan. The ^{11}B NMR spectrum again contained only resonances for the hydrolyzed borane(s) and $[BH_4]^-$ (Figure 10). However, the relative intensities of the signals clearly demonstrate that the reactive borane(s) dominates the product mixture obtained at the lower temperature. We conclude that the reactive borane is an intermediate in the two-step conversion of the triborane to $[BH_4]^-$. As seen in Scheme 1, the mechanism of Titov discussed above can be augmented to account for our observation of a metastable intermediate species when the hydrogenation is conducted in the presence of NaH. We propose that the transient B_2H_4 formed upon the

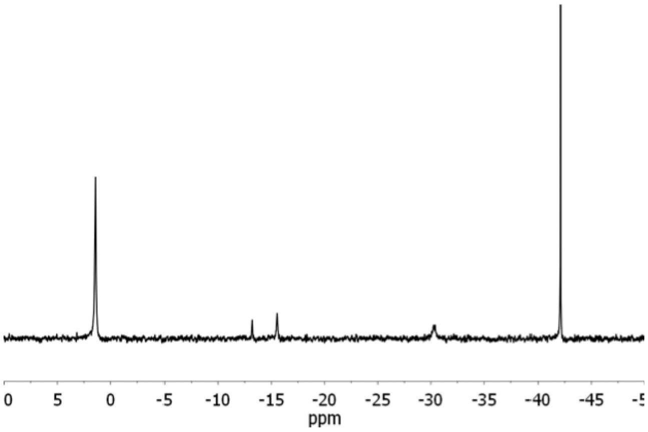

Figure 8. $^{11}B\{^{1}H\}$ NMR of $Mg(B_3H_8)_2{\cdot}2THF$ and NaH (1:4) after hydrogenation at 225 °C and 5 MPa H_2, immediately cooled.

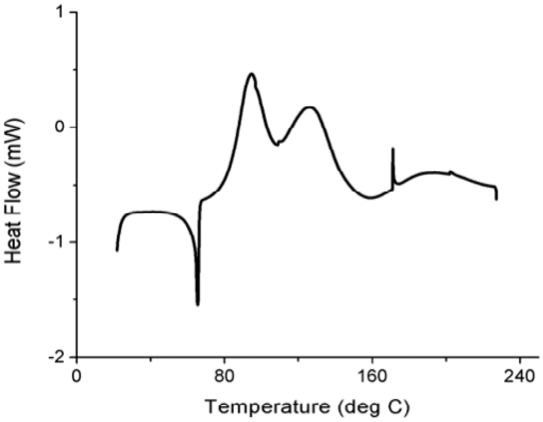

Figure 9. DSC profile of $Mg(B_3H_8)_2{\cdot}2THF$ and NaH (1:4) under 5 MPa H_2.

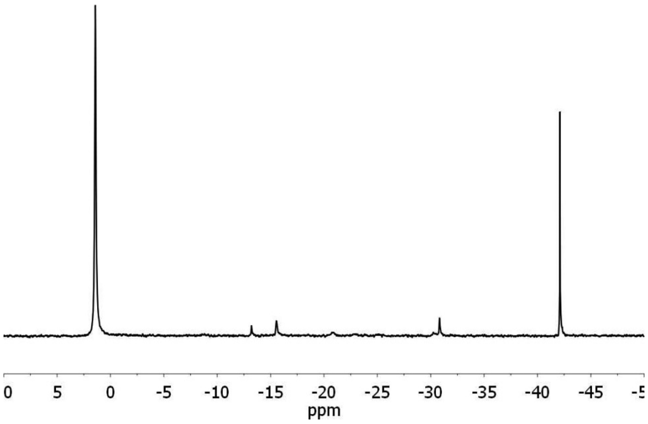

Figure 10. $^{11}B\{^{1}H\}$ spectra of $Mg(B_3H_8)_2{\cdot}2THF$ and NaH (1:4) after hydrogenation at 130 °C and 5 MPa H_2, immediately cooled.

Scheme 1. Proposed Reaction Pathway for the Hydrogenation of $[B_3H_8]^-$ to $[BH_4]^-$

$[BH_4{-}{-}{-}H_2B{-}BH_2]^-$ --> $[BH_4]^-$ + $H_2B{-}BH_2$

$MH + B_2H_4 + H_2$ --> $M[B_2H_7]$

$M[B_2H_7] + MH$ --> $2M[BH_4]$

elimination of BH_4^- from $[B_3H_8]^-$ undergoes addition of H_2 and reacts with the metal hydride to form the intermediate borane $[B_2H_7]^-$, which then reacts with another equivalent of metal hydride to give 2 equiv of the more thermodynamically stable $[BH_4]^-$. Mechanisms involving the alternative putative species $[B_2H_5]^-$ are also possible;[16] however, the reaction of B_2H_4 with H_2 as a Lewis acid seems much more likely than $[B_2H_5]^-$ reacting with H_2 as a Lewis base. Furthermore, the activation barrier to the conversion of the intermediate species to form $[BH_4]^-$ must be higher in the case of NaH versus MgH_2, thus allowing observation of the intermediate. Additionally, note that NaH, like MgH_2, appears to interact at a lower temperature than LiH thus circumventing the formation of $[B_{12}H_{12}]^{2-}$ through kinetic control.

To compare the results of hydrogenation of solvated triborane $Mg(B_3H_8)_2{\cdot}2THF$, prepared independently, with that of the unsolvated triborane $Mg(B_3H_8)_2$, prepared in situ, that is, from the low-temperature dehydrogenation of $Mg(BH_4)_2$, a sample of $Mg(BH_4)_2$ was dehydrogenated at low temperatures following the procedure outlined in a previous study.[2] The ^{11}B NMR spectra of the dehydrogenated powder and products resulting from subsequent hydrogenation under various conditions is presented in Figure 11. Hydrogenation results in direct conversion of unsolvated $Mg(B_3H_8)_2$ (−31 ppm) to $Mg(BH_4)_2$ (−42 ppm), although higher temperature and pressure is needed to achieve the complete transformation. The DSC profile for this reaction (Figure 12) did not exhibit a low-temperature endothermic feature corresponding to a phase change; thus, the lower kinetic barrier to hydrogenation of the adduct probably arises from higher molecular mobility in the gel state of the THF adduct. The profile contains only a broad exothermic feature with a maximum at 120 °C that is associated with the formation of $Mg(BH_4)_2$.

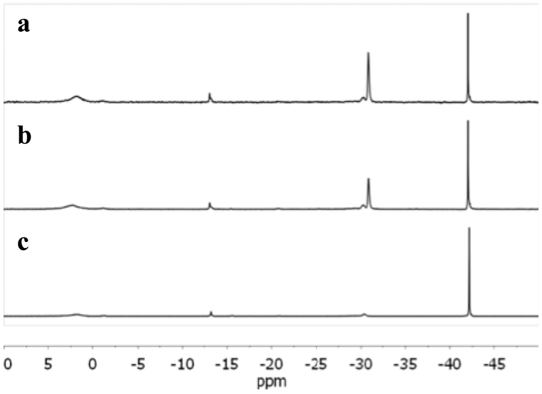

Figure 11. $^{11}B\{^1H\}$ NMR of (a) $Mg(BH_4)_2$ dehydrogenated five weeks, 200 °C; (b) rehydrogenation at 200 °C, 5 MPa H_2, cooled immediately; (c) rehydrogenation at 250 °C, 12 MPa H_2, 48 h.

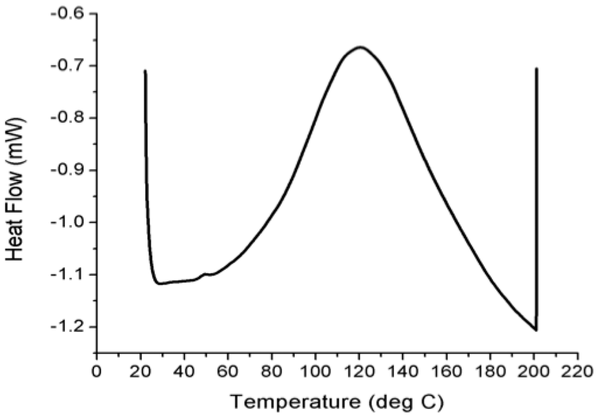

Figure 12. DSC profile of $Mg(BH_4)_2$ (dehydrogenated five weeks, 200 °C, 0 MPa), ramped at 5 °C/min to 200 °C under 5 MPa H_2.

CONCLUSIONS

Our results illustrate how the presence (and absence) of an alkaline metal hydride alters the dehydrogenation/rehydrogenation pathways of $Mg(BH_4)_2$. We have shown that the hydrogenation of $Mg(B_3H_8)_2$ as the THF adduct prepared independently or prepared unsolvated in situ without a hydride source results in some regeneration of $[BH_4]^-$ accompanied by the formation of higher boranes, most notably, $[B_{12}H_{12}]^{2-}$. However, hydride donors MgH_2 and NaH open a reaction pathway of lower activation that leads to selective hydrogenation to $[BH_4]^-$. MgH_2 and NaH appear to react at lower temperatures than LiH and are thus more effective in preventing the formation of $[B_{12}H_{12}]^{2-}$. The more stable the metal hydride, that is, LiH > NaH > MgH_2 ($\Delta H_f^\circ = -181.6$, -113, and -74.5 kJ/mol, respectively)[15] the lower the "regeneration" efficiency. Our DSC studies indicate that the conversion of the triborane to $[BH_4]^-$ occurs in a two-step process involving an intermediate like $[B_2H_7]^-$. The activation barrier to the conversion of the intermediate species to $[BH_4]^-$ must be higher in the case of NaH versus MgH_2, thus allowing observation of the intermediate. However, in the case of LiH, no intermediate is observed; thus, the barrier to the formation of the intermediate must be equal or greater than that for the conversion of the intermediate to products. These findings point to the possibility of finding mild polymer electrolyte membrane fuel cell relevant conditions for the reversible dehydrogenation of borohydrides that avoid thermodynamic sinks such as $[B_{12}H_{12}]^{2-}$.

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Notes

The authors declare no competing financial interest.

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