



Article Effects of Glymes on the Distribution of $Mg(B_{10}H_{10})$ and $Mg(B_{12}H_{12})$ from the Thermolysis of $Mg(BH_4)_2$

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Abstract: We examined the effects of concentrations and identities of various glymes, from monoglyme up to tetraglyme, on H₂ release from the thermolysis of Mg(BH₄)₂ at 160–200 °C for 8 h. ¹¹B NMR analysis shows major products of Mg(B₁₀H₁₀) and Mg(B₁₂H₁₂); however, their relative ratio is highly dependent both on the identity and concentration of the glyme to Mg(BH₄)₂. Selective formation of Mg(B₁₀H₁₀) was observed with an equivalent of monoglyme and 0.25 equivalent of tetraglyme. However, thermolysis of Mg(BH₄)₂ in the presence of stoichiometric or greater equivalent of glymes can lead to unselective formation of Mg(B₁₀H₁₀) and Mg(B₁₂H₁₂) products or inhibition of H₂ release.

Keywords: magnesium borohydride; glymes; boron cages; product selectivity; dehydrogenation; hydrogen storage

1. Introduction

The safe storage of hydrogen in a compact and efficient form remains a formidable challenge towards the realization of energy decarbonization. Among the wide range of complex hydride materials studied, Mg(BH₄)₂ has garnered tremendous interest from the storage community because of desirable physical and thermodynamic properties [1–4]. Mg(BH₄)₂ features a high gravimetric density of H₂ (ca. 14.7 wt% H₂), and a thermodynamic range that is ideal for H₂ release and H₂ uptake at moderate pressure and temperature. Despite these attractive physical and thermodynamic properties, one major drawback of Mg(BH₄)₄ is the slow rate of H₂ release at high temperature. To circumvent this high barrier towards reactivity, many studies have focused on generating complex mixtures of Mg(BH₄)₂ with additives composed of organic molecules [5–9], a different borohydride (e.g., LiBH₄) [10–12], and transition metals [13–16] to lower the temperature for H₂ release.

We have shown that the addition of a simple additive such as THF to Mg(BH₄)₂ can promote dehydrogenation of Mg(BH₄)₂ at temperature less than 200 °C compared to the dehydrogenation of solid Mg(BH₄)₂ at 250 °C and above [5,17]. Interestingly, in addition to lowering the dehydrogenation temperature, the presence of THF also favored the formation of B₁₀H₁₀²⁻ over B₁₂H₁₂²⁻ and B₃H₈⁻ from Mg(BH₄)₂ compared to the favored formation of B₃H₈⁻ over B₁₀H₁₀²⁻ and B₁₂H₁₂²⁻ for dehydrogenation of solid Mg(BH₄)₂ [17]. To our knowledge, the dehydrogenation of Mg(BH₄)₂ with triethylamine is the only system using an organic additive that favors the formation of B₃H₈⁻ over B₁₀H₁₀²⁻ and B₁₂H₁₂²⁻ [5]. Unfortunately, a structure–activity relationship on the dehydrogenation of Mg(BH₄)₂ with THF is limited by structural derivatives. We therefore turned to glymes because of their abundance, availability, and more importantly broad structural derivatives to probe the dehydrogenation activity of Mg(BH₄)₂. Additionally, the combination of glymes and Mg(BH₄)₂ have also drawn interest as electrolytes for battery energy storage [18–22]. In



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). addition, the thermodynamic affinity of the cation–glyme interaction is highly influenced by the number of chelating diether units, which may have some influence on Mg(BH₄)₂ dehydrogenation [23]. While structural studies of Mg(BH₄)₂ with monoglyme and diglyme are known [24,25], the effects of different glymes on the decomposition and product selectivity of Mg(BH₄)₂ have not been reported. Herein, we report the effects of a variety of glymes on the dehydrogenation of Mg(BH₄)₂ to form B₁₀H₁₀^{2–}, B₁₂H₁₂^{2–} and B₃H₈[–].

2. Results

We initiated our studies by performing parallel reactions of Mg(BH₄)₂ with 1.0 equiv. of monoglyme (G1), triglyme (G3), and tetraglyme (G4) at 180 °C for 8 h (Table 1). The results of these reactions showed that G1, G3, and G4 contain the highest activity with conversion of Mg(BH₄)₂ in the rage of 33–50%. Conversely, diglyme (G2) showed minimal activity for the dehydrogenation of Mg(BH₄)₂ even at 200 °C for 8 h (Table 1, entry 13) with no apparent selectivity for any boron products. Like THF, G1 selectively produced $B_{10}H_{10}^{2-}$ over $B_{12}H_{12}^{2-}$ and $B_3H_8^-$ (Table 1, entry 1). While the conversion of Mg(BH₄)₂ is higher for G4 (50%) than that of G3 (39%), G3 has higher selectivity of forming $B_{12}H_{12}^{2-}$ over $B_{10}H_{10}^{2-}$ than that of G4 with a ratio of $B_{12}H_{12}^{2-} / B_{10}H_{10}^{2-}$ is 2.5/1.0 for G3 and 1.4/1.0 for G4 (Table 1, entry 2 vs. entry 3). This preference for $B_{12}H_{12}^{2-}$ over $B_{10}H_{10}^{2-}$ for the longer chain glymes in a 1:1 reaction with Mg(BH₄)₂ is the reverse of that of G1 and THF.

| Entry | Additive | Equiv. | T (°C) | $B_{10}H_{10}^{2-}$ | $B_{12}H_{12}^{2-}$ | $B_3H_8^-$ | Unknown | Conv ^a | Mass Loss% ^b |
|-------|----------|--------|--------|---------------------|---------------------|------------|---------|-------------------|----------------------------|
| 1 | G1 | 1.0 | 180 | 29 | 1 | 1 | 2 | 33 | 11.5 |
| 2 | G3 | 1.0 | 180 | 10 | 25 | 1 | 3 | 39 | 40.3 |
| 3 | G4 | 1.0 | 180 | 19 | 27 | 1 | 3 | 50 | 53.8 |
| 4 | G1 | 1.5 | 180 | 37 | 14 | — | 2 | 53 | |
| 5 | G1 | 26 | 180 | 16 | 30 | — | 17 | 63 | |
| 6 | G4 | 0.25 | 180 | 15 | | 1 | | 16 | |
| 7 | G4 | 54 | 180 | _ | _ | _ | _ | 0 | |
| 8 | Me-THF | 1.0 | 180 | 3 | _ | 1 | 4 | 7 | |
| 9 | dodecane | 1.0 | 180 | _ | _ | _ | _ | 0 | |
| 10 | G1 | 1.0 | 160 | 7 | _ | 1 | 3 | 10 | |
| 11 | G4 | 1.0 | 160 | 3 | 8 | 3 | 5 | 19 | |
| 12 | G1 | 1.0 | 200 | 54 | 2 | 2 | 3 | 61 | |
| 13 | G2 | 1.0 | 200 | 5 | 2 | 5 | 5 | 17 | |
| 14 | G4 | 1.0 | 200 | 8 | 36 | 11 | 16 | 61 | |
| 15 | Me-THF | 1.0 | 200 | 22 | 1 | 4 | 8 | 35 | |
| 16 | dodecane | 1.0 | 200 | _ | _ | _ | _ | 0 | |

Table 1. Product distribution for the reaction of $Mg(BH_4)_2$ with 1.0 equivalent of additive at 180 °C for 8 h.

^a Characterization of B-containing products were analyzed by ¹¹B NMR spectroscopy using a mix solvent system of 2 D₂O: 1 THF. ^b Thermogravimetric analysis (TGA) (5 K/min ramp, 180 °C), the large mass loss can potentially result from the decomposition of glyme, see Ref. [26]. TGA data for the Mg(BH₄)₂ with G1, G2, G3, and G4 (Figures S1–S4) are provided in the Supplementary Materials. Abbreviations of Additives: G1 = monoglyme; G2 = diglyme; G3 = triglyme; G4 = tetraglyme; Me-THF = 2-methyltetrahydrofuran. Unknown borane is quartet at -13 ppm in ¹¹B NMR assumed as 1 boron.



We have previously shown that only sub-stoichiometric amounts of THF additive are necessary for the dehydrogenation of Mg(BH₄)₂ [5]. Therefore, we analyzed the effect of sub-stoichiometric and excess quantities of G1 versus G4 on the product distribution of boron species. Since 1.0 equiv. of G1 to Mg(BH₄)₂ is selective for $B_{10}H_{10}^{2-}$ formation,

we investigated the effect of slight excess of G1 because a lowered equivalent of G1 is expected to favor $B_{10}H_{10}^{2-}$ over $B_{12}H_{12}^{2-}$ based on the result of sub-stoichiometric THF and 0.25 equiv. of G4 (Table 1, entry 6). Interestingly, at 1.5 equiv. of G1 to Mg(BH₄)₂, the formation of $B_{10}H_{10}^{2-}$ remained favorable over $B_{12}H_{12}^{2-}$, but not selective because a 2.6:1.0 ratio of $B_{10}H_{10}^{2-}$: $B_{12}H_{12}^{2-}$ was observed (Table 1, entry 4). Additionally, increasing to 26 equiv. of G1 to Mg(BH₄)₂ now favors forming $B_{12}H_{12}^{2-}$ over $B_{10}H_{10}^{2-}$ with a ratio of 1.9 to 1.0 (Table 1, entry 5). The results for the reaction of 0.25 equiv. of G4 to Mg(BH₄)₂ showed preference for $B_{10}H_{10}^{2-}$ over $B_{12}H_{12}^{2-}$ (Table 1, entry 6), which is in contrast to that of 1.0 equiv. of G4 to Mg(BH₄)₂ (Table 1, entry 3). Moreover, in the presence of excess G4, there was no dehydrogenative conversion of Mg(BH₄)₂ (Table 1, entry 7).

Lastly, as expected, increasing the temperature of the reactions also increased the rates of dehydrogenation of Mg(BH₄)₂. The reactions of 1.0 equiv. of G1, Me-THF, and G4 with Mg(BH₄)₂ at 200 °C for 8 h showed high conversion of Mg(BH₄)₂ (35–61%) compared to conversion at 160–180 °C (Table 1, entry 12, 14, 15). More importantly, increasing the temperature for the 1:1 reaction of G1, Me-THF, and G4 and Mg(BH₄)₂ does not alter the product selectivity between $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. However, in case of G4, dehydrogenation at 200 °C leads to more side reactions of unknown boron products (16%). The ¹¹B NMR data for the reactions of Mg(BH₄)₂ with 1.0 equiv. of G1 and G4 at 200 °C are presented in Figure 1. The results of these systematic studies clearly indicate the diverse and complex effects of varying the identity and the concentration of $B_{10}H_{10}^{2-}$ over $B_{12}H_{12}^{2-}$ and vice versa can be controlled by using a single additive (e.g., G1) at different concentrations.



Figure 1. (a) ¹¹B NMR analysis of Mg(BH₄)₂, 1 equiv. tetraglyme (G4), 200 °C, 8 h to generate the major product of $B_{12}H_{12}^{2-}$; (b) ¹¹B NMR analysis of Mg(BH₄)₂, 1 equiv. monoglyme (G1), 200 °C, 8 h to generate the major product of $B_{10}H_{10}^{2-}$.

A working hypothesis for lowering the energy barrier for H₂ release from Mg(BH₄)₂ involves the ability of the oxygen atom of THF to form a Mg-O coordinative interactions with the oxophilic Mg²⁺ ion. It is well-known that *ortho*-substituted THF binds weakly compared to THF to metal ions because the lone pairs on the oxygen atom are less exposed. To probe the effect of the relative binding strength of this Mg-O interaction on the dehydrogenation of Mg(BH₄)₂, we performed the 1:1 reaction of Mg(BH₄)₂ to Me-THF at 180 °C for 8 h (Table 1, entry 8). The result of the reaction showed minor conversion of Mg(BH₄)₂ (7%), yet the selective formation of B₃H₈⁻ over B₁₀H₁₀²⁻ and B₁₂H₁₂²⁻ is similar to that of THF. However, at 200 °C, the conversion of Mg(BH₄)₂ showed significant improvement

with conserved selectivity for $B_{10}H_{10}^{2-}$ (Table 1, entry 15). To further demonstrate that only heteroatom-derived additives that can interact with the Mg²⁺ ion of Mg(BH₄)₂ or melt the Mg(BH₄)₂ upon heating can induce dehydrogenation, we performed the 1:1 reaction of Mg(BH₄)₂ and dodecane at 180–200 °C for 8 h and found no conversion of Mg(BH₄)₂ (Table 1, entry 9, 16). These two control studies suggest that the degree of interaction of Mg-O for THF and Me-THF might be critical for dehydrogenation activity and that nonpolar, high boiling, heteroatom-free hydrocarbons such as dodecane are not suitable to promote dehydrogenation of Mg(BH₄).

The lack of H₂ release from Mg(BH₄)₂ with dodecane is in stark contrast to the observation of H₂ release in Et₄NBH₄ in decane–dodecane mixture at 185 °C for ~ 10 h [27]. Some interaction of the glyme with the Mg²⁺ center may be important for the dehydrogenation of Mg(BH₄)₂. It is also clear that some glyme is beneficial to the selectivity of B₁₀H₁₀²⁻ over B₁₂H₁₂²⁻. However, excess G1 and G4 leads to complete loss of any selectivity for B₁₀H₁₀²⁻ or B₁₂H₁₂²⁻ and complete deactivation of H₂ release from Mg(BH₄)₂. These results suggest the strong complexation of the Mg²⁺ center by excess glymes inhibits dehydrogenative activity by disfavoring the formation of Mg-H by potentially locking up the Mg²⁺ center of Mg(BH₄)₂. Moreover, the loss of B₁₀H₁₀²⁻ selectivity in the presence of excess G1 (Table 1, entry 5) to give a mixture of products, including favoring formation of B₁₂H₁₂²⁻ over B₁₀H₁₀²⁻, also suggests that free G1 can interact with transient boron intermediates to drive different reaction pathways towards the formation of a variety of boron clusters.

3. Discussion

The complicated dependence of reaction conditions, pressure, and additives on the selectivity of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ formation during the dehydrogenation of borohydride complexes have been previously observed [27-30]. Additionally, the unselective formation of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ under varying reaction conditions suggests the factors controlling the reaction pathway to forming $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are close in energy. Interestingly, kinetic studies on the thermolysis of Et₄NBH₄ in refluxing decane–dodecane mixture at 185 °C generating $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^{-}$, $B_{12}H_{12}^{2-}$ as final products show that $B_3H_8^-$ is consumed over time with concomitant growth of $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ [27]. In fact, the relative rate of B₃H₈⁻ consumption corresponds more closely with the faster rate of formation of $B_{10}H_{10}^{2-}$ than that of the slower rate of formation of $B_{12}H_{12}^{2-}$, whereas the rate of $B_9H_9^{2-}$ and $B_{11}H_{14}^{-}$ formation appears independent under this reaction temperature. In a separate study, heating Cs₂B₉H₉ at 1 h at 600 °C was reported to give complete conversion to a mixture of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ products [29]. However, the initial formation of $B_3H_8^-$ before forming $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ products has been observed for the thermolysis of solid Mg(BH₄)₂. Heating B_2H_6 and NaBH₄ at 90 °C in diglyme leads to the formation of NaB₃H₈ suggesting that these $B_3H_8^-$ species can be generated at relative lower temperature. Thermolysis of NaB₃H₈ in diglyme at 162 °C leads to a mixture of products of Na₂B₆H₆, Na₂B₁₀H₁₀, and Na₂B₁₂H₁₂ [31,32]. While there are kinetic and reaction data to support that B₃H₈⁻ can readily form in the initial stages of constructing polyborane cages, it is unclear if the loss of $B_3H_8^-$ for the subsequent construction of larger polyboranes such as $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ is the direct result of construction from $B_3H_8^-$ or involves intermediate stages of $B_3H_8^-$ decomposition. For example, $B_3H_8^$ may disproportionate to B_2H_4 and BH_4^- , and the reactive B_2H_4 go on to form the various polyborane products.

In the current reaction involving $Mg(BH_4)_2$, keeping track of the stoichiometry of the individual steps enables the development of a hypothesis to follow the chemical evolution. For example, the stoichiometry of the decomposition reaction of $Mg(BH_4)_2$ to $Mg(B_3H_8)_2$ requires an accompanying production of MgH_2 (Equation (1)):

$$3 \text{ Mg}(BH_4)_2 \rightarrow \text{Mg}(B_3H_8)_2 + 2 \text{ MgH}_2 + 2H_2$$
 (1)

$$Mg(B_3H_8)_2 \to Mg(BH_4)_2 + 2[B_2H_4]$$
 (2)

The neutral B_2H_4 can then decompose to form B_2H_6 and B_5H_9 (Equation (3))

$$6B_2H_4 \rightarrow 2B_5H_9 + B_2H_6$$
 (3)

In the decomposition of $Mg(BH_4)_2$ studied here, MgH_2 is formed in concert with $B_3H_8^-$ opening additional pathways to compete with formation of B_2H_6 and B_5H_9 . For example, in the presence of the MgH_2 , a diborane anion may be formed through reaction of B_2H_4 with MgH_2 (Equation (4))

$$2MgH_2 + 2[B_2H_4] \to 2MgB_2H_6 \tag{4}$$

The $B_2H_6^{2-}$ has been proposed as an intermediate in the decomposition of Mg(BH₄)₂ on the pathway to forming $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ [33].

In a recent paper, Gigante et al. have compared the products observed in the decomposition of solvent free Mg(B₃H₈)₂ in the presence and absence of MgH₂ at 200 °C [34]. Indeed, they do report a difference in reaction products. In the absence of MgH₂, volatile pentaborane and diborane were observed and substantial quantities of B₁₀H₁₀^{2–} and B₁₂H₁₂^{2–} were produced. In contrast, in the presence of MgH₂, the reaction product was nearly all Mg(BH₄)₂, and substantially less pentaborane was observed in the gas phase. It is notable that, under the same reaction conditions, the presence of a two-fold stoichiometric excess MgH₂ switched the reaction products between B₁₀H₁₀^{2–} and B₁₂H₁₂^{2–} and Mg(BH₄)₂. This result is consistent with B₃H₈⁻ serving as a key intermediate connecting Mg(BH₄)₂ to B₁₀H₁₀^{2–}.

However, this does not explain the unique selectivity of $B_{10}H_{10}^{2-}$ formation over $B_{12}H_{12}^{2-}$ in the presence of G1, G4, THF, and MeTHF. At this time, we can only propose a hypothetical branching point that lowers the barrier of the pathway leading to the formation of $B_{10}H_{10}^{2-}$. One possible intermediate may be MgB₁₀H₁₂. Gaines and coworkers have shown that Na₂B₁₀H₁₂ decomposes to form B₁₀H₁₀ in high yield in the presence of glyme [35]. However, in the presence of MeCN, the $B_{10}H_{12}^{2-}$ decomposes to complex mixtures of boranes including both $B_9H_9^{2-}$ and $B_{10}H_{10}^{2-}$. If $B_{10}H_{12}^{2-}$ is a branching point, then the presence of glyme could reduce the barrier to form greater yields of $B_{10}H_{10}^{2-}$. However, this is supposition at this point and requires further study beyond the scope of the current work. Given the proposed role of MgH₂ intermediates in the initial decomposition of $Mg(BH_4)_2$ and in the subsequent reactivity with transient boranes during dehydrogenation, the detection of MgH_2 in the early stages of $Mg(BH_4)_2$ decomposition would provide key mechanistic evidence. The detection of MgH₂ formation is difficult and remains an acknowledged issue in the field of H_2 release from $Mg(BH_4)_2$ despite various efforts. However, MgH₂ has been observed by in situ diffraction at 350–360 °C, but, in both cases, this was more than 50 $^{\circ}$ C higher than the initial release of H₂ and constituted the formation of an amorphous intermediate [36,37].

Enhanced kinetics. In previous work, we have noted that the sub-stoichiometric adducts with THF induce a phase change from a polycrystalline $Mg(BH_4)_2$ compound to an amorphous phase at temperature below 100 °C [5,38]. We suggested that the diffusion rates of species in the amorphous phase will be enhanced, thus enhancing the rates of reaction. Therefore, a change in physical state enhances the rates of mass transfer and potentially increases the reactivity at lower temperatures compared to the neat bulk crystalline $Mg(BH_4)_2$. We offer another possibility involving the chemical nature of THF and Lewis base glyme adducts. It is well known that borane forms stable adducts with THF and other Lewis base adducts, e.g., dimethyl sulfide and amines. It is possible

that the presence of *catalytic* (sub-stoichiometric) quantities of these adducts reduces the activation barrier for borohydride to form intermediates such as B_2H_7 and B_3H_8 anions (Equations (5) and (6)):

 $THF^*MBH_4 \Leftrightarrow [THF^*BH_3] + MH$ (5)

$$[THF^*BH_3] + MBH_4 \Leftrightarrow THF^*MB_2H_7 \tag{6}$$

In this role, the THF, or glyme, lowers the barrier to form B_2H_7 by stabilizing the BH_3 transfer steps, i.e., [THF*BH3]. Glyme could perform a similar role as THF, thus the similar observations for enhanced reactivity, whereas the presence of a non-coordinating solvent, dodecane, shows no enhanced reactivity.

This does not directly explain the lack of reactivity in the experiments using diglyme (G2) or when excess tetraglyme (G4) is used. Recall that stoichiometric G4 showed enhanced reactivity, whereas an excess of G4 showed no dehydrogenation of BH_4^- . We propose that there is a competition between coordination of glyme and coordination of hydride and hydridoborate anions to Mg^{2+} . Small quantities of glyme are effective in transferring transient BH_3 as discussed above, but larger quantities introduce steric hindrance to the coordination of H^- , $B_2H_7^-$, $B_3H_8^-$, etc. to Mg^{2+} . We know that the THF or glyme coordinates to the Mg cation from X-ray crystal structures. The coordination of glymes to Mg^{2+} in solution has also been observed by NMR spectroscopy supported by ab initio calculations, which showed that the interaction increased with the glyme chain length [18]. Molecular dynamics simulations also showed differing arrangements of Mg^{2+} and BH_4^- when different glymes were present in excess [20]. G1 exhibited aggregate structures with larger numbers of Mg^{2+} and BH_4^- in relatively close proximity. G4, however, showed isolated Mg^{2+}/BH_4^- contact ion pairs surrounded by coordinated glyme, which would make further coordination of hydride or larger hydridoborates more difficult.

Assuming these proposed hypotheses are correct, we can then start to suggest adducts that will enhance reactivity of H_2 release from borohydrides by avoiding the *too much of a good thing dilemma*. The good news is that sub-stoichiometric amounts of additives will provide enhanced selectivity. A small amount of glyme can play the role of a catalyst, stabilizing the formation of borane and transferring borane to BH₄ and subsequent borane clusters to release hydrogen at temperatures below 200 °C. The glyme further destabilizes the crystalline phase, enabling the phase transformation to an amorphous phase where mass transfer reactions will be enhanced, as such additives that bind 'just right' not too strong and not too weak would benefit the reactivity. Glyme and THF appear to be candidates to achieve this benefit. An excess of adduct or one that binds too strongly will prevent formation of MH because the metal has no available sites to transfer the hydride. Other challenges are to maintain the amorphous phase of the reaction throughout hydrogen release. As the borohydride is consumed, the intermediates and products may form a less mobile phase and mass transfer rates becomes slower as barriers for diffusion increase.

4. Materials and Methods

4.1. General Considerations.

95% Mg(BH₄)₂ was purchased from Sigma Aldrich (St. Louis, MO, USA), stored inside a nitrogen glovebox, and used as received. Monoglyme, diglyme, triglyme, tetraglyme, 2-methyltetrahydrofuran, and *n*-dodecane were stirred over CaH₂ at 25 °C under N₂ for at least 48 h before purification by vacuum distillation with heating as required. These additives were taken into a nitrogen glovebox and stored in oven-dried glass bottles and dried over activated 4 Å molecular sieves. The integrity of the solvents was verified by ¹H NMR spectroscopy for purity before use. All sample preparation was conducted in a nitrogen glovebox.

4.2. General Procedure for Thermolysis Reaction of $Mg(BH_4)_2$ with Additives and ¹¹B NMR Spectroscopy

The Mg(BH₄)₂ etherates were prepared by combining the equivalent amounts of each at room temperature, then thoroughly mixed with a spatula until reaching homogeneous consistency. The contents were then transferred to a 10 mL high-pressure stainless-steel Swagelok reactor, secured with a Swagelok valve. Reactors were placed in pre-heated aluminum block containing 6 wells. The aluminum block was further covered with 3–5 layers of aluminum foil. Temperatures of the heating block were monitored using a thermocouple and a thermometer for verification. After the allocated reaction time, the reactors were cooled in the glovebox antechamber, taken into the glovebox, and the boron products were transferred into a vial for characterization by ¹H or ¹¹B NMR spectroscopy on a Varian 500 MHz spectrometer with ¹¹B chemical shifts were referenced to BF₃·Et₂O ($\delta = 0$ ppm) and ¹H chemical shifts were referenced to TMS ($\delta = 0$ ppm). A relaxation delay of 10 s was used for all ¹¹B analyses with a 45° pulse. The boron samples were extracted into 2:1 ratio of D₂O:THF. The calculation of percent composition of decomposition products was based on peak areas, and conversion is reported as the fraction of BH₄⁻ converted to other boron compounds.

5. Conclusions

We have shown that a variety of glymes can promote H₂ release in the thermolysis of Mg(BH₄)₂ from 160–200 °C. ¹¹B NMR analysis shows that boron clusters of B₁₀H₁₀^{2–} and B₁₂H₁₂^{2–} are the major products, in which the relative product distribution is strongly dependent on the identity and the concentration of the glyme employed in the thermolysis.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/inorganics9060041/s1, TGA and DSC data for Mg(BH₄)₂ with G1, G2, G3, and G4 (Figures S1–S4).

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