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Is $Y_2(B_{12}H_{12})_3$ the main intermediate in the decomposition process of $Y(BH_4)_3$?†

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Dodecaborates, *i.e.* the $[B_{12}H_{12}]^{2-}$ containing species, are often observed as main intermediates in the hydrogen sorption cycle of metal borohydrides, hindering rehydrogenation. In the decomposition process of $Y(BH_4)_3$, yttrium octahydrotriborate, *i.e.* $Y(B_3H_8)_3$, rather than the stable $Y_2(B_{12}H_{12})_3$, is formed as the main intermediate.

Metal borohydrides $M(BH_4)_n$ (n is the valence of metal M), with high gravimetric (18.4 wt% for $LiBH_4$) and volumetric (102 kg m^{-3} for $LiBH_4$) hydrogen densities, have been widely investigated for hydrogen storage in recent years.[1,2] The stability of $M(BH_4)_n$ was reported to depend on the charge transfer from M to $[BH_4]$, and thereby a correlation between the electronegativity (χ_p) of metal M and the stability of the corresponding $M(BH_4)_n$ was established.[3] Applying this empirical rule to Y (χ_p = 1.2), a decomposition temperature of 500 K, well below those of alkaline and alkaline earth metal borohydrides, is expected for $Y(BH_4)_3$. Combined with a hydrogen content of 9.1 wt%, it makes $Y(BH_4)_3$ an attractive candidate for solid hydrogen storage.

Experimentally, $Y(BH_4)_3$ was observed to release hydrogen below 200 °C.[4–6] The whole hydrogen release process occurs in multistep reactions with the formation of amorphous intermediates. Within the hydrogen sorption cycle, the reaction pathway and the intermediates involved determine the reversibility. For example, dodecaborates (*i.e.* the $[B_{12}H_{12}]^{2-}$ species), which are unwanted by-products and reduce the rehydrogenation performance, are often observed as intermediates in the decomposition process of alkaline and alkaline earth metal borohydrides.[7–14] F. C. Gennari reported the observation of the $[B_{12}H_{12}]^{2-}$ species using Fourier transform infrared spectroscopy during the decomposition of $Y(BH_4)_3$.[15] However, no further characterization was reported to support the formation of $Y_2(B_{12}H_{12})_3$. Here, we demonstrate that $Y(BH_4)_3$ decomposes *via* the formation of $Y(B_3H_8)_3$, and only traces of $Y_2(B_{12}H_{12})_3$ are detected using solution state ^{11}B nuclear magnetic resonance (NMR). Besides, $Y_2(B_{12}H_{12})_3$ was synthesized by ball milling $Y(BH_4)_3$ with B_2H_6 and its stability was examined.

The dehydrogenation of $Y(BH_4)_3$ (prepared according to ref. 6) was carried out by temperature programmed desorption (TPD) under a constant flow of 1, 5 and 10 bar H_2, respectively. The samples dehydrogenated at 240 to 350 °C were dissolved in D_2O and examined using ^{11}B NMR. Fig. 1a shows the solution state $^{11}B(^1H)$ NMR spectra of $Y(BH_4)_3$ decomposed under 1 bar H_2. A main resonance at −30.8 ppm together with some additional minor resonances is observed in the samples decomposed at 240, 255 and 280 °C, while no dissolved intermediates are observed in the sample decomposed at 350 °C. The chemical shift of −30.8 ppm agrees well with that of octahydrotriborate (*i.e.* the $[B_3H_8]^-$ species) reported in the literature.[16–18] In the 2D ^1H–^{11}B HMQC NMR spectrum of $Y(BH_4)_3$ after heating to 255 °C (Fig. 1b), a single correlation signal of $[B_3H_8]^-$ centered at 0.2 ppm (^1H) and −30.8 ppm (^{11}B) is observed. This single resonance is explained by the fact that all three boron atoms are equivalent and that each one couples with all eight of the hydrogen atoms.[16] In addition, the minor resonance in Fig. 1a at 19.6 ppm assigned to boric acid is attributed to the hydrolysis product of the remaining $Y(BH_4)_3$ in D_2O. The minor resonances at −15.2, −16.1 and −17.3 ppm suggest the existence of $[B_{12}H_{12}]^{2-}$ or its derivatives $[B_{12}H_{12-n}(OH)_n]^{2-}$ (n = 1 to 4),[19] and those at −8.4, −22.7 and −36.2 ppm are possibly related to the formation of $[B_{10}H_{14}]^{2-}$.[20]

The applied H_2 external pressure is known to influence the decomposition pathway of metal borohydrides.[13,21] Therefore, the experiment was repeated at 5 and 10 bar external H_2 pressures. The decomposition products were dissolved in D_2O and the corresponding $^{11}B(^1H)$ NMR spectra are shown in Fig. S1 (ESI†). $Y(B_3H_8)_3$ is also identified as the main phase in $Y(BH_4)_3$ decomposed at 300 °C under both 5 and 10 bar, and no dissolved intermediate species are observed in the samples

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† Electronic supplementary information (ESI) available: Experimental details of sample preparation and ^{11}B and ^1H NMR measurements, solution state $^{11}B(^1H)$ NMR spectra of $Y(BH_4)_3$ decomposed under 5 and 10 bar H_2 and hydrogen desorption performance of the as-synthesized $Y_2(B_{12}H_{12})_3$. See DOI: 10.1039/c3cc41184b

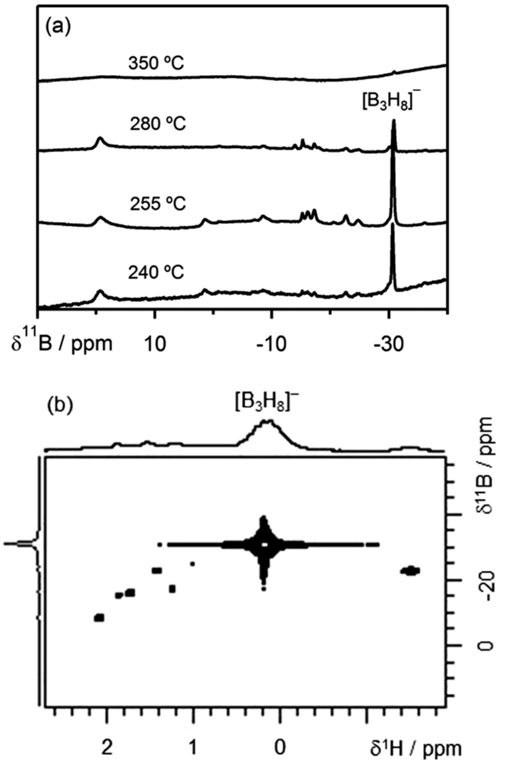

Fig. 1 (a) Solution state (D_2O) $^{11}B(^1H)$ NMR spectra (128.38 MHz) of $Y(BH_4)_3$ decomposed at 240 to 350 °C; (b) two dimensional ^1H–^{11}B HMQC NMR spectrum of $Y(BH_4)_3$ decomposed at 255 °C.

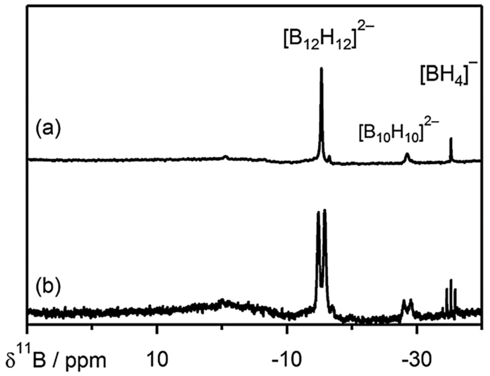

Fig. 2 ^{11}B NMR spectra (128.38 MHz) recorded in DMSO-d_6 of the as-prepared $Y_2(B_{12}H_{12})_3$: (a) ^1H decoupled and (b) ^1H coupled. Coupling constants of 124, 124 and 81 Hz were determined for $[B_{12}H_{12}]^{2-}$, $[B_{10}H_{10}]^{2-}$ and $[BH_4]^-$, respectively.

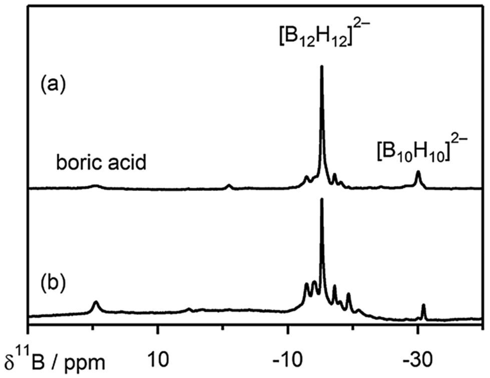

Fig. 3 $^{11}B(^1H)$ NMR spectra (128.38 MHz) recorded in D_2O of (a) the as-prepared $Y_2(B_{12}H_{12})_3$ and (b) $Y_2(B_{12}H_{12})_3$ after heating to 450 °C for 5 h.

decomposed at 400 °C. As a consequence, the above observations indicate that regardless of H_2 external pressures, $Y(BH_4)_3$ decomposes *via* the formation of $Y(B_3H_8)_3$ as the main intermediate according to eqn (1).

$$Y(BH_4)_3 \rightarrow 1/3Y(B_3H_8)_3 + 2/3YH_3 + H_2 \qquad (1)$$

The formation of the $[B_3H_8]^-$ species has also been observed in the decomposition process of $Mg(BH_4)_2$.[18] It was believed that the $[B_3H_8]^-$ species further convert to $MgB_{12}H_{12}$ as the main intermediate *via* a B–H condensation process. In contrast, only traces of $[B_{12}H_{12}]^{2-}$ were detected using ^{11}B NMR in the decomposition process of $Y(BH_4)_3$. To rule out the possibility that $Y_2(B_{12}H_{12})_3$ might not be detected using solution state NMR due to stability or solubility reasons, we synthesized $Y_2(B_{12}H_{12})_3$ by ball milling of $Y(BH_4)_3$ in B_2H_6 at 150 °C according to eqn (2).

$$2Y(BH_4)_3 + 15B_2H_6 \rightarrow Y_2(B_{12}H_{12})_3 + 39H_2 \qquad (2)$$

The solution state ^{11}B NMR spectra of the as-synthesized $Y_2(B_{12}H_{12})_3$ recorded in DMSO-d_6 and D_2O are shown in Fig. 2 and 3, respectively. The major resonance at −15.3 ppm with a coupling constant (J_{BH}) of 124 Hz (Fig. 2) agrees with those of the $[B_{12}H_{12}]^{2-}$ species reported in the literature.[8,20] In addition, the two resonances at −28.5 ppm (J_{BH} of 124 Hz) and −0.4 ppm assigned to $[B_{10}H_{10}]^{2-}$ as a side product are observed, together with the remaining $Y(BH_4)_3$ at −35.3 ppm (J_{BH} of 81 Hz). In the ^{11}B NMR spectrum recorded in D_2O (Fig. 3a), the $[B_{12}H_{12}]^{2-}$ species shows a typical chemical shift of −15.2 ppm,[20] and the $[B_{10}H_{10}]^{2-}$ species shows two resonances at −30.2 and −0.8 ppm, respectively. The observation of boric acid at 19.6 ppm is attributed to the hydrolysis of the remaining $Y(BH_4)_3$ in D_2O. Combining the ^{11}B NMR results recorded in both DMSO-d_6 and D_2O, it was found that $Y_2(B_{12}H_{12})_3$ was successfully formed according to eqn (2). Furthermore, the ^{11}B NMR spectra (Fig. 2) suggest that the $[B_{12}H_{12}]^{2-}$ species is the main phase in the as-synthesized $Y_2(B_{12}H_{12})_3$, as shown in Table 1.

To examine the stability of $Y_2(B_{12}H_{12})_3$, the as-synthesized $Y_2(B_{12}H_{12})_3$ was heated up to 450 °C under a constant flow of 1 bar H_2. Only limited hydrogen (1.4 wt%) is released in this process, as shown in Fig. S2 (ESI†), compared to the theoretical hydrogen capacity of 6.0 wt% of $Y_2(B_{12}H_{12})_3$. After heating to 450 °C for 5 h,

Table 1 Relative amounts of the boron species in the as-synthesized $Y_2(B_{12}H_{12})_3$, based on solution state ^{11}B NMR recorded in DMSO-$d_6$and D_2O. The remaining YH_3 is not taken into account. ^{11}B NMR chemical shifts are reported relative to the 1 M $B(OH)_3$ aqueous solution at 19.6 ppm

	DMSO-d_6		D_2O	
Compound	δ ^{11}B/ppm	Mol%	δ ^{11}B/ppm	Mol%
$Y_2(B_{12}H_{12})_3$	−15.3	60 ± 6	−15.2	42 ± 4
$Y_2(B_{10}H_{10})_3$	−28.5, −0.4	8 ± 1	−30.0, −0.8	7 ± 1
$Y(BH_4)_3$	−35.2	32 ± 3	—	—
Boric acid	—	—	19.6	51 ± 5

the signal of the $[B_{12}H_{12}]^{2-}$ species still belongs to the main resonance in the solution (D_2O) state $^{11}B(^1H)$ NMR spectrum (Fig. 3b), indicating its relatively high stability. The increase in the resonances at −12.8, −14.0, −17.1, −18.0, −19.3, −20.3 and −24.7 ppm assigned to the $[B_{12}H_{12-n}(OH)_n]^{2-}$ (n = 1–4) derivatives suggests that the dehydrogenation of $Y_2(B_{12}H_{12})_3$ might proceed through the formation of $Y_2(B_{12}H_{12-n})_3$ adducts.

The formation of higher boranes, such as the $[B_{12}H_{12}]^{2-}$ species, by the reaction of $[BH_4]^-$ with B_2H_6 has been reported for $LiBH_4$ and $NaBH_4$.[22–24] We demonstrated that this method is also applicable to $Y(BH_4)_3$ in the presence of B_2H_6 yielding $Y_2(B_{12}H_{12})_3$, a species which is stable up to at least 450 °C and readily soluble in water and DMSO-d_6. For the widely discussed borohydrides such as $LiBH_4$, $NaBH_4$, $Mg(BH_4)_2$ and $Ca(BH_4)_2$, the $[B_{12}H_{12}]^{2-}$ species have been identified as the main intermediates in the decomposition process.[7–14] In contrast to these borohydrides, $Y(BH_4)_3$ shows a different decomposition route. The absence of the dissolved B–H species in $Y(BH_4)_3$ decomposed at 350 °C (Fig. 1, top curve) implies that the stable $[B_{12}H_{12}]^{2-}$ species does not play a major role as an intermediate in the decomposition process. Instead, yttrium octahydrotriborate $Y(B_3H_8)_3$ was formed as the main intermediate.

The $[B_3H_8]^-$ species has been reported as an intermediate favorable for the rehydrogenation of $[BH_4]^-$ under moderate conditions in the case of $Mg(BH_4)_2$.[18] Although the reversible hydrogen release amount of $Y(BH_4)_3$ *via* the formation of $Y(B_3H_8)_3$ is not enough to meet the on-board storage target. Considering only traces of the stable $[B_{12}H_{12}]^{2-}$ species formed in the decomposition process (under an external pressure of 1 bar H_2), it can be anticipated that $Y(BH_4)_3$ can be further developed as a reversible hydrogen storage material under moderate conditions.

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