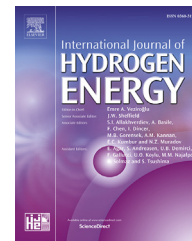




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# Hydrogen release from aqueous hydrazine bisborane

Eddy Petit, Umit B. Demirci\*

IEM (Institut Européen des Membranes), UMR 5635 (CNRS-ENSCM-UM2), Université de Montpellier, Place E. Bataillon, F-34095, Montpellier, France

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## ABSTRACT

Aqueous hydrazine bisborane  $\text{H}_3\text{B}-\text{N}_2\text{H}_4-\text{BH}_3$  (HBB) might be a possible liquid-state chemical H storage material at the conditions that the compound totally dehydrogenates in mild conditions. Herein we demonstrate such a potential. We report for the first time a work about the dehydrogenation of aqueous HBB. The compound is not stable in water. Its stability is even lower in alkaline conditions because of the likely formation of the unstable intermediate  $[\text{H}_3\text{BOH}]^-$ . The use of a metal-based catalyst accelerates the hydrolysis of the  $\text{BH}_3$  groups but the bimetallic NiPt catalyst is more active, being also able to decompose the  $\text{N}_2\text{H}_4$  moiety. The best kinetics is observed at 70 °C and in alkaline conditions. However, the dehydrogenation is not total, reaching a limit of 80% of conversion. Unfortunately the reason of that is not understood yet. As things stand, there are some challenges ahead, but HBB has shown to be a possible liquid-state chemical H storage material.

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## Introduction

The Pauling electronegativity of H (2.2) is between that of B (2.04) and that of O (3.44). The B–H and O–H bonds are thus polarized, and attractively the H of B–H is hydridic (or basic) and the other one is protic (or acidic). The former H may readily react with the latter H to form  $\text{H}_2$ . This description, simplistic though it may be, sheds light on the potential of boron-based compounds like sodium borohydride  $\text{NaBH}_4$  (SB) for easy  $\text{H}_2$  generation by hydrolysis or alcoholysis [1,2]. Boron-based compounds are old materials, but there is renewed interest in them, especially in the field of liquid- and solid-state chemical H storage [3]. Synthesis and hydrolysis of SB were first reported in 1953 [1] and today it is the most promising boron-based compound for  $\text{H}_2$  generation by

hydrolysis at ambient conditions [4]. Ammonia borane  $\text{H}_3\text{N}-\text{BH}_3$  (AB) was long sought [5,6] and its successful synthesis was finally published in 1955 [7]. Nowadays, AB is the most mature material for  $\text{H}_2$  generation in thermolytic conditions [8]. Hydrazine borane  $\text{H}_4\text{N}_2-\text{BH}_3$  (HB), which can be seen as a derivative of AB, was first reported in 1951 [9]. Subsequent works showed that it is more relevant to consider it for  $\text{H}_2$  generation by hydrolysis at near-ambient conditions [10] because its decomposition under heating gives rise to hazards [11–13]. In summary: “what’s past is prologue” [14].

Chronologically, the renewed interest in SB (from the early 2000s) was followed by that of AB (from the mid-2000s), which was followed by that of HB (from the early 2010s) [3]. Shortly after, hydrazine bisborane  $\text{H}_3\text{B}-\text{N}_2\text{H}_4-\text{BH}_3$  (HBB), a derivative of HB, has emerged [15,16]. It is also an old compound; it was first reported in 1951 [9]. The belated advent of HBB in the

\* Corresponding author.

E-mail address: [umit.demirci@umontpellier.fr](mailto:umit.demirci@umontpellier.fr) (U.B. Demirci).

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recent years is easily explained by its controversial behavior under heating. Originally, HBB was described to explode if heated rapidly much beyond 100 °C [12,17]. Recent contradictory reports indicate no unexpected hazardous phenomenon during thermolysis at heating rates up to 15 °C min<sup>-1</sup> [14,18]. However, we found that pure HBB explodes at 171 °C when heated at 10 °C min<sup>-1</sup> [19]. Furthermore, it is worth mentioning that, in the 1960s–1980s, HBB was considered as propellant for gas generators and rockets [20–24]. What seems most likely from Refs. [14–24] is that, like HB [11–13], HBB is not suitable for solid-state chemical H storage.

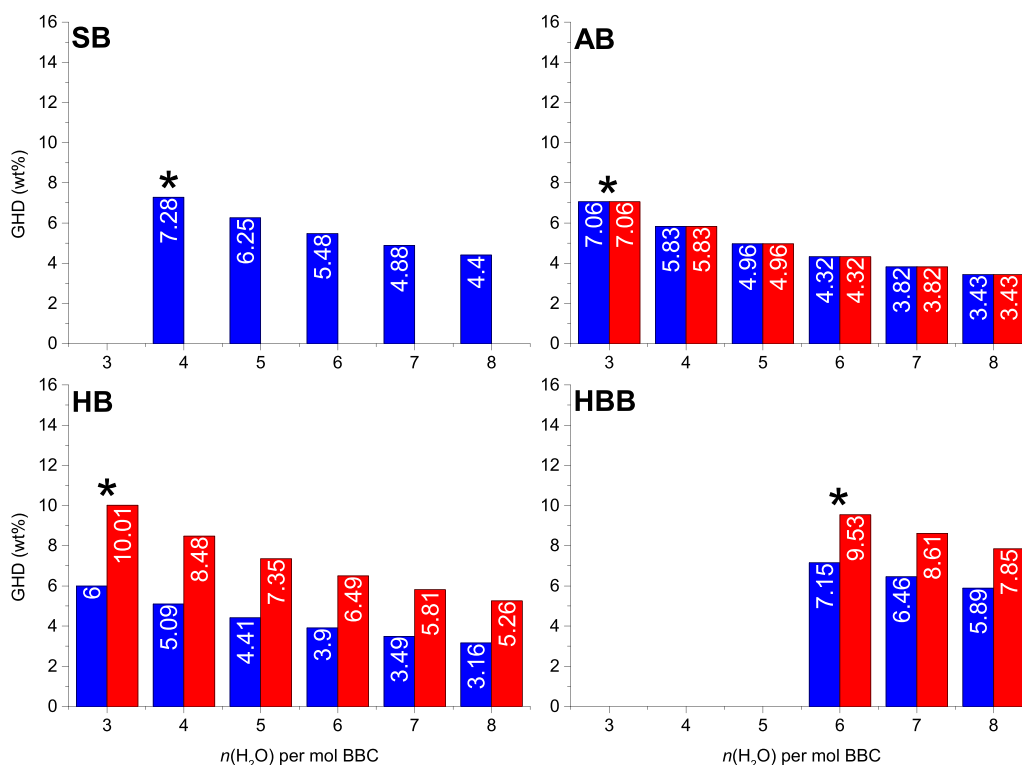
Like the other boron-based compounds, HBB may pave the way for prospects in liquid-state chemical H storage. Solubility in water (60.9 g L<sup>-1</sup>, or 1.020 mol L<sup>-1</sup>) and ability to be hydrolyzed are prerequisites of its [19]. Since HBB is compared to the other boron-based compounds, this raises one obvious and central question: would HBB have advantages over the other boron-based compounds? There are two answers to this question. Fig. 1 illustrates the first answer that is based on the gravimetric hydrogen densities. If HBB dehydrogenates through the BH<sub>3</sub> groups only, it is as attractive as SB and AB. If HBB dehydrogenates through the BH<sub>3</sub> groups as well as the N<sub>2</sub>H<sub>4</sub> moiety, it is as attractive as HB, both being much more interesting than SB and AB. HBB has thus, theoretically, a potential for liquid-state chemical H

storage. The second answer should be experimental. It is given hereafter. For the first time results on spontaneous and catalytic dehydrogenations of aqueous HBB at ambient conditions are reported.

## Experimental

HBB was synthesized by salt metathesis. Finely ground hydrazine sulfate [N<sub>2</sub>H<sub>5</sub>]<sup>+</sup>[SO<sub>4</sub>H]<sup>-</sup> (Sigma-Aldrich; 3.93 g), sodium borohydride NaBH<sub>4</sub> (Acros Organics; 2.28 g) and anhydrous tetrahydrofuran (Sigma-Aldrich; 150 mL) were transferred in a 250-mL three-necked round-bottom flask kept under argon flow. The mixture was allowed to react at 40 °C for 90 h. Then, the tetrahydrofuran solution of HBB was separated from insoluble Na<sub>2</sub>SO<sub>4</sub> by filtration, the solvent was removed by extraction under vacuum at room temperature for 4 h, and the as-obtained HBB was dried under dynamic vacuum at room temperature for 24 h. Details can be found in our previous work [19].

The gas (H<sub>2</sub> and/or N<sub>2</sub>) evolution experiments were performed on our set-up based on the inverted burette method, which was developed for HB [25]. The set-up consists of a glassy reactor placed in a thermostated bath (30, 40, 50, 60 or 70 °C), a trap filled with an aqueous solution of HCl (0.1 M) to



**Fig. 1** – Gravimetric hydrogen density (GHD, in wt%) of the couples NaBH<sub>4</sub>-H<sub>2</sub>O, NH<sub>3</sub>BH<sub>3</sub>-H<sub>2</sub>O, N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub>-H<sub>2</sub>O, N<sub>2</sub>H<sub>4</sub>(BH<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O as a function of the mole number of H<sub>2</sub>O (i.e.  $n(\text{H}_2\text{O})$  per mol BBC). The blue boxes are the GHD values when only the hydrolysis of the B–H bonds is taken into consideration. The red boxes are the GHD values when the hydrolysis of the B–H bonds and the dehydrogenation of the N–H bonds are both taken into account. The stars indicate the stoichiometric conditions for each BBC. With: SB as sodium borohydride; AB as ammonia borane; HB as hydrazine borane; HBB as hydrazine bisborane; and BBC as boron-based compound. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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