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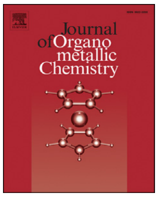

Review

The continuing story of the diammoniate of diborane

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ABSTRACT

The diammoniate of diborane ($[H_2B(NH_3)_2][BH_4]$, DADB) is an ionic dimer of ammonia borane (H_3NBH_3, AB). It has received much less attention in the past few decades than AB, although it has the same high hydrogen content (19.6%). In this review, the important events in the development of DADB are summarized: its serendipitous discovery, formulation, characterization, formation mechanism, preparation, and relationship with AB. Focus is given to its competing formation with AB and potential application as a hydrogen storage medium.

1. Introduction

As existing reserves of fossil fuels decrease, energy crises are a major threat to our way of life. Therefore, looking for alternative energy sources is a matter of global urgency. Hydrogen is proposed as a potential alternative energy carrier to mitigate these potential energy crises and minimize environmental impacts [1–4]. However, efficient and safe hydrogen storage techniques remain challenges in fuel cell power applications [5,6].

Current hydrogen storage systems can be divided into two main categories, namely physisorption and chemical storage media [7]. The former involves porous materials such as zeolites [8,9], MOFs [10,11], carbon materials (nanotubes, fullerenes, graphene) [12,13] and organic polymers [14–16]. The latter contains hydrogen in chemically bonded or complexed forms [17,18], or incorporated into organic molecules [19–22]. This may be represented by metal hydrides, borohydrides, ammonia-like complexes, alcohols, formic acid, and so on. Among these, ammonia borane (H_3NBH_3, AB) has attracted the greatest research interest due to its stability and high hydrogen storage capacity (19.6%) [23–26]. In comparison, the diammoniate of diborane ($[H_2B(NH_3)_2][BH_4]$, DADB), an ionic dimer of AB with the same hydrogen content (19.6%), has been much less studied.

In this review, we highlight important events in the development of the diammoniate of diborane: its serendipitous discovery, formulation, characterization, mechanism of formation, preparation and relationship with AB.

2. Serendipitous discovery of DADB

The DADB was first prepared by Alfred Stock in 1923 [27,28] from the reaction of ammonia (NH_3) and diborane (B_2H_6) under extreme conditions. As described in the literature, the crucial factors to obtain pure DADB include beginning with a low temperature (−140 °C) mixture of B_2H_6 in NH_3, and removing excess NH_3 as the temperature was allowed to rise to −80 °C. Subsequent research showed that the discovery of DADB was serendipitous, as if it was not treated with particular care, other by-products would appear, leading to erroneous conclusions [29–31].

Based on Lewis acid-base considerations, it is reasonable to expect that the addition reaction between NH_nR_{3-n} and B_2H_6 will take place to form $NH_nR_{3-n}\cdot BH_3$. For example, $N(CH_3)_3$ reacts with B_2H_6 to give trimethylamine-borane, $(CH_3)_3N\cdot BH_3$ (Eqn. (1)) [32,33]. However, the acid-base reactions of B_2H_6 and NH_3 are far more complex. As shown in Eqn. (2), one mole of B_2H_6 takes up two moles of NH_3, giving $B_2H_6\cdot 2NH_3$. The formula of $B_2H_6\cdot 2NH_3$ for the solid product was supported by a variety of careful experiments: the tensiometric study by Stock and Pohland [34], then molecular weight determinations (freezing-point depression by Rathjens and

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Pitzer [35], and high-precision freezing-point depression by Egan and Shore [36]). Furthermore, molecular weight measurements showed that the compound dissociated into 2 ions at high dilution, indicating that $B_2H_6 \cdot 2NH_3$ is not a simple, neutral adduct of B_2H_6 and NH_3. Thus the historical and accepted name, the diammoniate of diborane (DADB), stemming from the molecular formula $B_2H_6 \cdot 2NH_3$, does not genuinely represent its chemical formula.

$$B_2H_6 + 2\ N(CH_3)_3 \rightarrow 2(CH_3)_3N \cdot BH_3 \quad (1)$$

$$B_2H_6 + 2\ NH_3 \rightarrow B_2H_6 \cdot 2NH_3 \quad (2)$$

3. Formulation and characterization

3.1. History of the formulation of DADB

The structure of $B_2H_6 \cdot 2NH_3$ continued to puzzle boron chemists for decades. Four possible structural formulas were proposed before a series of experiments were conducted which identified the correct formula as $[H_2B(NH_3)_2][BH_4]$ (Fig. 1) [30,37–42].

Structure **I** was initially proposed by Stock [43] but was quickly rejected due to a lack of evidence to support its validity [44]. Later, Schlesinger and Burg proposed a second possible formula for DADB, $[NH_4][H_3BNH_2BH_3]$ (**II**), following replacement of the ammonium ion by sodium ion after reaction of $B_2H_6 \cdot 2NH_3$ with sodium in liquid ammonia (Eqn. (3)) [45]. That one equivalent of hydrogen was produced per mole of diborane offered only indirect proof for this formulation. It was not until 2010 that the existence of the $[H_3BNH_2BH_3]^-$ anion was confirmed as its sodium salt, $NaBH_3NH_2BH_3$, prepared by the reaction of Na or $NaNH_2$ with AB [46]. Further investigation of the reaction between an alkali metal and an ammonia solution of the diammoniate of diborane by Schaeffer, Adams and Koenig indicated that a hydride shift occurred within the anion $[H_3BNH_2BH_3]^-$ (Eqn. (4)). Accordingly, they proposed that the revised formula $[(NH_4)(H_2BNH_2)(BH_4)]$ (**III**) might be the best representation of the chemical nature of $B_2H_6 \cdot 2NH_3$ [47].

$$[NH_4][H_3BNH_2BH_3] + Na \rightarrow NaBH_3NH_2BH_3 + NH_3 + 0.5\ H_2 \quad (3)$$

$$[BH_3NH_2BH_2]^- \rightarrow [BH_4]^- + NH_2BH_2 \quad (4)$$

In 1958, Parry and Shore provided strong evidence that the borohydride ion, $[BH_4]^-$, was contained in DADB, and the data available were consistent with the structural formula $[H_2B(NH_3)_2][BH_4]$ (**IV**) [41]. Although this moiety was mentioned briefly in the literature as early as 1947 [48], it was excluded without further serious examination [38]. The direct proof provided by Parry and Shore includes the following: (a) the DADB can react with NH_4Cl or $(NH_4)_2SO_4$ to rapidly release H_2 (possible *via* the unstable salt NH_4BH_4) [42], but it does not react with $NaBH_4$, demonstrating that there is no $[NH_4]^+$ ion present in the formula of DADB; (b) the reaction between DADB and sodium in liquid ammonia is comparable to that of the bromide analogue $[H_2B(NH_3)_2]Br$, indicating the existence of the cation $[H_2B(NH_3)_2]^+$; (c) $[Mg(NH_3)_6](BH_4)_2$ can precipitate from a liquid ammonia solution of DADB and two thirds of the hydridic hydrogen in DADB hydrolyze easily, consistent with the presence of the $[BH_4]^-$ ion. In addition, the Raman spectrum obtained by Tayler, Schultz and Emery further confirms the presence of the $[BH_4]^-$ moiety [49]. Collectively, this evidence strongly supports the authentic formulation of $B_2H_6 \cdot 2NH_3$ as $[H_2B(NH_3)_2][BH_4]$.

$[NH_4]_2[B_2H_4]$ **I**

$[NH_4][H_3BNH_2BH_3]$ **II**

$[(NH_4)(BH_2NH_2)(BH_4)]$ **III**

$[H_2B(NH_3)_2][BH_4]$ **IV**

Fig. 1. Four proposed structures of DADB.

3.2. Solution NMR of DADB

Due to the instability of DADB in organic solvents at ambient temperature, almost all available spectroscopic characterizations (NMR and Raman) were carried out at temperatures below −35 °C [49–52]. The ^{11}B NMR spectrum at −40 °C contains a quintet at $\delta = -38.5$ ppm for BH_4 and a broad signal at $\delta = -15.2$ ppm related to BH_2 (Fig. 2) [50]. The broad signal of BH_2 is due to quadrupole interactions of boron at low temperatures, and is resolved into a triplet above 0 °C [53]. In liquid ammonia, a triplet for BH_2 could also be observed. In the ^1H NMR, two typical groups of peaks appear at $\delta = 0.10$ ppm (quartet) for BH_4 and around $\delta = 2.08$ ppm as a broad resonance for BH_2. Both signals are converted to sharp singlets at the corresponding chemical shifts in the boron-decoupled $^1H\{^{11}B\}$ NMR spectra (Fig. 2) [50].

3.3. Crystal structure of DADB

The crystal structure of DADB was first obtained by Autrey in 2010 by a combination of X-ray and neutron powder diffraction analyses [54] (Fig. 3). Similar to the previously reported $[H_2B(NH_3)_2]^+Cl^-$ [55], the DADB crystallizes in a tetragonal unit cell attributed to the space group *I*4/*mcm* but with differences in the arrangement of $[H_2B(NH_3)_2]^+$ ions. As observed in the crystal structure of AB, B—H···H—N dihydrogen bonds [56,57] are also observed in solid state of DADB (Fig. 3).

4. Formation mechanism and preparation

4.1. Formation mechanism

The confirmation of the solid state structure of DADB raised the question of how NH_3 might interact with B_2H_6 to give a different result from that observed for $N(CH_3)_3$. A plausible explanation may be given *via* a different cleavage pattern for B_2H_6, namely symmetric or asymmetric cleavage (Fig. 4) [41]. Symmetric cleavage (blue) leads to a non-ionic or covalent product, as in the case of $(CH_3)_3N \cdot BH_3$, whereas asymmetric cleavage (red) produces the ionic species $[H_2B(NH_3)_2][BH_4]$.

In consideration of the preparation of DADB, processes that should be borne in mind include (a) the adsorption of B_2H_6 onto solid NH_3 (at low temperature, −140 °C, and in the presence of excess NH_3) without affecting the bridging H atoms in B_2H_6; (b) upon subsequent increase of the temperature from −140 °C to −80 °C, it is believed that the system undergoes a rapid conversion to a more stable compound; (c) subsequent removal of excess NH_3 at −78 °C leads to DADB [47]. Based on the experimental facts, Shore and Parry suggested that the structure of the intermediate formed in step (b) might be a singly-bridged complex $NH_3BH_2(\mu\text{-}H)BH_3$ (ammonia diborane, AaDB), formed by breaking one B—H—B bond and can be assigned as an intermediate in the