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Ammonia borane, past as prolog

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ABSTRACT

Ammonia borane (NH_3BH_3), the simplest of the amine boranes, has yielded its secrets grudgingly since its first attempted synthesis in 1923. Here we review aspects of its history that yield insight into its chemistry and properties with special attention to current efforts to develop ammonia borane as a solid hydrogen storage material by improving its synthesis, dehydrogenation characteristics and spent fuel regeneration technologies.

1. Introduction

About a century ago, Alfred Stock, the pioneer of research on the boron hydrides, combined diborane (B_2H_6) and ammonia (NH_3), expecting to produce ammonia borane (NH_3BH_3, Fig. 1), the simplest possible amine borane, in the straightforward formation of a Lewis acid/base adduct [1,2]. Instead of producing ammonia borane, an unexpected ionic amine borane complex was isolated from the reaction mixture. The structure of the ionic product could not be characterized at that time so it was given an awkward name, the diammoniate of diborane (DADB), based on the starting materials from which it had been derived and a particular representation of its molecular formula, $B_2H_6 \cdot 2NH_3$ which gives no clue to the reaction that occurred [3,4]. It could have been named the dimer of ammonia borane ($(NH_3BH_3)_2$) but that would have implied some knowledge about the reaction but there was none. Neither formula was remotely related to the correct structure, $[H_2B(NH_3)_2][BH_4]$ (Fig. 1), which was established in 1958, one of several alternatives proposed following Stock's initial discovery [5–11]. In a 1955 structural study, a metathesis reaction expected to yield $[H_2B(NH_3)_2]Cl$ by the combination of $[H_2B(NH_3)_2][BH_4]$ and NH_4Cl in diethyl ether instead yielded a white powder with the same empirical formula as the diammoniate of diborane (BH_6N). However, molecular weight determination showed it to be a monomer rather than a dimer. Ammonia borane had been synthesized [12]. Interest in ammonia borane has continued to yield unexpected results even as attention has shifted recently to its potential as a solid hydrogen storage material. Numerous review articles about ammonia borane have been published [13–35]. Herein we highlight important developments in the history of ammonia borane that provide insight into its unique properties and potential.

2. Structure of ammonia borane

Ammonia borane has been analyzed by almost every possible spectroscopic technique: NMR, IR, and Raman spectroscopies, diffraction and scattering techniques such as X-ray crystallography and inelastic neutron scattering, many results are reviewed in depth in a 2010 report [20]. Here we trace the development of structural insights from X-ray crystallography and neutron diffraction.

When ammonia borane was prepared for the first time by Shore and Parry in 1955 [12], molecular weight measurements indicating that ammonia borane was a monomer were crucial to confirming the structure of ammonia borane. Their reported intensities and interplanar spacings obtained from the X-ray powder pattern were characteristic of a crystalline compound but could not be used to determine the structure of the solid [12]. From room-temperature X-ray experiments, Hughes [36] and Lipscomb [37] concluded that ammonia borane has a body-centered tetragonal structure while Sorokin et al. favored a face-centered orthorhombic unit cell [38]. Finally in 1983, Hoon and Reynhardt's, detailed powder X-ray

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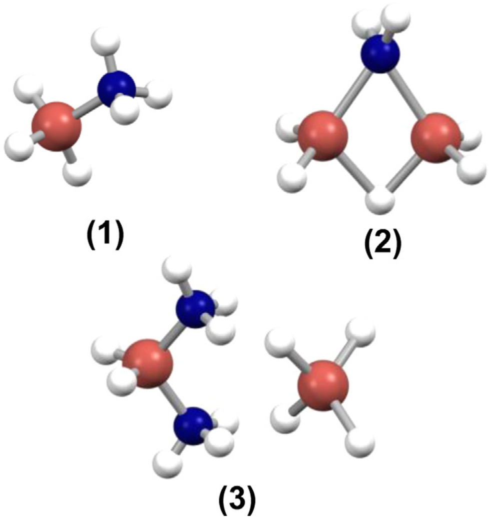


Fig. 1. Structures of Ammonia borane, NH_3BH_3, AB (1); Aminodiborane, $NH_2B_2H_5$, ADB (2); and the diammoniate of diborane, $[H_2B(NH_3)_2][BH_4]$, DADB (3) (N, blue; B, orange; H, light-gray).

diffraction study confirmed a body-centered tetragonal structure at room temperature and an orthorhombic $Pmn2_1$ phase at low temperature, which transforms into a tetragonal $I4$ mm phase at 225 K [39]. A single crystal X-ray study at 200 K assigned ammonia borane's structure to the primitive orthorhombic space group [40]. However, a neutron powder diffraction study of ammonia borane by Crabtree et al. demonstrated that B and N atom assignments in published X-ray analyses were incorrect and must be reversed. With the reversed assignment of B and N, the correct dihydrogen bond phase, bent B–H···H and linear N–H···H, was recognized in the closest intermolecular N–H…H–B interactions [41]. X-ray analysis of 18-crown-6 and related ethers with ammonia borane yields single crystal structure information for ammonia borane as well [42–47]. This approach is not only suitable for characterizing molecular recognition with boron-containing host molecules, but also for studying the single crystal structure of compounds such as aminodiborane ($NH_2B_2H_5$, ADB, Fig. 1), which are liquid at ambient temperature [48].

3. Chemistry of ammonia borane

The difference in electronegativity of boron and nitrogen accounts for the polarity of ammonia borane hydrogens, protic N–H and hydridic B–H, leading to an unique structural feature, an elaborate 3D network of stabilizing $N–H^{\delta+}\cdots{}^{\delta-}H–B$ proton–hydride (dihydrogen) interactions in solid ammonia borane [36,41,49–52]. Ubiquitous $H^{\delta+}\cdots{}^{\delta-}H$ interactions influence a number of very important physical and chemical properties of ammonia borane. Ammonia borane and ethane are isoelectronic but at room temperature ammonia borane is a stable crystal while ethane is a gas. The difference between their melting points is nearly 300 °C [41]. Ammonia borane is an effective reducing agent for reducing aldehydes or ketones to alcohols and recently has been shown to reduce a metal salt to a metal nanoparticle, serving both as reducing agent and surfactant to control particle size [53–56]. Ammonia borane contains three N–H and three B–H covalent bonds, and an N → B dative bond. Its reactions, which have been extensively reviewed [13,14,16–20,28], usually involve cleavage of at least one of these bonds and are highlighted in this section.

3.1. *Breaking the N → B dative bond*

Displacement reactions of ammonia borane are important for a variety of syntheses and energy storage applications. The N → B dative bond of ammonia borane breaks when NH_3 is displaced by a Lewis base or BH_3 is displaced by a Lewis acid. Nucleophilic substitution of NEt_3 on ammonia borane in THF is an equilibrium process. Simulation of the mechanism using the SM8 continuum solvation model shows the reaction most likely proceeds by a classical one-step S_N2 mechanism [57]. Addition of the Lewis acid, BF_3, to ammonia borane in ethereal solvents yields $NH_3 \cdot BF_3$, the simplest of the class of compounds, $NH_3 \cdot BR_3$, identified as the first known coordination compound [58,59], and used by G. N. Lewis to illustrate the dative bond [60]. In contrast, the reaction between ammonia borane and BCl_3 results in a complex mixture of $NH_3 \cdot BCl_3$, $NH_3 \cdot BHCl_2$ and $NH_3 \cdot BH_2Cl$ [58,61].

Ammonia borane is relatively stable to hydrolysis in neutral or basic aqueous solution [37], but hydrolysis occurs rapidly in acidic solution. The mechanism of acid-catalyzed hydrolysis can be interpreted as an example of electrophilic substitution in which a proton substitutes for borane at the ammonia nitrogen. The N → B dative bond breaks, NH_4^+ forms and the BH_3 released is rapidly hydrolyzed (Scheme 1) [62,63].

3.2. *Breaking protic N–H bond*

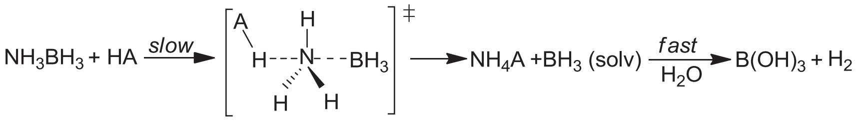
Protic N–H in ammonia borane is weakly acidic, removed by metal hydrides to form metal amidoboranes by solid-state mechanical milling [64–66] or wet-chemistry methods [67,68]. Generally, metal amidoborane can be synthesized by reacting metal hydrides (or organic hydrides) and ammonia borane, as illustrated in eqn (1) where n is the valence state of M (M = Li [64,66,69], Na [64,70], K [71], Mg [72], Ca [66,67,73], Sr [74], Y [75] etc).

$$MH_n + nNH_3BH_3 \rightarrow M(NH_2BH_3)_n + nH_2 \qquad (1)$$

The high hydrogen content of metal amidoboranes and their improved dehydrogenation properties compared to ammonia borane have attracted considerable attention to their application in hydrogen storage [30].

3.3. *Breaking hydridic B–H bond*

The hydrogen of B–H can be removed under a variety of circumstances. Photochemical or gamma radiolysis hydrogen radical abstraction produces the ammonia–boryl radical ($H_3N–BH_2\cdot$) in solution or in the solid state [76]. Boronium cations ($[BH_2(NH_3)(S)]^+$, S = ethereal solvent) form when ammonia borane is treated with strong Lewis or Brønsted acids in the absence of a strong nucleophile [77]. For example, $[BH_2(NH_3)(OEt_2)][A]$ has been obtained when ammonia borane was reacted the strong acid



Scheme 1. Brønsted acid-catalyzed hydrolysis of ammonia borane.