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Hydrogen Storage

In Situ Multinuclear NMR Spectroscopic Studies of the Thermal Decomposition of Ammonia Borane in Solution**

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The development of condensed-phase hydrogen-storage materials for fuel-cell-powered vehicles that meet the 2015 system target goals of the US Department of Energy of a volumetric density greater than 82 g H_2 per liter and a gravimetric density greater than 90 g H_2 kg^{-1} has attracted recent interest.[1,2] Ammonia borane, NH_3BH_3 (AB), which has a volumetric density of 146 g H_2 per liter and a gravimetric density of 194 g H_2 per kilogram, shows promise as a material that could meet these long-term storage targets.[3]

The details of the mechanisms for hydrogen release from AB are not completely understood; however, significant progress has been made in furthering our understanding of these mechanisms. Wolf and co-workers showed that the thermal decomposition of AB in the solid state occurs stepwise by a series of exothermic reactions to yield 12 wt% hydrogen.[4,5] The first step yields H_2 and polyaminoborane (PAB); subsequent decomposition of PAB yields another equivalent of H_2 and polyiminoborane (PIB). One important breakthrough for our understanding of the reaction mechanisms for H_2 release from AB was the recent in situ NMR spectroscopic study that showed formation of the diammoniate of diborane, $[NH_3BH_2NH_3]^+[BH_4]^-$ (DADB), to be an essential first step for hydrogen release from solid-state AB.[6] Once DADB is formed, hydrogen release from AB follows, whereby the release of the first equivalent of H_2 yields acyclic amineborane oligomers.

DADB is also observed in the decomposition of AB in ionic liquids;[7] however, no one has reported the observation of DADB in organic solvents. Indeed, Mayer observed that the addition of DADB to a glyme solution results in decomposition and the evolution of hydrogen at −20 °C.[8] Wang and Geanangel followed the decomposition of AB at 80 °C in several solvents by ex situ NMR spectroscopy.[9] They did not report the observation of DADB or linear decomposition products in glyme, but they did observe the formation of cyclic $(\text{-}BH_2NH_2\text{-})_n$ species. Unfortunately, the lower resolution did not permit them to discriminate between the $n=2$, $n=3$, and $n=4$ cyclic products. These results suggest that the decomposition of AB in organic solvents occurs by a different reaction mechanism to that observed in the solid state or ionic liquids. It is important to understand the mechanism of hydrogen release, as this mechanism should provide critical insight into the stability of AB solutions that may be used as hydrogen-storage media. For example, Rassat et al. were able to predict the thermal stability of AB at 60 °C on the basis of the mechanism of hydrogen release in the solid state.[10] The mechanistic details of decomposition permit the evaluation of the long-term thermal stability of the storage compound, whether it is stored in the solid or solution phase.

Herein, we revisit the initial thermolysis pathways of AB in the solution phase. In the process, we introduce a new high-pressure, spinning NMR cell that enables the in situ observation of the decomposition of AB by ^{11}B NMR spectroscopy. We provide evidence for the existence of DADB as a critical intermediate in the release of hydrogen from AB in organic solvents, and we use ^{11}B and ^{15}N NMR spectroscopy to characterize a new intermediate, B-(cyclodiborazanyl)aminoborohydride, *cyc*$[NH_2BH_2NH_2BH]\text{–}NH_2BH_3$.

The decomposition of AB (1 M and 2 M) in glyme follows second-order kinetics for over three half-lives (Figure 1). Figure 1 b shows the expected linear dependence of 1/[AB] as a function of time for the temperature range 50–95 °C. Arrhenius treatment of the measured rates (see Table S1 in the Supporting Information) as a function of temperature provides the Arrhenius rate expression $\log(k) = (12\pm2) - (25\pm2)/\theta$ (in which the units for k are $M^{-1}s^{-1}$), $\theta = 2.303/RT$ kcal mol^{-1}. The second-order decomposition has considerable implications for the storage of AB in solution. Specifically, it explains why, at low concentrations (<0.15 M), AB appears to be stable at temperatures up to 80 °C for several hours, whereas at high concentrations (> 2 M), AB undergoes decomposition at 50 °C just a few hours.

The first products observed during the decomposition of AB were detected in the BH_2 region of the ^{11}B NMR spectrum at $\delta \approx -11$ to -15 ppm. The evolution of this region of the $^{11}B\{^1H\}$ NMR spectrum at 80 °C is shown in Figure 2. The first product observed during AB thermolysis had a BH_2 resonance at $\delta = -10.8$ ppm. This peak is different from that for cyclotriborazane (CTB, c-$B_3N_3H_{12}$), as deter-

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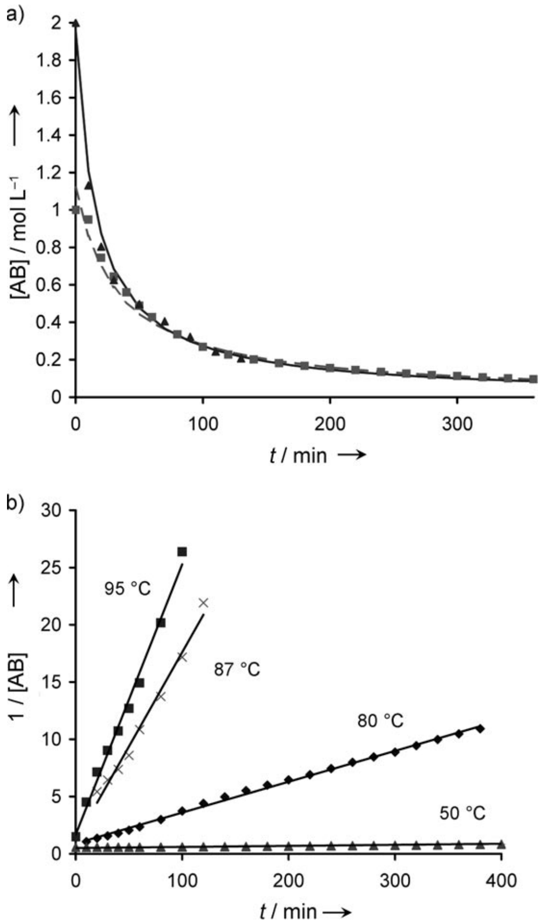


Figure 1. a) Thermal decomposition of AB as a function of time at 80 °C. Initial concentration of AB: 1 M (squares), 2 M (triangles). b) Plots of 1/[AB] versus time showing the second-order kinetics of the decomposition of AB at various temperatures. Initial concentration of AB: 1 M (2 M for the experiment at 50 °C).

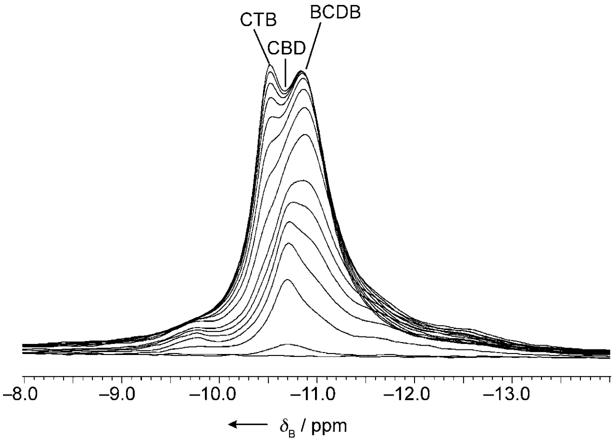


Figure 2. Time-dependent $^{11}B\{^1H\}$ NMR spectra for the first 3.5 h (0, 10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, 180, 200, 220 min, from bottom to top) of the thermolysis of NH_3BH_3 (1 M) at 80 °C. Cyclodiborazane was the first species to appear.

mined by comparison with the $^{11}B\{^1H\}$ NMR spectrum of authentic CTB dissoved in glyme. We tentatively assign this peak to cyclodiborazane (CDB, c-$B_2N_2H_8$). The next peak to appear was initially visible as a shoulder on the CDB peak at $\delta = -10.9$ ppm. This peak appeared concurrently with the new BH ($\delta = -5.0$ ppm) and BH_3 ($\delta = -23.4$ ppm) peaks.[7] These three peaks integrated to approximately 1:1:1 over the course of their growth and decay. This evidence suggests that these three boron peaks belong to a single species, which we believe to be B-(cyclodiborazanyl)aminoborohydride (BCDB; see Figure S2 in the Supporting Information). Subsequent to the appearance of the signals for the BH_2 group of CDB at $\delta = -10.8$ ppm and for that of BCDB at $\delta = -10.9$ ppm, another BH_2 resonance appeared at $\delta = -10.6$ ppm. We assigned the BH_2 signal observed at $\delta = -10.6$ ppm to CTB on the basis of its chemical-shift identity with that observed for an authentic sample of CTB. Following the initial growth of the BH_2 peak for CDB and concurrent with the growth of peaks for BCDB and CTB, we observed new resonances due to borazine and polyborazylene ($\delta = 27$–31 ppm).

To strengthen our assignment of the BH_2 peaks at $\delta = -5.0$, -10.9, and -23.4 ppm to BCDB, we measured the ^{15}N NMR spectrum at a similar point of conversion. Figure 3 shows the proton-coupled and proton-decoupled room-temperature ^{11}B and ^{15}N NMR spectra of the decomposition products formed by heating a solution of AB (1 M) in glyme at 80 °C for 7.5 h in a sealed PEEK (polyetheretherketone) NMR tube. The ^{11}B NMR spectrum shows one BH_3, one BH, and three BH_2 resonances (Figure 3 a); the ^{15}N NMR spectrum indicates the presence of four NH_2 groups, with no evidence of new NH_3 or NH groups (Figure 3 b). This observation is important, as it indicates conclusively that AB reacts with CDB only at the BH_2 ring position. No linear product or trigonally substituted (singly protonated) nitrogen species are observed in this decomposition reaction by ^{15}N NMR spectroscopy; thus, any significant reaction between NH_3BH_3 and the NH_2 ring position can be ruled out.

Together, the ^{11}B and ^{15}N NMR spectroscopic data provide evidence for the three identifiable BH_2- and NH_2-containing products depicted in Scheme 1. The initial BH_2

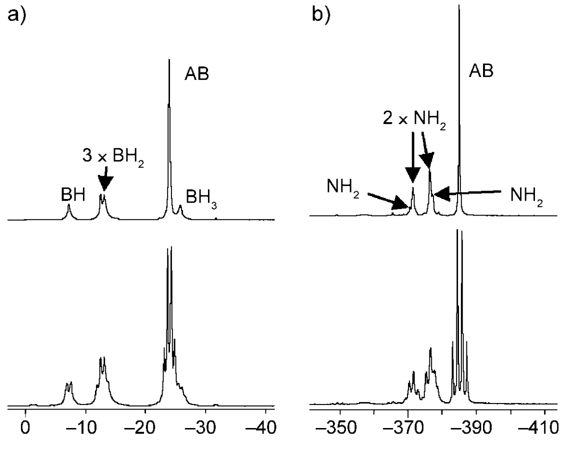


Figure 3. a) ^{11}B and b) ^{15}N NMR spectra recorded at room temperature following the heating of $^{15}NH_3BH_3$ (1 M) at 80 °C for 7.5 h (top: decoupled; bottom: ^1H-coupled). The upfield regions of both spectra are consistent with the presence of BCDB, CDB, and CTB. The region of the spectrum in which signals for sp^2-hybridized B centers occur ($\delta = 20$–40 ppm, not shown) is consistent with the presence of borazine- and polyborazylene-type species.

signal observed is consistent with CDB, which is also consistent with the observation of only NH_2 products. The assignment of the second product, characterized by a BH_3, a BH_2, and a BH signal in the ^{11}B NMR spectrum, as BCDB, in which the ammonia borane addition product is bound through a boron (and not a nitrogen) center, is supported by the observation of NH_2 groups and the absence of sp^3 NH or NH_3 groups in the ^{15}N NMR spectrum. Our ^{11}B NMR spectra and assignments are consistent with the spectrum of BCDB prepared by an alternate method. The third BH_2 signal observed between 1 and 3 h was assigned as CTB. This interpretation is also in agreement with the observation of only NH_2 resonances in the ^{15}N NMR spectrum of the product mixture. Table 1 summarizes the chemical-shift data and structural assignments for this reaction.

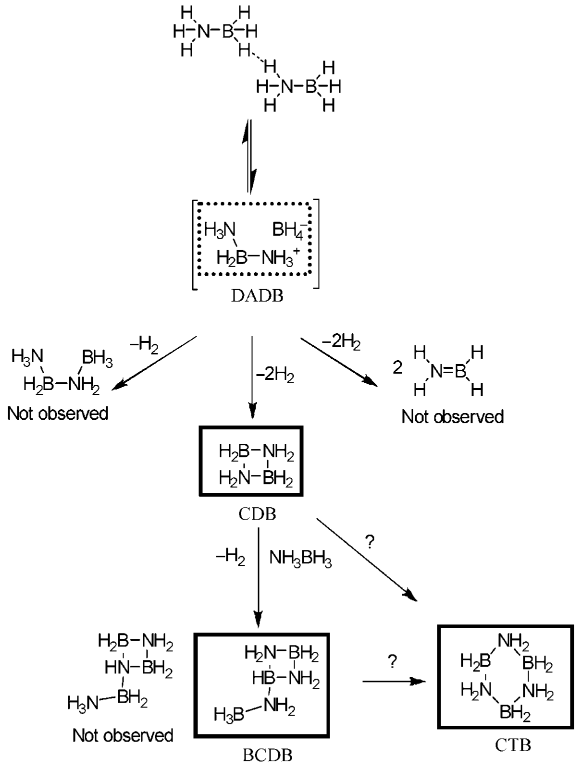
At the lowest temperature of 50 °C, we observed a small peak at $\delta = -37$ ppm in the ^{11}B NMR spectra. The signal for the borohydride anion of DADB appears at this position in the ^{11}B NMR spectra of DADB in the solid state and in ionic liquids.[7] The observation of small quantities of DADB suggests that the initial decomposition step is the isomerization of AB to DADB. The observation of DADB in glyme parallels the observation of DADB in the solid state; however, we propose that in an organic solvent, DADB cyclizes to CDB in competition with the bimolecular reaction with AB that appears to be the dominant pathway in the solid state and in ionic liquids. In an organic solvent, the tight binding interaction of the ion pair may enhance the rate of cyclization of DADB to form neutral CDB. To test this hypothesis, we added authentic DADB to glyme and monitored the formation of products by ^{11}B NMR spectroscopy. However, when solid DADB was added to glyme, the cyclization and subsequent reactions occurred so rapidly that we observed a mixture of BH_2 species, as well as a BH and a BH_3 resonance (Figure 3). The observation of the cyclization products is consistent with the report by Mayer that hydrogen evolves from DADB upon dissolution in glyme.[8]

Table 1: AB-dehydrogenation products identified by ^{11}B and ^{15}N NMR spectroscopy, in order of appearance.

Species	^{11}B [ppm][a] (80 °C)	$^{1}J_{B,H}$ [Hz]	^{15}N [ppm][b] (20 °C)	$^{1}J_{N,H}$ [Hz]
NH_3BH_3	−21.6 (BH_3)	96 (q)	−384.5 (NH_3)	70 (q)
CDB	−10.8 (BH_2)	104 (t)	−376.7 (NH_2)	65 (t)
BCDB	−23.4 (BH_3)	93 (q)	−375.9 (NH_2)	65 (t)
	−10.9 (BH_2)	104 (t)	−370.9 (NH_2)[c]	66 (t)
	−5.0 (BH)	114 (d)		
CTB	−10.6 (BH_2)	102 (t)	−370.0 (NH_2)	66 (t)
borazine	31.1 (BH)	133 (d)	−281.7 (NH)	102 (d)
polyborazylene	27.2 (B)	–	−324.4 (NH)	75 (d)

[a] ^{11}B chemical shifts relative to the IUPAC standard $BF_3{\cdot}OEt_2$ (δ=0 ppm) at 20 °C (Ξ=32.083974). [b] ^{15}N chemical shifts referenced to NH_4Cl ($\delta = -360.2$ ppm) relative to the IUPAC standard CH_3NO_2 (δ=0 ppm; Ξ=10.136767). [c] Signal for the NH_2 group outside the ring.

On the basis of the combined NMR spectroscopic results of our study, we propose a pathway for the decomposition of AB in glyme (Scheme 1). The observed second-order rate for the disappearance of AB is consistent with dimerization to form a DADB intermediate. DADB is not stable in glyme and undergoes either conversion back into AB or cyclization to form CDB. In a subsequent reaction, CDB reacts with AB to form the new species BCDB. As the kinetics of this process are relatively complex, we could not determine whether the cyclic trimer was derived from BCDB or formed in another competing reaction between CDB and AB. We can rule out the unimolecular loss of H_2 to form $H_2N{=}BH_2$ followed by rapid [2+2] cycloaddition.[11] The results presented herein are also consistent with previous isotopic-labeling studies in which hydrogen production from dimethylamine borane was observed to be intermolecular in nature.[12,13]



Scheme 1. Initial decomposition pathways of AB based on the results of in situ NMR spectroscopy. Solid boxes denote species observed by ^{15}N and ^{11}B NMR spectroscopy. DADB was only observed at very low concentrations in the thermolysis study at 50 °C.

In our experiments on the decomposition of AB, the appearance of borazine in the ^{11}B NMR spectrum (δ = 31.1 ppm) was evident before significant quantities of CTB were present. Indeed, it was difficult to tell whether borazine appeared before or after CTB. Previous studies showed little or no conversion of CTB into borazine at temperatures below 130 °C.[14] Both of these observations indicate that the mechanism for the formation of borazine (and polyborazalene) does not involve the dehydrogenation of CTB. Further research into the mechanism of formation of borazine at these low temperatures is warranted.

It is interesting to compare the reactivity of AB in the solid state with its reactivity in solution to learn more about the important pathways that lead to the release of hydrogen. Both in solution and in the solid state, it appears that the formation of DADB by an isomerization reaction is a first key step. However, the fate of the DADB formed depends strongly on the reaction conditions. In glyme solution, DADB cyclizes rapidly to form CDB, and CDB reacts by a dehydrogenation pathway with the remaining AB; however, in the solid state, cyclization is much slower, and DADB reacts by a dehydrogenation pathway with the remaining AB. The observation by Sneddon and co-workers of DADB-like products in ionic liquids[7] leads us to suggest that under such conditions the ability of the reaction medium to stabilize the ionic species promotes the formation of oligomers of DADB-like species with AB. On the other hand, the previous observations by Wang and Geanangel[9] and those reported herein suggest that organic solvents facilitate the cyclization of ionic DADB species. The relative stability of DADB in the solid state and its relative instability in organic solvents can be explained in terms of the polarity of its environment: In solid DADB or AB, the environment is sufficiently polar to stabilize the ionic species; however, in an organic solvent, the ion pair $[NH_3BH_2NH_3]^+[BH_4]^-$ is destabilized, and the barrier to cyclization is lower. Thus, when neat DADB is added to glyme, it cyclizes rapidly to form a mixture of new species containing BH_2 structural units.

The formation of sp^2-hybridized BH structural units (the signals for which appear in the ^{11}B NMR spectrum where those for borazine-like species are expected) at early reaction times is also a curiosity. An alternative mechanism for the production of borazine from non-CTB intermediates may be required to explain the present results; we are currently investigating possible mechanisms. More detailed kinetic analysis of the appearance and disappearance of the products of AB thermolysis to create a more accurate mechanistic picture of hydrogen loss from AB is in progress. The decomposition of AB by second-order reaction pathways will have profound consequences in terms of the thermal stability of the storage media. At the high concentrations required to meet volumetric and gravimetric targets, the addition of a stabilizer or an on-board mixer will be required to meet the demands of long-term thermal stability.

Experimental Section

Materials: Glyme was purchased from Aldrich and distilled from sodium prior to use. Ammonia borane was purchased from Aviabor and was used as received.

Synthesis of $^{15}NH_3BH_3$: In a 1 L flask, $^{15}NH_3$ (1 L) was condensed to approximately 1 mL at −78 °C. $BH_3{\cdot}THF$ (1 M, 50 mL) was syringed into the flask under nitrogen, and the resulting mixture was stirred for 1 h. The THF was then removed under vacuum, and the product $^{15}NH_3BH_3$ was recrystallized from ether and stored in a glove box.

Sample preparation: Solutions of the appropriate concentration of natural-abundance or ^{15}N-labeled AB in glyme were prepared in a glove box. An aliquot of the solution (0.2 mL) was transferred to a high-pressure spinning PEEK cell (see the Supporting Information), which was sealed to prevent exposure to air.

NMR spectroscopy: ^{15}N and ^{11}B NMR spectroscopic experiments were performed at 7.06 and 11.75 T. The cell was placed in the magnet, and spectra were recorded at room temperature. The sample was then heated to the appropriate temperature, and the ^{11}B NMR spectrum was monitored as a function of time. This procedure was repeated reproducibly several times with natural-abundance AB. A similar experiment under identical conditions was carried out with ^{15}N-labeled AB. The samples were cooled to room temperature, and the sealed PEEK NMR tube was transferred to an instrument with a ^{1}H-resonance frequency of 500 MHz. Higher-resolution ^{11}B and ^{15}N DEPT[15] NMR spectra were then recorded. In all cases, spectra were recorded both with and without decoupling. The ^{11}B chemical shifts are referenced to $BF_3{\cdot}OEt_2$ ($\delta = 0$ ppm) at 20 °C, and the ^{15}N chemical shifts to $^{15}NH_4Cl$ (1 M) in water ($\delta = -341$ ppm).

PEEK NMR cell: The PEEK NMR cell used in this study evolved from a static, nonspinning cell designed previously by Yonker and Linehan[16] (see Figure S1 in the Supporting Information). The current PEEK-cell design has the NMR spinner built into the approximately 6.5 cm long high-pressure PEEK liquid-sample chamber with an inside diameter of 2 mm and an outside diameter of 5 mm. This novel design facilitates pressurization of the sample (or in this case, the performance of reactions that generate pressure) and enables the spinning of the sample. A simple valve can be tightened to seal the spinning NMR cell under pressure. The advantage of this design is that the spinning of the cell improves the resolution of the NMR signals.

Safety considerations: The cell design was tested hydrostatically at room temperature to failure at 1000 bar and beyond, and the time that elapsed prior to failure was measured. To build in a 10 times safety factor, the failure time at 1000 bar was never exceeded for pressures of 100 bar, maximum. However, unlike for metal vessels, it is impossible to specify a maximum working pressure or time limit for the PEEK NMR cell. As with all high-pressure experiments, laboratory personnel should not be exposed directly to the pressurized vessel. Use of the PEEK NMR cell should follow established protocols for the length of exposure to pressure and temperature, and for the determination of the radial dimension for any sign of polymer stress.

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