Aminoboranes

Ammonium Aminodiboranate: A Long-Sought Isomer of Diammoniate of Diborane and Ammonia Borane Dimer

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Abstract: Ammonium aminodiboranate ([NH₄] [BH₃(NH)BH₄]) is a long-sought isomer of diammoniate of diborane ([NH₄BH₃(NH)BH₄]) and ammonia borane (NH₃BH₃) dimer. Our results show that [NH₄][BH₃(NH)BH₄] is stable in tetrahydrofuran at –18 °C and decomposes rapidly to NH₄BH₃NHBH₄ and H₂ at elevated temperatures. The decomposition pathway is dictated by the dihydrogen bonding between H₃⁺ on NH₄⁺ and H₂⁺ on BH₄⁻ as confirmed by theoretical calculations. This is in contrast to the interconversion between [NH₄BH₃(NH)BH₄] and (NH₄BH₃)₂, although all three have dihydrogen bonds and the same stoichiometry.

Ammonia borane (NH₃BH₃, abbreviated as AB), which was synthesized in the 1950s but received sparse interest in the last century, has attracted extensive investigations in recent years as a potential hydrogen storage candidate, as the most used precursor to boron nitride nanosheets, and as a building block for other novel boron-nitrogen-containing compounds.[1] Around 20 years prior to the discovery of AB, an ionic isomer of AB dimer with the empirical formula of B₃H₆·2NH₃ (known as diammoniate of diborane, abbreviated as DADB) and four possible structures, ([NH₄]BH₃(NH)BH₄), [NH₄][BH₃(NH)BH₄], [NH₄][BH₃(NH)BH₄], [NH₄][BH₃(NH)BH₄], and [NH₄][BH₃(NH)BH₄] were reported.[2] After a series of investigations,[2,3] the structure of the borohydride salt [NH₃BH₃(NH)BH₄] was confirmed using ¹¹B nuclear magnetic resonance spectroscopy (NMR) and X-ray diffraction (XRD).[4] In the literature, DADB is thus often referred to as [NH₃BH₃(NH)BH₄]. The interconversion between DADB and AB has been known for over 50 years.[3a,3]

The synthesis of one other possible ionic isomer, named ammonium aminodiboranate ([NH₄][BH₃(NH)BH₄] abbreviated as AADB), which was mentioned in computational works, has been unsuccessful.[4] This is probably due to the fact that AADB is ≈ 16.4 and 5.8 kcal/mol less stable than AB dimer and DADB at 0 K, respectively, as suggested by computational studies.[5] Sodium aminodiboranate Na(BH₃(NH)BH₄), which possesses the anion in AADB, was first isolated by Girolami and co-workers in 2010, and its single-crystal structure with a crown ether was recently resolved by Chen et al.[6] Replacing Na⁺ with NH₄⁺ through metathesis seems a logical way to synthesize AADB. After numerous attempts, we found that a reaction between Na(BH₃(NH)BH₄) and NH₃SCN in tetrahydrofuran (THF) leads to the formation of AADB, but it is only stable at –18 °C in THF solution. Unlike DADB, which isomerizes into AB among other B, N polymers in solution,[5,9] AADB dehydrogenates 1 equiv H₂ to form NH₄BH₃(NH)BH₄ (abbreviated as NBNB) at elevated temperatures.

The initial syntheses were performed in liquid ammonia by reacting Na(BH₃(NH)BH₄) and NH₃Cl at –20 °C. After removing the ammonia at this temperature and warming the resultant powders to room temperature, rapid gas release was observed. The XRD pattern of the final powder is dominated by NaCl diffract peaks (Figure S1 in the Supporting Information), which is indicative of a metathesis reaction between Na(BH₃(NH)BH₄) and NH₃Cl. To further investigate the reaction process, ¹¹B NMR was employed to monitor the reaction at low temperatures. Na(BH₃(NH)BH₄) and NH₃SCN were employed due to their good solubility in THF. A new set of quartet resonance centered at −19.2 ppm (q, Jυυ = 90 Hz, BH₄⁻ 6H), different from the −19.9 ppm of pristine Na(BH₃(NH)BH₄), was observed once the two reagents were mixed together in a 1:1 molar ratio at −18 °C (Figure 1). The intensity of the −19.2 ppm peaks remained the same after 1 h, which indicated that the newly formed compound was relatively stable at −18 °C. A clear high-field shift in ¹¹Na NMR was detected (Figure S2 in the Supporting Information) at the same time due to the formation of NaSCN. XRD characterization of the final products, collected after removing the THF, featured NaSCN diffraction peaks (Fig-
ure S3 in the Supporting Information). Based on these results, we believe that AADB was formed at $-18^\circ$C in accordance with [Eq. (1)]:

$$\text{Na(BH}_3\text{NH}_2\text{BH}_3\text{)} + \text{NH}_2\text{SCN} = [\text{NH}_4][\text{BH}_3\text{NH}_2\text{BH}_3] + \text{NaSCN} \quad (1)$$

Empirical scaling was used to predict the chemical shifts based on a set of diverse boron-containing molecules (details can be found in the Supporting Information, Figures S6 and S7 in the Supporting Information). The results show that AADB has a $^1$B chemical shift of $-19.0$ ppm, consistent with our experimental result ($-19.2$ ppm; Table S1 in the Supporting Information). Calculations of relative energies were carried out in THF solution using the solvation model (SMD) at M062X/6-311 + + (G,d,p)-SMD + ZPE calculations. The next question to be answered is why AADB does not transform to AB dimer as DADB does, but rather undergoes dehydrogenation to NBNB. We thus performed simulations to disclose the relevant mechanism. As shown in Figure 2, the decomposition pathways for AADB in THF solution goes through a transient transition state of 18.8 kcal mol$^{-1}$ (transition state TS1), which is substantially more stable than the transition state to AB dimer (33.0 kcal mol$^{-1}$, transition state TS2). Specifically, TS1 to NBNB involves the close contact of NH$_4^+$ with (BH$_3$NH$_2$BH$_3$)$^-$, in which the N--H (in NH$_4^+$) bond length is elongated by 0.62 Å (1.65 Å versus 1.03 Å) and the B--H bond by 0.13 Å (1.35 Å versus 1.22 Å). The HH distance in B--H$^+$--H$_2$--N of TS1 is 0.86 Å, favorable to the formation of H$_2$. Once H$_2$ is released, NBNB is produced. The TS2 state, on the other hand, involves the migration of H on NH$_4^+$ to -NH$_2$, leading to the formation of two AB molecules, in which a higher energy barrier needs to be overcome.

Because H$_2$ is derived from the combination of H$^+$ and H$^-$, N(CH$_3$)$_2$Cl was employed to replace NH$_2$SCN in order to obtain a stable AADB derivative. Liquid ammonia was chosen as the reaction medium due to the good solubility of N(CH$_3$)$_2$Cl in it. The $^11$B NMR spectrum of the resultant sample (Figure 3a) shows a down-field shift of the BH$_3$ group compared to that of Na(BH$_3$NH$_2$BH$_3$). In the $^1$H NMR spectrum (Figure 3b), a sharp resonance appears at 3.14 ppm, indicative of H(C). The broad resonance of H(N) at 1.6 ppm and the quartet of H(B) centered at 22.4 ppm, respectively, emerged simultaneously, which can be assigned to NH$_4^+$BH$_3$NH$_2$BH$_3$. At the same time, H$_2$ was detected by mass spectroscopy (MS; Figure S4 in the Supporting Information). Quantitative measurement revealed that the amount of H$_2$ was equal to that of NH$_2$SCN and also Na(BH$_3$NH$_2$BH$_3$). By combining NMR and MS analysis and quantitative measurements, we propose the reaction in [Eq. (2)].

$$[\text{NH}_4][\text{BH}_3\text{NH}_2\text{BH}_3] = \text{NH}_2\text{BH}_3\text{NH}_2\text{BH}_3 + \text{H}_2 \quad (2)$$

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ing the integrity of the BH₃NH₂BH₃ group. The center of H(B) peaks in ¹H NMR is also down-field shifted compared with that of Na(BH₄NH₂BH₃). The integration shows a H(C)/(H(N) + H(B)) ratio of 1:0.62, which close to the theoretical value (1:0.66). NaCl was also detected by XRD in the final product (Figure S5 in the Supporting Information). Furthermore, the elemental analysis of the sample reveals a ratio of C:N:H = 7:12.5:4.2, close to the theoretical value of 7:12:5. Summarizing the above results, we believe that a derivative of AADB with the composition of [N(CH₃)₃][BH₃NH₂BH₃] (denoted as TM-AADB) is formed as shown in [Eq. (3)].

\[
\text{Na(BH}_3\text{NH}_2\text{BH}_3) \text{+Na} = \text{NaCl} + [\text{N(CH}_3\text{)}_3\text{][BH}_3\text{NH}_2\text{BH}_3]
\] (3)

In conclusion, this work both experimentally and theoretically demonstrates the presence of AADB, a long-sought compound for more than 90 years. AADB is stable at -18 °C, but decomposes to NH₃BH₄BH₃ and H₂ at elevated temperatures. The decomposition is from the result of the dihydrogen bond interaction between H⁺ on NH₃⁺ and H⁺ on BH₃, which is further proved by the good stability of TM-AADB. This finding may shed light on how to prepare new B-, N-, H-containing chain compounds assisted by dihydrogen bond interactions. Hybrid chain compounds containing C, B, N, and H are currently under investigation by reacting methyl-substituted ammonium salts with Na(BH₄NH₂BH₃). These C-, B-, N-, H-containing compounds could be precursors to carbon-doped hexagonal boron nitride nanosheets.

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