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Experimental and Computational Study of the Formation Mechanism of the Diammoniate of Diborane: The Role of Dihydrogen Bonds

Xuenian Chen,[†,‡,⊥] Xiaoguang Bao,[‡,⊥] Ji-Cheng Zhao,[*,†] and Sheldon G. Shore[*,‡]

[†]Department of Materials Science and Engineering and [‡]Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, United States

Supporting Information

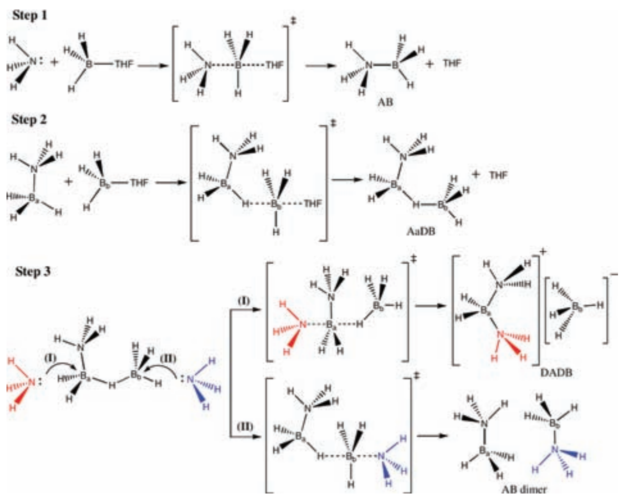
ABSTRACT: The mechanism of formation of ammonia borane (NH_3BH_3, AB) and the diammoniate of diborane ($[H_2B(NH_3)_2][BH_4]$, DADB) in the reaction between NH_3 and THF·BH_3 was explored experimentally and computationally. Ammonia diborane ($NH_3BH_2(\mu\text{-H})BH_3$, AaDB), a long-sought intermediate proposed for the formation of DADB, was directly observed in the reaction using ^{11}B NMR spectroscopy. The results indicate that dihydrogen bonds between the initially formed AB and AaDB accelerate the formation of DADB in competition with the formation of AB.

A dihydrogen bond is an attractive interaction between a positively charged H atom (such as N−H, O−H, or other proton donor) and a negatively charged H atom (such as M−H or B−H, where M is usually a transition metal).[1] Such H···H interactions were first noticed by Brown through solution IR spectra in the late 1960s.[2] Although substantial progress has been made over the past two decades in the identification and characterization of the dihydrogen bond,[3] its possible applications in synthetic chemistry have not been widely explored.[4] Recent investigations of the role of the dihydrogen bond in amine−borane systems indicate that N−H···H−B dihydrogen bonds could promote new syntheses/reactions.[5]

A diborane ammonia complex, which was first observed in the 1920s by Stock et al. in a reaction between ammonia (NH_3) and diborane (B_2H_6),[6] was characterized with the empirical formula B_2H_6·$2NH_3$ and thus was called the diammoniate of diborane (DADB).[7] Over the years, four possible structural formulas were proposed on the basis of the chemical composition: (a) $[NH_4]_2[B_2H_4]$,[8] (b) $[NH_4][H_3BNH_2BH_3]$,[9] (c) $[(NH_4)(BH_2NH_2)(BH_4)]$,[10] and (d) $[NH_3BH_2NH_3][BH_4]$.[11b] The structure of DADB was shown to be formula d in a series of papers from Parry's group in 1958.[11] Recently, the crystal structure of DADB was also reported.[12] Interestingly, the anion in the structural formula b, $[H_3BNH_2BH_3]^-$, was synthesized very recently through the reaction of Na or $NaNH_2$ with ammonia borane (NH_3BH_3, AB) under reflux in THF.[13] DADB was also found as a side product in a simple displacement reaction between NH_3 and tetrahydrofuran borane (THF·BH_3) along with the desirable product AB,[14] which is a widely studied compound for hydrogen storage.[15]

The mechanism of DADB formation has attracted considerable attention.[16] Factors such as steric effects and solvent properties were considered[16] but were found to be insufficient to explain the DADB formation.[17] Ammonia diborane ($NH_3BH_2(\mu\text{-H})BH_3$,[18] denoted as AaDB in order to distinguish it from aminodiborane ($NH_2B_2H_5$, ADB[5,19])), has long been contemplated as an intermediate associated with the formation of DADB, although it was never identified experimentally.[18] Here we present the first direct ^{11}B NMR evidence for the existence of the AaDB intermediate in the reaction of NH_3 with a THF·BH_3 solution. Moreover, the mechanism leading to DADB formation from the AaDB intermediate is experimentally and computationally explored.

Scheme 1. Proposed Mechanism Leading to DADB and AB



A three-step mechanism for the formation of a mixture of AB and DADB is proposed (Scheme 1). In step 1, AB is produced in a displacement reaction. AB further reacts with THF·BH_3 to form the AaDB intermediate in step 2. In step 3, NH_3 can react with AaDB in one of two pathways: (I) NH_3 attacks B_a to form DADB or (II) NH_3 attacks B_b to form two molecules of AB.

To study the mechanism of the DADB formation, ^{11}B NMR spectroscopy, which can easily distinguish AB from DADB, was employed to follow the reaction. Figure 1 shows a stacked plot of ^{11}B NMR spectra recording an 11 min period from the beginning to completion of the reaction of NH_3 gas with a THF·BH_3 solution at −78 °C. As the reaction proceeded, the THF·BH_3 signal (δ −0.9 ppm) decreased, and a new signal characteristic of AB (δ −22.5 ppm) increased after a slight delay. Two additional small signals at δ −13.8 and −25.5 ppm appeared within 3 min and were assigned respectively to B_aH_2 (triplet) and B_bH_3 (quartet) in the AaDB intermediate (Scheme 1). At ~7 min, a broad peak emerged at δ −38.0 ppm, which gradually increased in amplitude and changed

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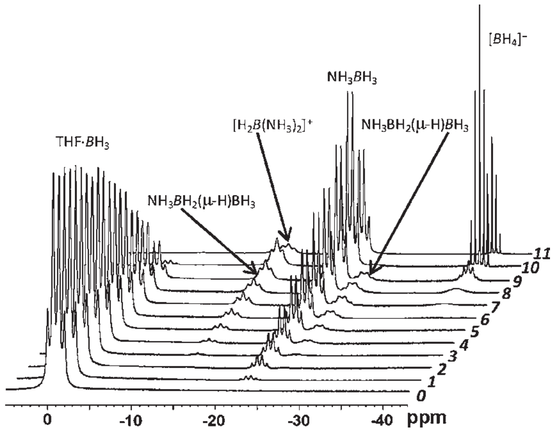

Figure 1. ^{11}B NMR spectra of the reaction of NH_3 with a THF·BH_3 solution at −78 °C. Samples were extracted at 1 min intervals and stored at −78 °C. After the reaction was complete, spectra were rapidly recorded for each sample as it warmed to ambient temperature.

to a quintet characteristic of BH_4^-. Finally, after 11 min of reaction, only signals due to AB and DADB were present in the spectrum.

The transformation from the AaDB intermediate to DADB product is clearly reflected in the formation of the BH_4^- anion in the ^{11}B NMR spectra. When the quartet signal at δ −25.5 ppm, assigned to B_bH_3 in the AaDB, gradually decreased and finally disappeared, a new BH_4^- peak at δ −38.0 ppm appeared and gradually increased at the same time. In contrast, the triplet at δ −13.8 ppm assigned to B_aH_2 increased steadily in the same period of time rather than producing the corresponding chemical shift change. One possible explanation is the coincidence of the chemical shifts of B_aH_2 and $[H_2B(NH_3)_2]^+$ at δ −13.8 ppm.

The observed values of ^{11}B chemical shifts, δ −13.8 and −25.5 ppm, for B_aH_2 and B_bH_3 groups in AaDB are not consistent with the results calculated at the B3LYP/6-311++G(d,p) level of theory with GIAO method.[20] This discrepancy is attributed to a dihydrogen bond effect on the ^{11}B NMR spectra of AaDB. When an AB binds AaDB through B−H···H−N dihydrogen bonds, the value calculated for B_b shifts significantly to δ −19.8 ppm. When two AB molecules interact with AaDB, the calculated B_b chemical shift is δ −24.4 ppm, in good agreement with the observed result. For comparison, the solvation effect of THF on the ^{11}B chemical shifts of AaDB is less pronounced because the N−H···O H-bonds formed are remote from B_b. A calculated chemical shift of δ −17.9 ppm for B_b was obtained when three THF molecules were H-bonded to AB (see Supporting Information for computational details).

Attempts to identify the AaDB intermediate by ^{1}H, ^{1}H{^{11}B}, and two-dimensional NMR spectroscopies were unsuccessful. The weak signals from AaDB were obscured by the large THF·BH_3 and AB signals. However, a control experiment clearly revealed separate resonances for $NH_3BH_2NH_2BH_3$ and AaDB, proving that the resonances at δ −13.8 and −25.5 ppm are not from $NH_3BH_2NH_2BH_3$ (Figures S3 and S4).

The proposed mechanism in Scheme 1 is supported by a variety of experimental results. When THF·BH_3 reacted with a large excess of liquid NH_3 at −78 °C, pure AB (Figure S8) was obtained, indicating that only step 1 had occurred. No THF·BH_3 remained for the formation of AaDB in step 2. In contrast, when NH_3 gas was passed over a THF·BH_3 solution at −78 °C, the reaction proceeded along all three steps to produce a mixture of AB and DADB (Figure 1).

Table 1. Relationship between Dihydrogen Bonds and the Ratio of DADB to AB

	H-bonds	ratio DADB/AB[a]
THF·BH_3 (1 M) + NH_3	H···H	1:4.0
THF·BH_3 (1 M) + ND_3	D···H	1:4.1
THF·BH_3 (0.5 M)/AB (0.5 M) + NH_3	H···H[b]	1:2.6
THF·BH_3 (0.5 M)/TMAB (0.5 M)[c] + NH_3	H···H[b]	1:15

[a] The ratio of DADB to AB is based on the integrated values of the $[BH_4]^-$ anion and formed AB in ^{11}B{^{1}H} NMR spectra. [b] The intentionally added AB is much more effective in forming dihydrogen bonds than the intentionally added TMAB. [c] The actual concentration of TMAB is ca. 0.3 M.

Formation of DADB (pathway I) was perhaps enhanced by the dihydrogen bond formation between AB and AaDB. To test this hypothesis, NH_3 gas was passed over an equimolar solution (0.5 M) of THF·BH_3 and AB at −78 °C. The ratio of DADB to AB in the product increased, consistent with increased dihydrogen bonding to AaDB promoted by the high concentration of AB. When NH_3 gas was passed over an equimolar solution (0.5 M) of THF·BH_3 and trimethylamine borane (TMAB) at −78 °C, the ratio of DADB to AB decreased significantly. The presence of methyl groups makes TMAB less effective than AB in forming dihydrogen bonds with AaDB. When ND_3 gas was passed over a THF·BH_3 solution at −78 °C, the deuterium isotope effect was found to be minimal (Table 1).

The proposed mechanism presented in Scheme 1 and the role of dihydrogen bonds between AB and AaDB in the formation of DADB were supported by computational studies carried out at the MP2/6-31++G(d,p) level of theory (see Supporting Information for computational details). Step 1 is recognized as a typical S_N2 reaction. In the transition state, the borane moiety is planar, and breaking of the B−O bond and formation of the N−B bond occur simultaneously. The calculated activation energy barrier is 8.4 kcal/mol, and the reaction is exothermic (−5.6 kcal/mol) (Table S1).

The optimized reactant complex (RC), transition state (TS), and product complex (PC) for step 2 are shown in Figure 2. In the RC, AB interacts with THF·BH_3 via a bifurcated dihydrogen bond. The transition state is created by binding a hydridic H of AB (negative charge −0.11 according to natural population analysis (NPA), Figure S26) to the borane moiety on THF·BH_3. In the TS, a planar borane moiety of THF·BH_3 is identified, suggesting simultaneous cleavage of the B−O bond and formation of an H−B bond. The predicted reaction energy barrier is 15.5 kcal/mol (Table 2). In the PC, a N−H···O hydrogen bond with THF stabilizes AaDB. The formation of AaDB from AB and THF·BH_3 is slightly endothermic (1.4 kcal/mol), suggesting that formation of AaDB may be reversible.

In step 3 of Scheme 1, NH_3 attacks either B_a or B_b of the AaDB intermediate (pathway I or II, respectively). The calculated energy barrier for pathway I (30.6 kcal/mol in a vacuum) was significantly higher than the barrier of pathway II (14.3 kcal/mol) (Table 3, Figure S28). When the THF solvation effect was included (a polarizable continuum model (PCM) method), the resulting energy barrier for pathway I was still much higher than that for pathway II (Table 3). NPA charge analysis for the TS of pathway I showed that the BH_4 moiety has a negative charge (−0.79) and the NH_3BH_2 moiety has a positive charge (+0.65) (Figure S29). Their strong attractive interaction may be responsible for the high energy barrier to create the BH_4^- anion and the

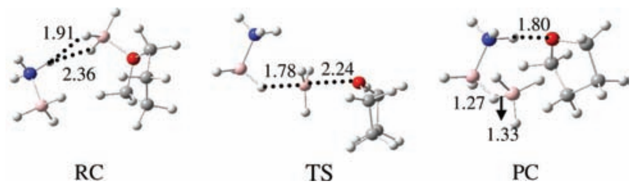

Figure 2. Optimized RC, TS, and PC for the reaction between AB and $THF \cdot BH_3$ to produce the AaDB intermediate. Colors: C, gray; H, white; N, blue; B, pink; and O, red. Bond lengths are shown in Å.

Table 2. Energetics of the Reaction between AB and $THF \cdot BH_3$ To Produce AaDB (kcal/mol at 0 and 195 K), Calculated at the MP2/6-31++G(d,p) Level of Theory[a]

	ΔE_0	ΔH_0	ΔH_{195}	ΔG_{195}	ΔH_0(PCM)	ΔG_{195}(PCM)
RC	0.0	0.0	0.0	0.0	0.0	0.0
TS	16.9	15.5	15.5	15.1	15.2	14.9
PC	1.2	1.3	1.3	1.7	3.4	3.8

[a] The THF solvation effect was analyzed using the PCM approach. The single-point energies were calculated using optimized geometries in a vacuum with dielectric constant ε = 7.4257.

$NH_3BH_2NH_3^+$ cation for formation of DADB. In contrast, there was no significant charge separation for the TS of pathway II. As a consequence, AB formation has a lower energy barrier.

Computational analysis of the reaction of NH_3 with AaDB in the presence of one, two, three, and four AB molecules provides a possible explanation for DADB formation as the reaction nears completion (Table 3). As the proportion of AB increases, the activation energies for pathways I and II become nearly comparable. Dihydrogen bonds from one AB to AaDB reduced the calculated activation energy barrier leading to DADB by 5.7 kcal/mol. Figure 3 contains the relevant RC, TS, and product structures for pathways I and II of step 3. TS1, a protonic H of AB, forms a dihydrogen bond with the BH_4 group, facilitating the separation of BH_4^- to produce DADB. More dihydrogen bonds form when two AB molecules interact with AaDB, providing assistance in the separation of BH_4^-. The calculated energy barrier of pathway I decreases to 20.7 kcal/mol. When four AB molecules are considered, the predicted activation energy for pathway I is only 15.9 kcal/mol, compared to 11.8 kcal/mol for pathway II.

The catalytic role of AB molecules in the formation of DADB is attributed to the fact that the AB molecule has a partially positively charged protonic end and a partially negatively charged hydridic end. The partially positively charged end favors the BH_4^- group, and the partially negatively charged end prefers to interact with the NH_3BH_2 moiety through B−H···H−N dihydrogen-bonding interactions in the TS leading to DADB. As a consequence, the attractive interaction between the BH_4^- group and the NH_3BH_2 group is weakened. Therefore, the reaction energy barrier for the formation of DADB is lowered due to the assistance of AB molecules via the intermolecular dihydrogen bonds, rendering pathway I to form DADB feasible. In comparison with pathway II to form AB, pathway I still has a relatively higher energy barrier. Therefore, one can expect AB to be the major product and DADB a minor product, which is consistent with the experimental observations.

Here we have explicitly analyzed the influence of dihydrogen bonds on the activation energy of pathways I and II. The solvation effect of polar solvents[21] or ionic liquids[22] plays a similar role through dipole−dipole or ion−dipole interactions. However, the dihydrogen bond may play a dominant role in determining the product types, based on this experimental and computational study. For instance, in

Table 3. Energetics of the Reaction between NH_3 and AaDB in the Presence of Zero, One, Two, Three, and Four AB (at the MP2/6-31++G(d,p) Level, in kcal/mol, at 0 and 195 K)[a]

	ΔE_0	ΔH_0	ΔH_{195}	ΔG_{195}	ΔH_0(PCM)	ΔG_{195}(PCM)
Without AB Molecule						
Pathway I: Attack B_a						
RC1	0.0	0.0	0.0	0.0	0.0	0.0
TS1	32.1	30.6	30.1	31.9	19.9	21.1
DADB	−3.0	−1.8	−2.6	−0.4	−9.5	−8.0
Pathway II: Attack B_b						
RC2	0.0	0.0	0.0	0.0	0.0	0.0
TS2	16.1	14.3	14.5	14.0	12.4	12.1
2AB	−14.6	−13.1	−13.3	−12.8	−15.8	−15.5
With One AB Molecule						
Pathway I: Attack B_a						
RC1	0.0	0.0	0.0	0.0	0.0	0.0
TS1	26.5	24.9	24.5	26.0	18.2	19.3
DADB···AB	−10.2	−9.0	−9.7	−7.1	−13.7	−11.8
Pathway II: Attack B_b						
RC2	0.0	0.0	0.0	0.0	0.0	0.0
TS2	14.2	12.5	12.6	12.4	11.0	10.9
2AB···AB	−14.0	−12.4	−12.6	−12.5	−16.1	−16.2
With Two AB Molecules						
Pathway I: Attack B_a						
RC1	0.0	0.0	0.0	0.0	0.0	0.0
TS1	22.1	20.7	20.3	21.4	18.2	18.9
DADB···2AB	−12.7	−11.3	−11.9	−10.1	−14.1	−13.0
Pathway II: Attack B_b						
RC2	0.0	0.0	0.0	0.0	0.0	0.0
TS2	12.9	11.5	11.4	11.8	10.9	11.2
2AB···2AB	−21.2	−18.7	−19.4	−17.2	−19.0	−17.5
With Three AB Molecules						
Pathway I: Attack B_a						
RC1	0.0	0.0	0.0	0.0	0.0	0.0
TS1	19.5	18.0	17.7	18.6	16.8	17.4
DADB···3AB	−16.0	−14.5	−15.1	−13.6	−15.9	−15.0
Pathway II: Attack B_b						
RC2	0.0	0.0	0.0	0.0	0.0	0.0
TS2	13.6	12.6	12.3	13.5	11.2	12.1
2AB···3AB	−21.1	−19.1	−19.7	−17.2	−19.1	−17.3
With Four AB Molecules						
Pathway I: Attack B_a						
RC1	0.0	0.0	0.0	0.0	0.0	0.0
TS1	17.5	15.9	16.0	16.0	15.6	15.7
DADB···4AB	−22.8	−20.7	−21.4	−18.2	−18.6	−16.2
Pathway II: Attack B_b						
RC2	0.0	0.0	0.0	0.0	0.0	0.0
TS2	12.4	11.8	11.8	12.1	11.1	11.3
2AB···4AB	−24.8	−22.6	−22.8	−21.8	−20.6	−19.7

[a] The THF solvation effect was considered by using the PCM approach. The single-point energies were calculated using optimized geometries in a vacuum with dielectric constant ε = 7.4257.

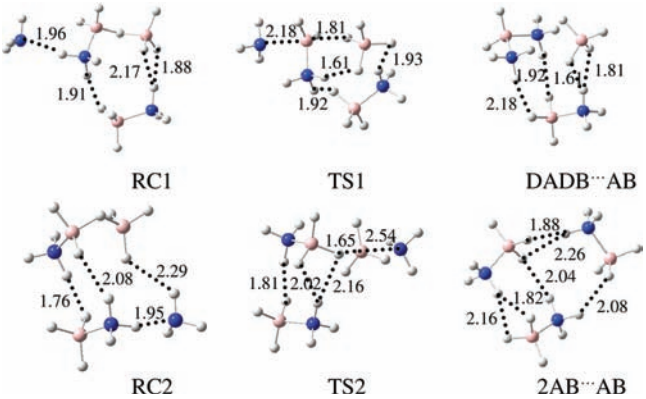

Figure 3. Optimized RC, TS, and products for both reaction pathways of NH_3 to AaDB in the presence of one AB. Colors: H, white; N, blue; B, pink. Bond lengths are shown in Å.

the intentional additions of AB or TMAB discussed above, the solvation effect of the reaction systems should be similar. However, the alteration of dihydrogen bonding between AB/TMAB and AaDB causes a significant difference in the ratio of DADB to AB.

In summary, both experimental and computational investigations have been applied to the classic displacement reaction between NH_3 and $THF \cdot BH_3$ to explore the formation mechanism of DADB, a side product. The results indicate that the initially produced AB reacts with $THF \cdot BH_3$ to yield an AaDB intermediate, which has been directly observed in the reaction using ^{11}B NMR spectroscopy. AB, produced by NH_3 reacting with either $THF \cdot BH_3$ or B_b of AaDB, facilitates the separation of the BH_4^- via dihydrogen bond interactions with AaDB that lower the reaction energy barrier to DADB production. Dihydrogen bonds may play a significant, but previously unrecognized, role in other reactions where reactants, intermediates, or products have both hydridic and protonic hydrogens.

■ ASSOCIATED CONTENT

S Supporting Information. Experiments, computations, and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors
zhao.199@osu.edu; shore.1@osu.edu

Author Contributions
⊥These authors contributed equally.

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