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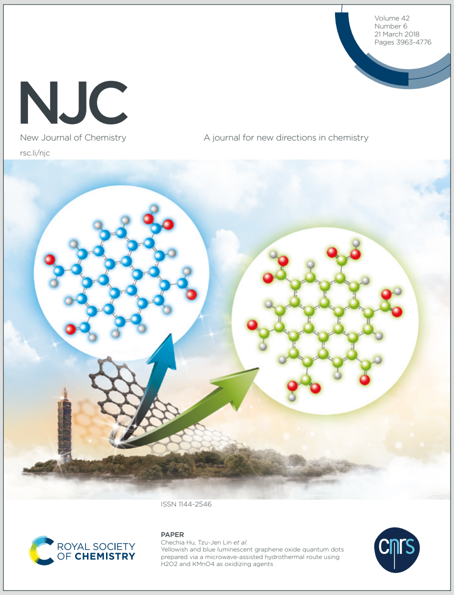

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ARTICLE

Reactivity and mechanisms of hydridic hydrogen of B-H in ammonia borane towards acetic acids: the ammonia B-monoacyloxy boranes

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The non-classical acid-base neutralization reactions of ammonia borane ($NH_3{\cdot}BH_3$, AB) with acetic acids are moderate, affected by the strengths of acetic acid and its chloro derivatives, the concentrations and ratios of the reactants. The experiment results indicate that only one hydridic hydrogen of B–H in AB is substituted and fortunately, four ammonia B-monoacyloxy boranes ($NH_3{\cdot}BH_2OOCR$, R = CH_nCl_{3-n}, n = 0, 1, 2, 3) are prepared. Two single crystals of $2NH_3BH_2OOCCH_2Cl{\cdot}C_{12}H_{24}O_6$ and $2NH_3BH_2OOCCHCl_2{\cdot}C_{12}H_{24}O_6$ were obtained and analyzed firstly. Theoretical calculations demonstrated that these reactions are two-step elimination-addition process that takes advantage of the formation of dihydrogen bond (DHB) and hydrogen bond (HB), and aminoborane (NH_2BH_2, AoB) is identified as the key intermediate.

Introduction

Burgeoning research interest in boron–nitrogen–hydrogen (B–N–H) compounds resurrected during the past decades, not just because of their potential use in hydrogen storage[1-7] but also for a new understanding of their particular structure and properties.[8-16] Furthermore, the B–N–H compounds have been utilized as reducing agent[17] for CO_2,[18] graphene,[19] aldehyde/ketone,[20] alkenes[21] and precursors to prepare boron nitride nanotube/ball,[22-23] boron nitride polymer,[24] white graphene,[25] and metal nanoparticles.[26-27] Amongst the B–N–H family, ammonia borane ($NH_3{\cdot}BH_3$, AB) is the most widely studied Lewis acid-base adduct, in which three types of bonds (N→B dative bond, N–H, and B–H bonds) connected both protonic ($N{-}H^{\delta+}$) and hydridic ($B{-}H^{\delta-}$) hydrogens together. Intermolecular dihydrogen bond (DHB), $N{-}H^{\delta+}{\cdots}{}^{\delta-}H{-}B$ and expected bent B–H···H and linear N–H···H moieties were present in AB.[10] On the one hand, the amphoteric reactivity of AB can be explained by the standard view that electron-deficient BH_3 acts as a Lewis acid and the electron-rich NH_3 as a Lewis base. In the presence of a strong Lewis acid or base, such as BF_3/BCl_3[28-29] or $Me_3N/Et_3N/C_5H_5N$,[30-32] the N→B dative bond was broken, and the displacement of BH_3 or NH_3 occurred to form new Lewis acid-base adducts. The breaking of the N→B dative bond also occurred in the acid-catalyzed hydrolysis of AB, in which proton substitutes for BH_3 at the ammonia nitrogen, NH_4^+ formed and the released BH_3 was rapidly hydrolyzed.[33-34] Interestingly, AB can also serves as an efficient substoichiometric (10%) precatalyst for the direct amidation of both aromatic and aliphatic carboxylic acids. [35]

On the other hand, the amphoteric characteristics of AB can be understood from a new perspective that protic hydrogen ($H^{\delta+}$) is acidic coupled to basic $NH_2BH_3^-$ and hydridic hydrogen ($H^{\delta-}$) is basic coupled to acidic $NH_3BH_2^+$. The hydrogenation of polar unsaturated compounds (such as olefins and imines) with AB is proposed to be a double-hydrogen-transfer reaction (both $H^{\delta+}$ and $H^{\delta-}$ atoms).[36-38] While AB was treated with Lewis base, such as M, MH (M = Li, Na, K), the N–H bond was broken, a metal cation replaced only $H^{\delta+}$, and metal amidoboranes formed.[39-42] Boronium cations including $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-[H(OEt_2)_2]^+$ and $[BH_2(amine)(S)]^+$ (amine = NH_3, Me_2NH, $MeNH_2$; S = ethereal solvent) can be obtained from the reactions of amine borane with some strong Lewis or Brønsted acids, such as $[H(OEt_2)_2][A]$ (A^- = $B[3,5\text{-}(CF_3)_2{-}C_6H_2]_4$, $B(C_6F_5)_3$ and $HOSO_2CF_3$.[43-45] Similarly, NH_3BH_2Cl was obtained when AB reacted with dry HCl in Et_2O at -40 °C.[46] A mixture of $NH_3{\cdot}BCl_3$, $NH_3{\cdot}BHCl_2$ and $NH_3{\cdot}BH_2Cl$ was found in the products of the reaction of AB with BCl_3.[28]

The hydrolysis product of the released BH_3 from the acid-catalyzed hydrolysis of AB was $B(OH)_3$,[33-34] while the product of the reaction of AB with oxalic acid was a spiral bis(oxalate)borate ($[B(C_2O_4)_2]NH_4$),[47] which is because of the strong interaction between the electron-deficient B and electron-rich O, the chelation effect of the oxalic acid may also play an essential role in promoting the formation of spiroborate compounds. Also, the B–H of AB can initially displace L from $L{\cdot}BH_3$ (L = weaker base) to form a new Lewis acid/base adduct, ammonia diborane $[NH_3BH_2(\mu{-}H)BH_3]$, with a newly formed B–H–B (3c–2e) bond, which is usually unstable so that further transformation occurs easily.[48] The analogous B–H–Al bonds were also observed in aluminum complexes of AB, which resulting from the coordination of the B–H bonds in AB to Al in AlX_3 (X = Br,

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C_6F_5).[49] Thus it can be seen that the reactivity of $H^{\delta-}$ of B–H bond in AB is far more complicated than it had been expected; an in–depth understanding of the intrinsic properties of AB is still limited. Therefore, we tested the reactions of AB with about fifty acids, including alcohol, phenols, and carboxylic acid. However, there are no significant reactions of AB with series of alcohols, phenols under mild conditions without a catalyst. Only carboxylic acids can react with AB at moderate speed, which is suitable to investigate its reactivity and reaction mechanism. In the present study, we systematically studied the reactions of AB with acetic acids. The experimental results revealed that only one $H^{\delta-}$ of B–H in AB was substituted by acyloxy of acetic acid, the ammonia B–monoacyloxy borane ($NH_3{\cdot}BH_2OOCR$, R = CH_nCl_{3-n}, n = 0, 1, 2, 3), as the main product was obtained for the first time, and X-ray single-crystal structure of two ammonia B–monoacyloxy boranes were also determined. Furthermore, theoretical DFT calculations have indicated that the reaction of AB with acetic acids is an elimination-addition process promoted by the DHB and HB, unveiling the chemical nature of a stepwise dehydrogenation process.

EXPERIMENTAL SECTION

General Methods

Unless stated otherwise, all manipulations were carried out using standard Schlenk techniques or a nitrogen-filled glove box or glove bag. Ammonia borane (AB), CH_3COOH, $CH_2ClCOOH$, $CHCl_2COOH$, and CCl_3COOH were purchased from Aldrich and used as received without further purification. Solvents used for the reactions (THF, Et_2O) were dried over sodium/benzophenone and freshly distilled prior to use. Crystalline 18-crown-6 ether (Aldrich) was ground to a powder and dried over P_2O_5 under vacuum.

A standard reaction procedure was usually followed: a solution of acids was added dropwise to the solution of AB at room temperature. The reaction mixture was monitored by ^{11}B NMR at different intervals. All NMR spectra were recorded with a Bruker AV400 (^{11}B 128.0 MHz; ^{1}H 400.1 MHz; ^{13}C 100.6 MHz). The ^{11}B NMR spectra were externally referenced to $BF_3{\cdot}OEt_2$ in C_6D_6 ($\delta = 0.00$ ppm). IR spectra were obtained using a Nicolet–Magana 550 FT–IR spectrophotometer in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. Elemental analysis data were recorded using an Elementar (Vario EL) instrument.

Preparation and Characterization of $NH_3BH_2OOCCH_3$

At room temperature, a solution of acetic acid was added dropwise to AB solution with constant stirring. The initial molar ratio of n_{AB}: n_{acid} and c_{AB} were adjusted according to Table 1 (the same below). Several crystal growing techniques had been tried to prepare $NH_3BH_2OOCCH_3$ crystal, and no crystal had been obtained yet. After the reaction finished, the solvent was evaporated under a dynamic vacuum to leave a wax product. ^{11}B NMR (d_3- CD_3CN, 128 MHz, δ): -6.5 (*t*, BH_2).

Preparation and Characterization of $2NH_3BH_2OOCCH_2Cl{\cdot}C_{12}H_{24}O_6$ (1)

A similar procedure to that of $NH_3BH_2OOCCH_3$ was used to prepare $NH_3BH_2OOCCH_2Cl$ (yield: ~86%). A 10 mL THF solution of $NH_3BH_2OOCCH_2Cl$ (0.12 g, 1 mmol) was prepared and 0.13 g (0.5 mmol) of 18-crown-6 was added to the solution. The mixture was stirred for 5 min and filtered. The clear solution was kept in the refrigerator at -10 ºC, and colorless transparent block crystals (**1**) were obtained. ^{11}B NMR (d_3- CD_3CN, 128 MHz, δ): -6.8 (*t*, BH_2) ^{1}H NMR (d_3- CD_3CN, 400 MHz, δ): 4.6 (*br*t, 3H, NH_3), 4.1 (*t*, 2H, CH_2), 3.6 (*t*, 24H, $12CH_2$), 3.6 (*q*, 2H, BH_2, overlapped with 24H, CH_2). $^{13}C\{^{1}H\}$ NMR (d_3- CD_3CN, 101 MHz, δ): 169 (*s*, CO), 118 (*s*, C of CN), 71 (*s*, 12C of $12CH_2$), 43(*s*, C, CH_2), 0.4 (*s*, C, CH_3). Anal. Calcd for $C_2H_7BNClO_2$ (123.35): C, 19.47; H, 5.72; N, 11.36. Found: C, 19.18; H, 5.96; N, 11.58.

Preparation and Characterization of $2NH_3BH_2OOCCHCl_2{\cdot}C_{12}H_{24}O_6$ (2)

A similar procedure to that of $NH_3BH_2OOCCH_3$ was used to prepare $NH_3BH_2OOCCHCl_2$ (yield: ~88%). A 10 mL THF solution of $NH_3BH_2OOCCHCl_2$ (0.16 g, 1 mmol) was prepared and 0.13 g (0.5 mmol) of 18-crown-6 was added to the solution. The mixture was stirred for 5 min and filtered. The clear solution was kept in the refrigerator at -10 ºC, and colorless transparent block crystals (**2**) were obtained. ^{11}B NMR (d_3- CD_3CN, 128 MHz, δ): -5.5 (*t*, BH_2). ^{1}H NMR (d_3- CD_3CN, 400 MHz, δ): 4.6 (*br*t, 3H, NH_3), 4.1 (*t*, 2H, CH_2), 3.6 (*t*, 24H of $12CH_2$), 3.6 (*q*, 2H of BH_2, overlapped with 24H, CH_2).$^{13}C\{^{1}H\}$ NMR (d_3- CD3CN, 101 MHz, δ): 168 (*s*, CO), 118 (*s*, C, CN), 70 (*s*, 12C, $12CH_2$), 67 (*s*, C, CH_2), 0.3 (*s*, C, CH_3). Anal. Calcd for $C_2H_6BNCl_2O_2$ (157.79): C, 15.22; H, 3.83; N, 8.88. Found: C, 15.40; H, 4.19; N, 8.36.

Preparation and Characterization of $NH_3BH_2OOCCCl_3$

A similar procedure to that of $NH_3BH_2OOCCH_3$ was used to prepare $NH_3BH_2OOCCCl_3$. Several crystal growing techniques had been tried to prepare $NH_3BH_2OOCCCl_3$ crystal, and no crystal had been obtained yet. After the reaction finished, the solvent was evaporated under a dynamic vacuum to leave a wax product.^{11}B NMR (d_3- CD_3CN, 128 MHz, δ): -4.8 (*t*, BH_2).

X-ray Crystallography

Single-crystal XRD analyses were conducted on Bruker Kappa CCD diffractometers. The measurement of **1** and **2** were recorded using Mo *Kα*, λ = 0.71073 Å. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography. The structures were solved using the direct method and refined through the full-matrix least-squares method on F^2 using SHELXS-97. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Further details on the crystal structure investigation can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/ on quoting the depository numbers CCDC-1957962 (**1**), CCDC-1957961 (**2**).

Computational Details

The Gaussian-09 program suite has been used to investigate the potential energy landscape associated with ammonia borane and acetic acid or substituted acetic acid. All the geometrical structures were optimized at the B3LYP/6-311++G(2d,p) level of theory. The vibrational frequencies calculations indicate that all the species are stationary points that the transition states with one imaginary frequency and other species without imaginary frequency. The single-point energy calculations for the stationary points are carried out to get the more reliable and authentic information at the M06/6-

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311++G(2d,p) level of theory with Solvation Model Based on Density (SMD).

RESULTS AND DISCUSSION

The reactions of AB with acetic acids: the syntheses and structure of ammonia B–monoacyloxy boranes

Generally, the reactions of $H^{\delta+}$ with $H^{\delta-}$ can be regarded as non–classical acid–base neutralization reactions. Elimination of H_2 as oppositely charged hydrogens combine and a new covalent bond forming has been known for a long time, which can be used to synthesize new compounds and design new materials.[16,50-51] From this perspective, the $H^{\delta-}$ of B–H in AB and $H^{\delta+}$ of O–H in Brønsted acid can be easily engaged in the intermolecular DHB $O–H^{\delta+}\cdots{}^{\delta-}H–B$ and subsequent dihydrogen elimination. At room temperature, AB can react with an excess amount of acetic acid and chloroacetic acids in THF or Et_2O. Fortunately, four ammonia B–monoacyloxy boranes ($NH_3{\cdot}BH_2OOCR$, $R = CH_nCl_{3-n}$, n = 0, 1, 2, 3) were obtained with H_2 release (Eq 1, Table 1, Figures S1–4).

$$NH_3{\cdot}BH_3 + RCOOH \rightarrow H_2 + NH_3{\cdot}BH_2OOCR \ (R = CH_nCl_{3-n},\ n = 0, 1, 2, 3) \quad \text{(Eq 1).}$$

Table 1. The reactions of AB with acetic acids.

Entry	Reactants (the initial molar ratio of n_{AB}: n_{acid}, c_{AB})	Conditions	Products	Conversion of AB^a (%)
1	AB + CH_3COOH (1:1, 0.50 M)	RT^b, THF	NR^c	-
2	AB + $ClCH_2COOH$ (1:1, 0.50 M)	RT, THF, 30 d	$NH_3BH_2OOCCH_2Cl$, H_2	20
3	AB + $Cl_2CHCOOH$ (1:1, 0.50 M)	RT, THF, 56 h	$NH_3BH_2OOCCHCl_2$, H_2	100
4	AB + Cl_3CCOOH (1:1, 0.50 M)	RT, THF, 7 h	$NH_3BH_2OOCCCl_3$, H_2	100
5	AB + CH_3COOH (1:1, 1 M)	RT, THF, 14 h	NR	-
6	AB + CH_3COOH (1:1, 2 M)	RT, THF, 14 h	$NH_3BH_2OOCCH_3$, H_2	4
7	AB + CH_3COOH (1:1, 3 M)	RT, THF, 14 h	$NH_3BH_2OOCCH_3$, H_2	12
8	AB + CH_3COOH (1:1, 4 M)	RT, THF, 14 h	$NH_3BH_2OOCCH_3$, H_2	35
9	AB + CH_3COOH (1:1, 5 M)	RT, THF, 14 h	$NH_3BH_2OOCCH_3$, H_2	50
10	AB + CH_3COOH (1:1, 6 M)	RT, THF, 14 h	$NH_3BH_2OOCCH_3$, H_2	56
11	AB + CH_3COOH (1:3, 1 M)	RT, THF, 67 h	$NH_3BH_2OOCCH_3$, H_2	100
12	AB + CH_3COOH (1:6, 1 M)	RT, THF, 24 h	$NH_3BH_2OOCCH_3$, H_2	100
13	AB + Cl_3CCOOH (1:1.2, 0.13 M)	RT, THF, 45 min	$NH_3BH_2OOCCCl_3$, H_2	21
14	AB + Cl_3CCOOH (1:1.2, 0.38 M)	RT, THF, 45 min	$NH_3BH_2OOCCCl_3$, H_2	73
15	AB + Cl_3CCOOH (1:1.2, 0.50 M)	RT, THF, 45 min	$NH_3BH_2OOCCCl_3$, H_2	85
16	AB + Cl_3CCOOH (1:1.2, 0.63 M)	RT, THF, 45 min	$NH_3BH_2OOCCCl_3$, H_2	91
17	AB + Cl_3CCOOH (1:1.2, 0.75 M)	RT, THF, 45 min	$NH_3BH_2OOCCCl_3$, H_2	97
18	AB + $ClCH_2COOH$ (1:2, 1 M)	RT, Et_2O, 76 h	$NH_3BH_2OOCCH_2Cl$, H_2	100
19	AB + $ClCH_2COOH$ (1:2, 1 M)	RT, Et_2O, 10 d	$NH_3BH_2OOCCH_2Cl$, $NH_3BH(OOCCH_2Cl)_2$, H_2	100
20	AB + CH_3COOH (1:1, 3 M)	70 °C, THF, 7 h	complex	100

a: calculated by the resonance intensities of boron signals in the ^{11}B NMR spectra of the reaction mixture; b: RT, room temperature; c: NR, no reaction.

The reactions of AB with acetic acids were monitored by ^{11}B NMR, and the products have been characterized by ^{11}B NMR, ^{1}H, ^{13}C NMR, FTIR, Elemental analyses, and single–crystal X–ray diffraction (SI). Notable features of the ^{11}B NMR, including a triplet of BH_2, indicate that only one $H^{\delta-}$ of B–H is substituted by acyloxy (Figures S1a, 2a, 3a, 4). Furthermore, the chemical shifts of B in the ammonia B–monoacyloxy boranes move downfield slightly (Table S1), which is in line with the electron-withdrawing effect of chlorine in chloroacetic acids. The disappearance of characteristic O–H stretching vibration centered at 3400 cm^{-1} and the new B–O stretching vibration centered at 1380 cm^{-1} in FTIR spectra demonstrate unequivocally that the $H^{\delta-}$ of B–H in AB are substituted by acyloxy, and the B–H stretching vibration centered at 2390 cm^{-1} show that not all $H^{\delta-}$ of B–H are substituted (Figures S2d, 3d).

It is significant to note that most acyloxyboranes are transient species, and the intermediates characterization is often challenging.[47, 52-56] Only few acyloxyboranes were synthesized[57] and used as catalyst for asymmetric Diels-Alder reactions, [58] P. Helquist and O. Wiest studied the stereoselectivity in (acyloxy)borane–catalyzed Mukaiyama Aldol reactions by theoritacal calculations. [59] To the best of our knowledge, there are no ammonia B–monoacyloxy borane has been isolated. We utilized 18–crown–6 ether to bind the ammonia B–monoacyloxy boranes by weak HBs and two single crystals, $2NH_3BH_2OOCCH_2Cl{\cdot}C_{12}H_{24}O_6$ (**1**), $2NH_3BH_2OOCCHCl_2{\cdot}C_{12}H_{24}O_6$ (**2**), were obtained. Single-crystal X-ray diffraction analysis (Fig. 1, Table S2) shows that the two ammonia B–monoacyloxy boranes and 18–crown–6 adducts are both crystallized with 0.5 equiv of 18–crown–6, which are monoclinic and belong to the P21/n space group. The structures of the two adducts are stabilized by hydrogen-bonding interactions between the hydrogen atom of an $–NH_3$ of two adjacent ammonia B–monoacyloxy boranes and an oxygen atom of 18–crown–6 (Fig. 1). The HBs in **1** and **2** are similar to those in $2NH_2B_2H_5{\cdot}C_{12}H_{24}O_6$, $NH_2BH_2NH_2BH_3{\cdot}C_{12}H_{24}O_6$, $Na[H_2N(BH_3)_2]{\cdot}C_{12}H_{24}O_6{\cdot}2THF$, $NH_2B_2H_5{\cdot}THF$.[12, 60]

For comparison, the critical bond lengths and bond angles are summarized in Tables S3, 4. As shown in Table S3, 4, similar to the N–B bond length in AB, the N(1)–B(1) bond length is 1.581(3) Å and 1.590(7) Å for **1** and **2**, which are not affected by one more Cl substituent on C(2). The B(1)–O(1), C(1)–C(2) bond lengths for **2** (1.513(7) Å, 1.536(9) Å) are slightly longer than those of **1** (1.505(3) Å, 1.505(4) Å). However, the C(1)–O(2), C(2)–Cl(1) bond lengths for **2**

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(1.205(9) Å, 1.750(7) Å) are slightly shorter than those of **1** (1.217(3) Å, 1.779(3) Å). The N(1)−B(1)−O(1) angles (109.1(5)°) in **2** is consistent with sp^3 hybridization, while the N(1)−B(1)−O(1) angles (102.7(2)°) in **1** is slightly smaller.

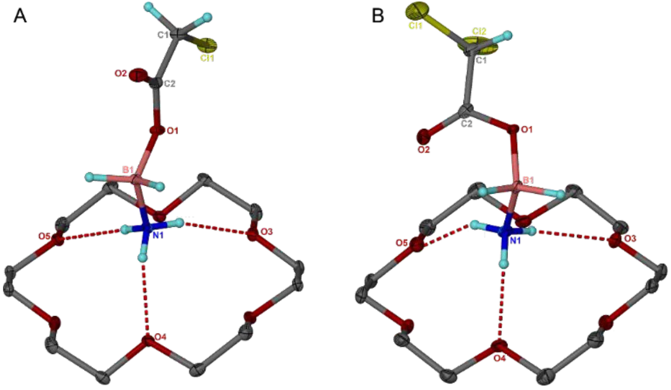

Fig. 1 The molecular structures with 35% of displacement ellipsoids for A) $2NH_3BH_2OOCCH_2Cl·C_{12}H_{24}O_6$ (1), B) $NH_3BH_2OOCCHCl_2·C_{12}H_{24}O_6$ (2). Colors: N, blue; B, pink; O: red; C, gray; H, light−blue; Cl, yellow (red dash lines show hydrogen bonds).

Affecting factors of the reactions of AB with acetic acids

The reaction rate of AB with acetic acids is strongly dependent on the acidity of acetic acids. At the same conditions (the initial ratio of n_{AB}: n_{acid} = 1:1, c_{AB} = 0.5 M), there was no reaction between AB and CH_3COOH (Table 1, entry 1), the conversion of AB was only 20% in 30 days for the reaction of AB with $CH_2ClCOOH$ (Table 1, entry 2), while AB can react with $CHCl_2COOH$ and CCl_3COOH at a moderate speed, which took 76 h and 7 h, respectively, to complete (Table 1, entries 3, 4). Because of the Cl substituents effect, the relative acidity of acetic acids is known to increase along with the series CH_3COOH < $CH_2ClCOOH$ < $CHCl_2COOH$ < CCl_3COOH and their *pKa* are 4.76, 2.86, 1.30 and 0.22, respectively. The reaction rates of AB with acetic acids increased along with the same trend.

Both increasing the concentration of reactants (AB and acetic acids) and the molar ratio of acetic acids can accelerate the reaction. Controlling the initial molar ratio of n_{AB}: n_{acid} = 1:1, increasing c_{AB} can accelerate the reaction significantly. For example, when the reactions of AB with CH_3COOH were monitored by ^{11}B NMR spectroscopy in 14 h, increasing c_{AB} from 1 M to 6 M resulted in increased conversion of AB from 0 to 56% (Table 1, entries 5−10, Figure S5), the fastest reaction could complete in 24 h (Table 1, entry 10). With increasing c_{AB} over 6 M, byproducts were significantly increased because the reaction was exothermic. Similarly, increasing the molar ratio of acetic acid can also promote the reaction. By optimizing the initial ratio of n_{AB}: n_{acid} to 1:3 and 1:6, the reactions of AB with CH_3COOH took 67 h and 24 h to complete, respectively (Table 1, entries 11, 12). A similar phenomenon was observed for the reaction of AB with CCl_3COOH when increasing the c_{AB} by optimizing the initial ratio of n_{AB}: n_{acid} to 1:1.2. The conversion of AB was increasing from 21 to 97%, with the c_{AB} being set at a range of 0.13−0.75 M (Table 1, entries 13−17, Figure S6), the reaction of entry 17 was the most rapid, which can complete within 1 h.

Quite unexpectedly, only one hydridic (B−$H^{\delta-}$) hydrogen was substituted despite different acidity and quantities of acetic acids (t, BH_2, Figure S1a, 2a, 3a, 4), indicating that more substitution of hydrides of ammonia B−monoacyloxy boranes is difficult. It is only when the reaction time is long enough, such as 10 days, a small quantity of ammonia B−diacyloxy boranes can be observed in the ^{11}B NMR spectrum by the reaction of the formed ammonia B−monoacyloxy boranes with excess $ClCH_2COOH$ in Et_2O (Table 1, entries 18−19, Figure S7), which can be probably rationalized with the appropriate nucleophilicity of the B−H bonding pair electrons and the suitable acidity of acetic acids. Further investigations in the substitution process of the second hydridic hydrogen in AB are still in our group's progress. Besides, the reaction of AB with acetic acids was strongly dependent on temperature (Table 1, entry 20, Figure S8). However, the products are too complicated, indicating increasing the reaction temperature may result in the byproducts and the dissociation of the main product.

The formation mechanism of ammonia B−monoacyloxy boranes by the reaction of AB with acetic acids

The relatively mild reaction conditions and speed make the reactions of AB with acetic acids very suitable for mechanistic study when compared to other highly reactive boranes. To figure out the reaction mechanism, whether the reaction is carried out kinetically or thermodynamically, theoretical calculations with density functional theory (DFT) are performed (SI). The formation mechanism of ammonia B−monoacyloxy boranes ($NH_3·BH_2OOCR$, R = CH_nCl_{3-n}, n = 0, 1, 2, 3) by the reaction of AB with acetic acids is shown in Scheme 1. The energy profile of these reactions at M06/6-311++G(2d,p)//B3LYP/6-311++G(2d,p) level of theory with SMD solvent model is shown in Fig. 2 and Fig. S9a-c, 10. The calculated energies and rate constants are listed in Tables S4-9. The optimized geometries of all the species are shown in Figures S11a, b.

As shown in Scheme 1, the mechanism includes two steps. In the first step, the RCOOH catalyzes AB to release hydrogen by the DHB between the $H^{\delta-}$ of B−H in AB and $H^{\delta+}$ of O-H in RCOOH and HB between $H^{\delta+}$ of N−H in AB and $O^{\delta-}$ of C=O in RCOOH. The transition states (TS) TS1 has an eight-membered ring via $B{-}H^{\delta-}\cdots{}^{\delta+}H{-}O$ and $N{-}H^{\delta+}\cdots{}^{\delta-}O{-}C$, in which the H···H bond distance is at a range of 0.815~0.862 Å and the H···O distance is at a range of 1.148~1.202 Å (Fig. 2, Figures S9a-c, Figures S11a, b). The short $H^{\delta-}\cdots{}^{\delta+}H$ and $H^{\delta+}\cdots{}^{\delta-}O$ distance suggest the elimination of H_2 resulting in the formation of aminoborane (NH_2BH_2, AoB) and RCOOH. We have tried to trap AoB by cyclohexene but failed. Synchronously, the $H^{\delta+}$ of N−H in AoB can be captured by the terminal O of C=O and the $H^{\delta+}$ of O−H captured by the N in AoB, an intermediate complex with a six-membered ring form (Fig. 2, Figures S9a-c, Figures S11a, b). For the reaction of AB with CCl_3COOH, the intermediate complex (IM4) has a different structure via an $N\cdots H^{\delta+}{-}O$ interaction in which the N···H distance is 2.028 Å (Fig. 2, Figure S11b).

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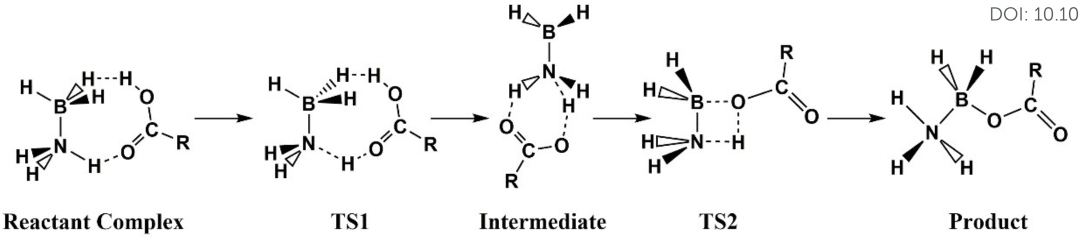
Scheme 1 Proposed formation mechanism of ammonia B−monoacyloxy boranes ($NH_3{\cdot}BH_2OOCR$, R = CH_nCl_{3-n}, n = 0, 1, 2, 3)



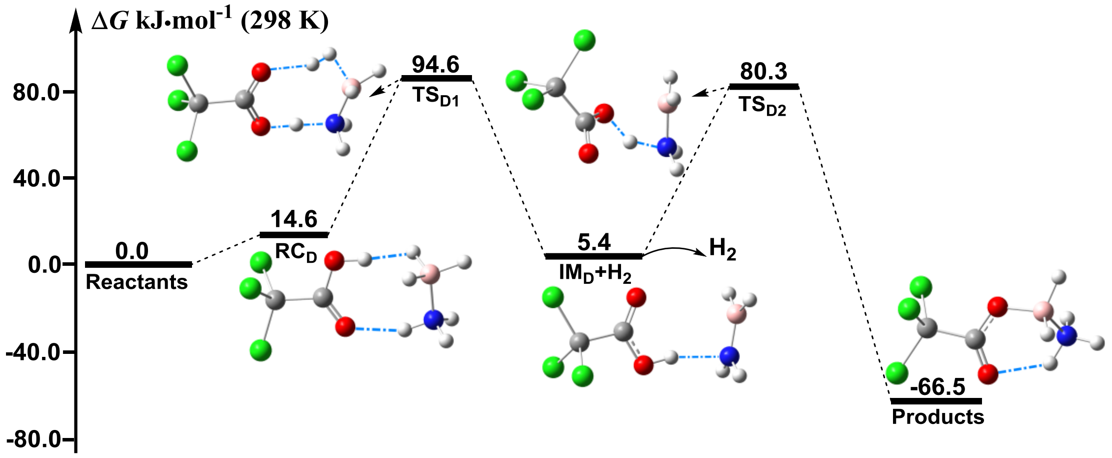


Fig. 2 Potential energy surface for the reaction of AB with CCl_3COOH.

In the second step, a concerted hydrogen transfer from O−H in RCOOH to N in AoB and the addition of O in RCOO to the B of AoB occurred, resulting in the formation of TS2 with a four−membered ring via $N{\cdots}H^{\delta+}$−O and B···O interaction, the N···H and B···O distance is 1.215~1.307 and 1.734~2.107 Å respectively, and finally the ammonia B−monoacyloxy borane formed ($NH_3{\cdot}BH_2OOCCH_nCl_{3-n}$, n = 0, 1, 2, 3), which does not favor the further reduction of acetic acid. In a word, the reaction of AB with RCOOH (R = CH_nCl_{3-n}, n = 0, 1, 2, 3) can be regarded as an elimination−addition process promoted by hydrogen transfer.

All the total free energies (*ΔG*) are negative (-36.4/-62.3/-62.8/-66.5 kJ·mol^{-1}), indicating that those reactions are thermodynamically controlled and can occur spontaneously. The free energy barrier of TS1 is slightly higher than that of TS2 for the reactions of AB with acetic acids (Tables S5-8, Figure S9a-c, Figure 2). Simultaneously, all the free energy barriers of TS decreased with the acidity of acetic acids increases, which is consistent with the changes in the reaction rates. Furthermore, the free energy barriers of TS of the reactions of AB with acetic acids (94.6~124.3 kJ·mol^{-1}, Tables S5-8, Figure S9a-c, Figure 2) are much smaller than that of the direct decomposition of AB into AoB and H_2 (175.7 kJ·mol^{-1}, Table S9, Figure S10), which demonstrating that acetic acid is an efficient catalyst and hydrogen−transfer reagent. Table S10 listed the calculated rate constants with a temperature range from 258 to 398 K, which shows that the rate constants are also increasing (*k1-k4*) with the acidity of acetic acids.

Conclusions

In summary, using the moderate reactions of AB with acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid at room temperature, the reactivity of AB towards Brønsted acids has been systematically investigated. The reaction of AB with acetic acids constitutes an important fundamental reaction mode of B−N−H compounds, which was not only related to the activity of the B−H bond and the acidity of Brønsted acid but also affected by the ratio and concentration of reactants. Only one hydridic hydrogen in AB can be substituted by acetic acid and series chloroacetic acid, dichloroacetic acid, trichloroacetic acid, and four ammonia B−monoacyloxy boranes ($NH_3{\cdot}BH_2OOCCH_nCl_{3-n}$, n = 0, 1, 2, 3) are firstly obtained, in which two single crystals of $2NH_3BH_2OOCCH_2Cl{\cdot}C_{12}H_{24}O_6$ and $2NH_3BH_2OOCCHCl_2{\cdot}C_{12}H_{24}O_6$ were obtained firstly, and their crystal structures were analyzed. DFT calculations indicate that the reactions are a two−step elimination−addition process; both DHB and HB play an essential role in the reaction pathways. The calculated negative total free energies (*ΔG*) and lower energy barriers are consistent because the reaction can spontaneously occur at room temperature. The reactions of AB with acetic acids not only offer a facile synthetic procedure for the synthesis of ammonia B−monoacyloxy boranes with high yield and purity but also provide a unique opportunity to study the structure, stability, and behavior of the new monoacyloxyboranes species. What is more, the ammonia

B–monoacyloxy boranes may suggest and allow many interesting syntheses, incredibly selective and asymmetric reductions in the future.

Author Contributions

[⊥] Y. Li and J. Kang contributed equally.

Conflicts of interest

The authors declare no competing financial interest.

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