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Hydrogen Release Studies of Alkali Metal Amidoboranes

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A series of metal amidoboranes $LiNH_2BH_3$ (LAB), $NaNH_2BH_3$ (SAB), $LiNH(Me)BH_3$ (LMAB), $NaNH(Me)BH_3$ (SMAB), $KNH(Me)BH_3$ (PMAB), and $KNH(^tBu)BH_3$ (PBAB) were synthesized by solution phase methods, and the thermal release of H_2 in the solid state was studied. The mechanism of hydrogen release from metal amidoboranes, a *metal ion assisted hydride transfer*, is very different than the mechanism of hydrogen release from the parent compound ammonia borane (AB). On the basis of the observed trends in reaction rates of H > Me > ^{t}Bu, K > Na > Li, and the kinetic isotope effect, the mechanism of hydrogen release from MAB compounds was found to proceed through a bimolecular mechanism involving the intermediacy of a MH (M = Li, Na, or K). The non-volatile products formed from MABs are significantly different than the products formed after hydrogen release from AB. The boron containing products resulting from the release of 1 equiv of hydrogen from the metal amidoboranes were characterized by MAS ^{11}B NMR spectroscopy and found to contain both BH_3 and sp^2 hybridized BH groups, consistent with the general structure $MN(R){=}BHN(R)MBH_3$.

Introduction

The fixation of hydrogen in the form of a solid hydride containing lightweight elements is a promising and actively investigated approach to energy storage.[1] One main group hydride that has received significant interest because of the high gravimetric density of hydrogen and low temperatures for release is ammonia borane (NH_3BH_3, AB).[2−7] More recently, metal amidoboranes [$M^{n+}(NH_2BH_3)_n$, MAB; M = Li (LAB),[8−14] Na (SAB),[12,14−16] and Ca (CAB)[17]] have drawn intense interest. Experimental studies on the decomposition of LAB have shown that the temperature for H_2 liberation is lower, the thermolysis to release H_2 is less exothermic, and the H_2 purity is greater for LAB and SAB compared to AB.[12,13,15]

While progress has been made in elucidating the mechanism of H_2 release from solid AB,[3,18] experimental reports on metal amidoborane (MAB) compounds have not included many details on the mechanism of H_2 release.[9−17] This lack of mechanistic details is likely due to difficulty in characterizing the products of the thermolysis of MAB compounds and that kinetic studies have focused on maximizing the quantity and rate of H_2 released and not on understanding the mechanism.[9−13,15] However, in two recent computational studies on the dehydrogenation LAB, a bimolecular mechanism involving the intermediacy of lithium hydride was predicted to be the lowest energy pathway in the gas phase.[19,20] To gain insight into the mechanism of H_2 release

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(1) Orimo, S.; Nakamori, Y.; Eliseo, J. R.; Zuttel, A.; Jensen, C. M. *Chem. Rev.* **2007**, *107*, 4111.

(2) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.* **2009**, *38*, 279.

(3) Stowe, A. C.; Shaw, W. J.; Linehan, J. C.; Schmid, B.; Autrey, T. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1831.

(4) Wolf, G.; Baumann, J.; Baitalow, F.; Hoffmann, F. P. *Thermochim. Acta* **2000**, *343*, 19.

(5) Hu, M. G.; Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta* **1978**, *23*, 249.

(6) Shaw, W. J.; Linehan, J. C.; Szymczak, N. K.; Heldebrant, D. J.; Yonker, C.; Camaioni, D. M.; Baker, R. T; Autrey, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7493.

(7) Bluhm, M. E.; Bradley, M. G.; Butterick, R., III; Kusari, U.; Sneddon, L. G. *J. Am. Chem. Soc.* **2006**, *128*, 7748.

(8) Myers, A. G.; Yang, B. H.; Kopecky, D. J. *Tetrahedron Lett.* **1996**, *37*, 3623.

(9) Graham, K. R.; Kemmitt, T.; Bowden, M. E. *Energy Environ. Sci.* **2009**, *2*, 706.

(10) Wu, H.; Zhou, W.; Yildirim, T. *J. Am. Chem. Soc.* **2008**, *130*, 14834.

(11) Xiong, Z.; Chua, Y. S.; Wu, G.; Xu, W.; Chen, P.; Shaw, W.; Karkamkar, A.; Linehan, J.; Smurthwaite, T.; Autrey, T. *Chem. Commun.* **2008**, 5595.

(12) Xiong, Z.; Yong, C. K.; Wu, G.; Chen, P.; Shaw, W.; Karkamkar, A.; Autrey, T.; Jones, M. O.; Johnson, S. R.; Edwards, P. P.; David, W. I. F. *Nat. Mater.* **2008**, *7*, 138.

(13) Kang, X.; Fang, Z.; Kong, L.; Cheng, H.; Yao, X.; Lu, G.; Wang, P. *Adv. Mater.* **2008**, *20*, 2756.

(14) Ramzan, M.; Silvearv, F.; Blomqvist, A.; Scheicher, R. H.; Lebègue, S.; Ahuja, R. *Phys. Rev. B* **2009**, *79*, 132102.

(15) Xiong, Z.; Wu, G.; Chua, Y. S.; Hu, J.; He, T.; Xu, W.; Chen, P. *Energy Environ. Sci.* **2008**, *1*, 360.

(16) Fijałkowski, K. J.; Grochala, W. *J. Mater. Chem.* **2009**, *19*, 2043.

(17) Diyabalanage, H. V. K.; Shrestha, R. P.; Semelsberger, T. A.; Scott, B. L.; Bowden, M. E.; Davis, B. L.; Burrell, A. K. *Angew. Chem. Int. Ed.* **2009**, *15*, 5598.

(18) Heldebrant, D. J.; Karkamkar, A.; Hess, N. J.; Bowden, M. B.; Rassat, S.; Zheng, F.; Rappe, K.; Autrey, T. *Chem. Mater.* **2008**, *20*, 5332.

(19) Kim, D. Y.; Singh, N. J.; Lee, H. M.; Kim, K. S. *Chem.—Eur. J.* **2009**, *15*, 5598.

(20) Lee, T. B.; McKee, M. L. *Inorg. Chem.* **2009**, *48*, 7564.

from MAB compounds in the solid phase and to test the predictions from the computational studies on LAB dehydrogenation in the gas phase, we prepared a series of metal amidoboranes for experimental studies. Using in situ magic angle spinning (MAS) ^{11}B NMR spectroscopy to identify the reaction products and volumetric gas analysis to determine relative rates of H_2 release from various MAB compounds and selectively deuterated LAB, we provide experimental evidence in favor of a bimolecular reaction pathway involving loss of metal hydride.

Experimental Section

General Considerations. All manipulations were done under an inert atmosphere in a nitrogen filled drybox or using standard vacuum line techniques. Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Tetrahydrofuran (THF) and hexanes were purified by passage through a column of activated alumina. THF-d_8 was stored over Na/benzophenone and vacuum transferred prior to use. KH was obtained as a suspension in mineral oil and washed with hexane prior to use. AB was purchased from Aviabor, and methylaminoborane (MeAB) and *tert*-butylaminoborane (tBuAB) were purchased from Callery Chemical. MeAB was sublimed prior to use and stored at −35 °C, and tBuAB was stored at 2 °C. ND_3BH_3 was prepared as previously reported.[21] NH_3BD_3 was prepared by addition of NH_3 to a solution of $THF \cdot BD_3$ (1 M) in THF at ambient temperature followed by removal of the volatiles. Both ND_3BH_3 and NH_3BD_3 were sublimed at 60 °C prior to use. Solution ^{1}H and ^{11}B NMR spectra were acquired on a Varian Unity INOVA (500 MHz for ^{1}H) or a Varian (300 MHz for ^{1}H) spectrometer. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent signal (^{1}H) or externally to neat $Et_2O \cdot BF_3$ (^{11}B).

Lithium Amidoborane (LAB). Using a procedure adapted from that previously reported for $Ca(NH_2BH_3)_2$,[17] AB (392 mg, 12.7 mmol) and THF (17 mL) were added to a glass reaction vessel fitted with a stir bar. LiH (151 mg, 19.1 mmol) was added in small aliquots over 5 min to the stirring THF/AB solution and allowed to react for an additional 70 min. The reaction mixture was filtered through a frit followed by a syringe fitted with a PTFE filter tip, and the volatiles were removed under vacuum. The colorless powder was washed with hexanes (4 mL), and the volatiles were removed by remaining under vacuum for 18 h. Yield: 401 mg (86%). ^{1}H NMR (500 MHz, THF-d_8) δ 1.45 (m, J_{BH} = 86 Hz, 3H), −0.82 (s, 2H). ^{11}B NMR (160 MHz, THF-d_8) δ −21.99 (q, J_{BH} = 85 Hz). IR spectrum (THF, cm^{-1}) 2215 (*BH*), 2133 (*BH*).

Sodium Amidoborane (SAB). A procedure similar to the synthesis of LAB described above was followed using AB (187.3 mg, 6.07 mmol), THF (80 mL), and NaH (172.9 mg, 7.20 mmol) and allowing them to react in a drybox for 30 min prior to filtering and removal of the volatiles by remaining under vacuum for 16 h. Yield: 248.6 mg (77%). ^{1}H NMR (300 MHz, THF-d_8) δ 1.55 (m, J_{BH} = 83 Hz, 3H), −1.01 (s, 2H). ^{11}B NMR (96 MHz, THF-d_8) δ −21.50 (q, J_{BH} = 83 Hz). IR spectrum (THF, cm^{-1}) 2182 (*BH*), 2124 (*BH*).

Lithium *N*-methylamidoborane (LMAB). A procedure similar to the synthesis of LAB described above was followed using MeAB (314.3 mg, 7.00 mmol), THF (30 mL), and LiH (130.2 mg, 16.4 mmol) and allowing them to react in a drybox for 70 min prior to filtering and removal of the volatiles by remaining under vacuum for 24 h. This procedure gave LMAB that contained residual THF and minor impurities signals at 3.0−2.4 ppm in the ^{1}H NMR spectrum. ^{1}H NMR (300 MHz, THF-d_8) δ 2.21 (s, 3H), 1.40 (m, J_{BH} = 85 Hz, 3H), −0.77 (s, 1H). ^{11}B NMR (96 MHz, THF-d_8) δ −18.15 (q, J_{BH} = 86 Hz).

Sodium *N*-methylamidoborane (SMAB). A procedure similar to the synthesis of LAB described above was followed using MeAB (238 mg, 5.30 mmol), THF (40 mL), and NaH (168 mg, 7.00 mmol) and allowing them to react in a drybox for 30 min prior to filtering and removal of the volatiles by remaining under vacuum for 18 h. Yield: 315 mg (89%). ^{1}H NMR (300 MHz, THF-d_8) δ 2.28 (s, 3H), 1.46 (m, J_{BH} = 83 Hz, 3H), −0.95 (s, 1H). ^{11}B NMR (96 MHz, THF-d_8) δ −17.99 (q, J_{BH} = 83 Hz). IR spectrum (THF, cm^{-1}) 2186 (*BH*), 2101 (*BH*).

Potassium *N*-methylamidoborane (PMAB). A procedure similar to the synthesis of LAB described above was followed using MeAB (211.2 mg, 4.70 mmol), THF (30 mL), and KH (291.0 mg, 7.26 mmol) and allowing them to react in a drybox for 45 min prior to filtering and removal of the volatiles by remaining under vacuum for 17 h. Yield: 306.9 mg (79%). ^{1}H NMR (500 MHz, THF-d_8) δ 2.29 (s, 3H), 1.43 (m, J_{BH} = 82 Hz, 3H), −0.89 (s, 1H). ^{11}B NMR (160 MHz, THF-d_8) δ −16.51 (q, J_{BH} = 82 Hz). IR spectrum (THF, cm^{-1}) 2176 (*BH*), 2080 (*BH*).

Potassium *N*-*tert*-butylamidoborane (PBAB). A procedure similar to the synthesis of LAB described above was followed using tBuAB (448 mg, 5.15 mmol), THF (20 mL), and KH (250 mg, 6.23 mmol) and allowing them to react in a drybox for 16 h. This procedure gave PBAB that contained residual THF impurities signals in the ^{1}H NMR spectrum even after remaining under vacuum for 16 h. Yield: 608 mg (94%). ^{1}H NMR (500 MHz, THF-d_8) δ 1.34 (m, J_{BH} = 83 Hz, 3H), 1.00 (s, 9H), −0.73 (s, 1H). ^{11}B NMR (160 MHz, THF-d_8) δ −21.72 (q, J_{BH} = 83 Hz).

$LiNH_2BD_3$. A procedure similar to the synthesis of LAB described above was followed using NH_3BD_3 (261.2 mg, 7.71 mmol), THF (30 mL), and LiH (122 mg, 15.4 mmol) and allowing them to react in a drybox for 70 min prior to filtering and removal of the volatiles by remaining under vacuum for 17 h. Yield: 146 mg (48%). ^{1}H NMR (300 MHz, THF) δ −0.87 (s). ^{11}B NMR (96 MHz, THF) δ −22.33 (m, J_{BD} = 12 Hz). ^{2}H NMR (46 MHz, THF) δ 1.43 (q, J_{BD} = 12 Hz).

$LiND_2BH_3$. A procedure similar to the synthesis of LAB described above was followed using ND_3BH_3 (196.7 mg, 5.81 mmol), THF (30 mL), and LiH (134 mg, 16.9 mmol) and allowing them to react in a drybox for 70 min prior to filtering and removal of the volatiles by remaining under vacuum for 17 h. Yield: 187 mg (83%). ^{11}B NMR (96 MHz, THF) δ −22.09 (q, J_{BH} = 85 Hz). ^{2}H NMR (46 MHz, THF) δ −0.86 (s).

Hydrogen Volume Measurements. The volume of gas released during thermolysis reactions was measured using an automated buret system modified from a previously reported apparatus for good precision with small sample masses and short thermal equilibration times.[22] A pressure transducer mounted at the top of the buret was used to determine the change in pressure (ΔP_b) in the buret. The change in volume (ΔV_b) in the buret was calculated using the equations

$$\Delta h_b = \frac{A_r}{A_r + A_b} \times \frac{\Delta P_b - \Delta P_r}{\rho g}$$

and

$$\Delta Vb = A_b \times \Delta h_b$$

where Δh_b is the change in height of oil in the buret, ΔA_b is the change in internal area of the buret, ΔA_r is the change in area of the reservoir, ΔP_r is the change in pressure above the reservoir, ΔP_b is the change in pressure in the buret, ρ is the density of the oil, and g is the force of gravity. The moles of hydrogen released were calculated from ΔV_b and the ideal gas law. Finely

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(21) Cho, H.; Shaw, W. J.; Parvanov, V.; Schenter, G. K.; Karkamkar, A.; Hess, N. J.; Mundy, C.; Kathmann, S.; Sears, J.; Lipton, A. S.; Ellis, P. D.; Autrey, S. T. *J. Chem. Phys. A* **2008**, *112*, 4277.

(22) Zheng, F.; Rassat, S. D.; Helderandt, D. J.; Caldwell, D. D.; Aardahl, C. L.; Autrey, T.; Linehan, J. C.; Rappé, K. G. *Rev. Sci. Instrum.* **2008**, *79*, 084103.

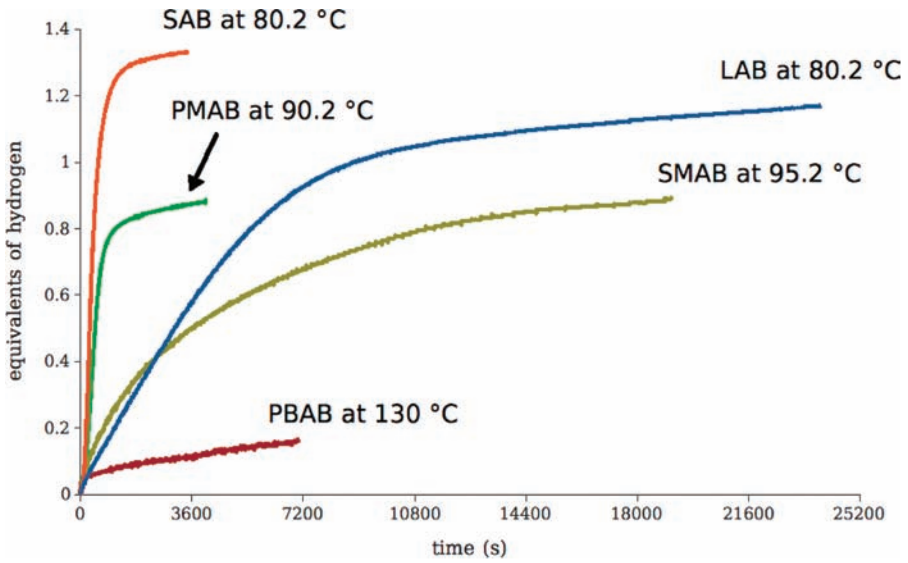

Figure 1. Plots of the equivalents of H_2 liberated upon heating LAB, SAB, SMAB, PMAB, and PBAB.

powdered samples were packed into a medium walled NMR tube that was shortened to 6−7 cm. The NMR tube was fitted to a #15 O-ring joint using a 3/8−1/4 in. Cajon Ultra-Torr reducing union and connected to the top of the buret system through a 180° connecting adaptor and Tygon tubing. Data points were collected every 4−8 s depending upon reaction time, and the NMR tubes were submerged into a digital temperature controller and circulator after 2 min of null data collection. The temperature of the oil was measured using a calibrated mercury thermometer with a precision of ±0.2 °C.

Results

The compounds LAB, SAB, LiNH(Me)BH_3 (LMAB), NaNH(Me)BH_3 (SMAB), KNH(Me)BH_3 (PMAB), and KNH(^{t}Bu)BH_3 (PBAB) were synthesized by addition of excess LiH, NaH, or KH to a THF solution of AB or alkyl aminoborane and allowing them to react for 30−70 min at ambient temperature (eq 1). The insoluble solids were removed by filtration. Removal of the volatiles under vacuum for 16−18 h gave LAB, SAB, SMAB, or PMAB as a THF free solid as characterized by ^{1}H NMR, ^{11}B NMR, and IR spectroscopies. A ^{1}H NMR spectrum of LMAB or PBAB in THF-d_8 shows a signal for THF-h_8 slightly downfield of the residual solvent signal even after the solid compound was subject to active vacuum for 24 h (LMAB) or 16 h (PBAB). The ^{1}H NMR spectrum of metal amidoboranes LAB, SAB, LMAB, SMAB, PMAB, and PBAB in THF-d_8 have in common a singlet corresponding to the NH group between −0.73 and −1.01 ppm, which moves downfield with increasing concentration of aminoborane starting material. Attempts to synthesize potassium amidoborane (PAB) of adequate purity were unsuccessful as PAB is not soluble in THF or 1,2-dimethoxyethane and could neither be separated from any unreacted KH nor characterized by NMR spectroscopy.

$$NH_2(R)BH_3 + MH \xrightarrow[THF]{-H_2} (THF)_nMNH(R)BH_3 \qquad (1)$$

$n \approx 0$
M = Li; R = H
M = Na; R = H, Me
M = K; R = Me

$n > 0$
M = Li; R = Me
M = K; R = ^{t}Bu

Table 1. Measured Times for the Release of 0.5 equiv of H_2 from LAB, SAB, SMAB, PMAB, and PBAB at Various Temperatures

compound		T (°C)	time to 0.5 equiv. H_2 (s)
$LiNH_2BH_3$	LAB	80.2	3070(30)
		85.2	698(8)
		90.2	138(6)
$NaNH_2BH_3$	SAB	70.0	2040(10)
		75.2	684(6)
		80.2	94(2)
NaNH(Me)BH_3	SMAB	95.2	3620(84)
		100.2	705(9)
KNH(Me)BH_3	PMAB	85.2	992(8)
		90.2	486(6)
KNH(^{t}Bu)BH_3	PBAB	130	negligible H_2 observed

The rate of decomposition of solid LAB, SAB, SMAB, and PMAB was measured by monitoring the volume of H_2 release over the course of the reaction as a function of temperature. The MAB (ca. 50 mg) was packed into a shortened medium walled NMR tube and fitted to an automated buret system.[22] The tube was submerged into a temperature controlled bath, and the volume of oil displaced in the buret was recorded until minimal change in volume was observed. Attempts to study the hydrogen release from LMAB were unsuccessful as the compound rapidly expanded out of the reaction vessel when heated at 80 °C. A plot of the equivalents of hydrogen released versus time for the thermolysis of LAB, SAB, SMAB, PMAB, and PBAB is shown in Figure 1. Relative rate data inferred from the measured time to release 0.5 equiv of H_2 at various temperatures is summarized in Table 1. The times to reach 0.5 equiv of H_2 are used to compare reaction rates as opposed to the rate constants because a single rate law that fits all the data for this complex solid state reaction could not be obtained. The temperatures studied were chosen such that the rate of H_2 released was within the detection limits of the buret system. Unfortunately, no one temperature gave reasonable reaction rates for all compounds studied. Unlike the SAB thermolysis reported previously,[16] no NH_3 was found in the gas released from LAB or SAB as measured by sampling the gas in the buret through a Drägar tube that measures NH_3 between 10 and 1000 ppm.

Analysis of the data on the reactivity of metal amidoboranes in Table 1 suggests several trends in reaction rates. First,

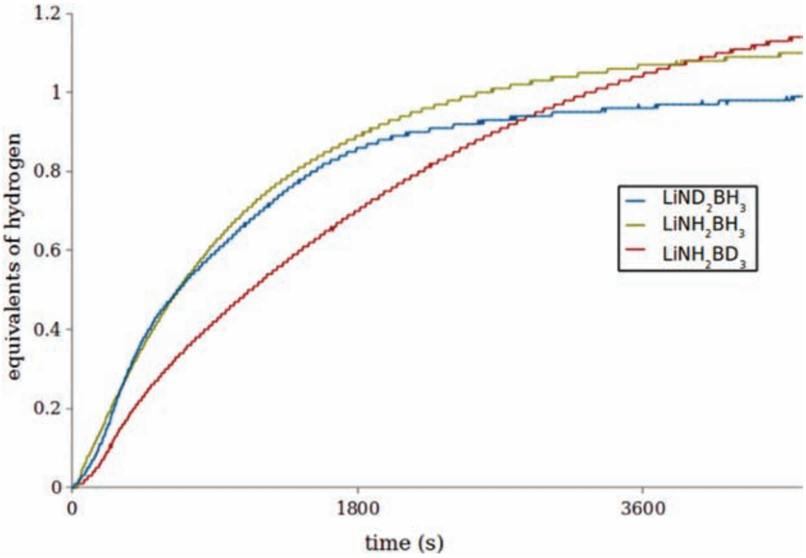

Figure 2. Plots of equivalents of H_2 released at 85.2 °C for LAB, $LiNH_2BD_3$, and $LiND_2BH_3$ showing that there is a normal KIE for $LiNH_2BD_3$ but none for $LiND_2BH_3$.

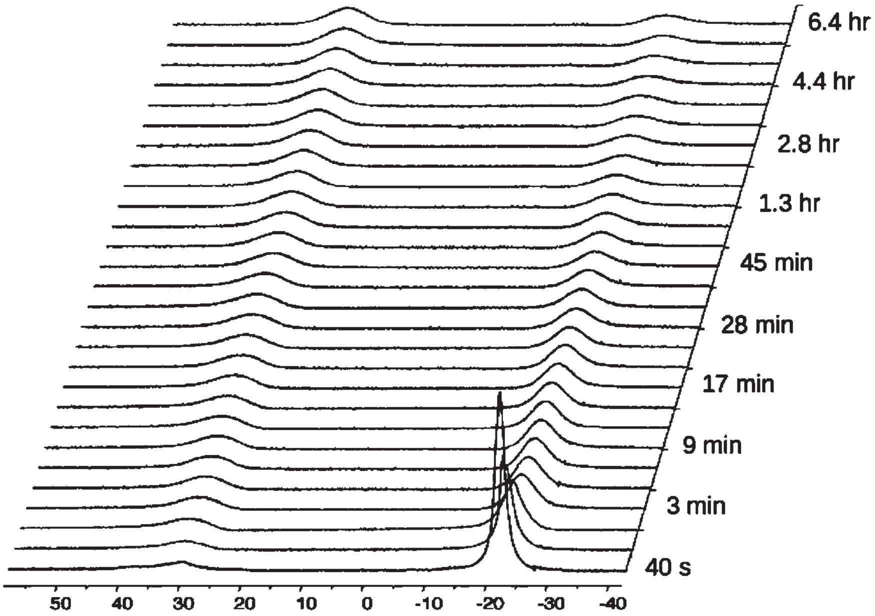

Figure 3. Solid state MAS ^{11}B NMR spectra of LAB at 90 °C and a frequency of 257 MHz.

there is a remarkably large temperature dependence on the rate of H_2 release from LAB, SAB, SMAB, and PMAB. Specifically, a 10 °C increase in temperature results in over 20-fold decrease in time to release 0.5 equiv of H_2 for LAB. Second, substitution of hydrogen for a bulkier alkyl group lowers the rate of hydrogen liberation. The compound SMAB at 95.2 °C releases hydrogen much slower than SAB at 80.2 °C and while PMAB reacts rapidly at 90.2 °C, PBAB does not release H_2 at an appreciable rate even at 130 °C.[23,24] And third, the metal ion has a notable effect on the rate of H_2 liberation with an apparent trend in reactivity of K > Na > Li.

The kinetic isotope effect (KIE) for the decomposition of LAB was determined by comparing the time required to release 0.5 equiv of hydrogen from $LiNH_2BH_3$ to $LiNH_2BD_3$ and $LiND_2BH_3$ at 85.2 °C (Figure 2). These plots show the rate of hydrogen release and time to release 0.5 equiv of H_2 is similar for both $LiNH_2BH_3$ (698 s) and $LiND_2BH_3$ (669 s) but slower for $LiNH_2BD_3$ (1125 s). This indicates that there is a normal KIE for hydrogen loss from $LiNH_2BD_3$ but no significant KIE for $LiND_2BH_3$ over the first half-life of the reaction. Although slower over the majority of the reaction, the equivalents of hydrogen lost from $LiNH_2BD_3$ crosses that for $LiNH_2BH_3$ and $LiND_2BH_3$ between 0.9 and 1 equiv. Apparently, the second equivalent of hydrogen is lost slowly for $LiNH_2BH_3$ and $LiND_2BH_3$ compared to $LiNH_2BD_3$.

To gain insight into the compounds formed during the release of H_2 from LAB, the compound was heated in a NMR spectrometer, and the reaction was followed by MAS ^{11}B NMR spectroscopy (Figure 3). At time zero and ambient temperature, the MAS ^{11}B NMR spectrum for LAB shows a single signal at −22 ppm assigned to the BH_3 group in the

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[23] A ^1H and ^{11}B NMR spectrum in THF-d_8 after heating PBAB at 130 °C showed only signals for PBAB and no THF-h_8.

[24] The H_2 quantity released for PBAB appears to start at 0.06 equiv. This is likely due to residual THF, which was not removed under vacuum at room temperature, being liberated upon heating.

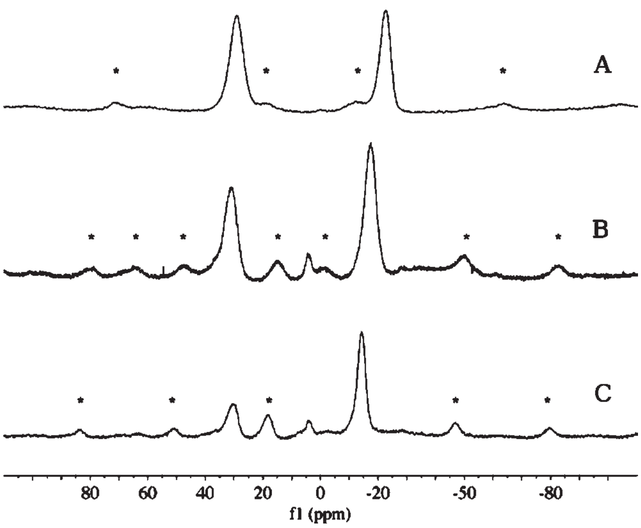
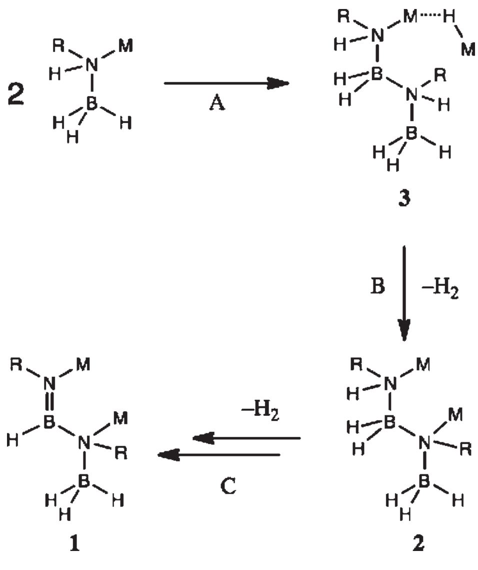


Figure 4. Solid state MAS ^{11}B NMR spectra of the thermolysis products of (A) SAB, (B) SMAB, and (C) PMAB at a frequency of 289 MHz. Spinning side bands are denoted with an asterisk.

starting material. Upon heating at 90(5) °C the MAS ^{11}B NMR spectrum shows broadening and loss of intensity of the peak at -22 ppm concurrent with the appearance of a new signal at $+29$ ppm (Figure 3). Similar signals at 30 ppm in the MAS ^{11}B NMR spectrum were observed as the product of thermolysis for SAB, SMAB, and PMAB (Figure 4). Although one might expect the initial product of H_2 loss from LAB to give a BH_2 containing species analogous to observations for the thermolysis of AB,[3] the chemical shift of 29 ppm for the product of LAB thermolysis is not consistent with a tetrahedral BH_2 linkage, which are expected between $+5$ and -15 ppm.[7,25,26] The absence of BH_2 signals in the ^{11}B NMR spectrum during the thermolysis of LAB suggests that any BH_2 species formed are rapidly consumed under the reaction conditions.

On the basis of the MAS ^{11}B NMR spectra of the decomposition products after loss of 1 equiv of hydrogen from solid LAB, SAB, SMAB, or PMAB, the major product formed is a species containing BH and BH_3 groups. One compound with these features is $MN(R){=}BHN(R)MBH_3$ (**1**) as shown in Scheme 1. However, **1** contains a potentially reactive BH_3 group and for R = H, there is a potentially reactive NHM (M = Li or Na) functionality as well. Therefore, the actual product in the solid state decomposition may be a mixture of compounds of varying length containing internal sp^2 BH and terminal BH_3 groups. For LAB and SAB, where R is H, the double bond in **1** may be on the internal B$-$N bond giving the compound $MNHBH{=}NMBH_3$ (**1′**). The MAS ^{11}B NMR spectra of the boron containing products of the thermolysis of SMAB and PMAB shows a minor signal at 4 ppm (Figure 4), which may be $MNH(R)BH_2N(R)MBH_3$ (**2**) (Scheme 1) or an unrelated side product such as $[MN(Me)BH_2]_2$. A complex similar to **1** was recently reported as the product of the thermolysis of $(nacnac)CaNH_2BH_3(THF)_2$ {nacnac = $[(2,6\text{-}^{i}Pr_2\text{-}C_6H_3)NC(Me)]_2CH$} in THF,[27] and **1** was also predicted as the product in computational studies of H_2 loss from LAB.[19,20]

Scheme 1



Discussion

The kinetics of H_2 liberation from MAB compounds and MAS ^{11}B NMR studies presented here are consistent with the mechanism shown in Scheme 1, which is similar to the L* pathway that was proposed as the mechanism with the lowest activation barrier in previous computational studies on LAB decomposition.[19,20] The trends in reaction rates of SAB > SMAB and PMAB > PBAB suggest a slower rate of H_2 release with increasing sterics, ruling out unimolecular loss of H_2. The observation of a normal KIE for $LiNH_2BD_3$ and absence of a KIE for $LiND_2BH_3$ can be explained if the N$-$H,D bond is broken after the rate determining step. In this case, **2** is formed by rate limiting loss of MH to give $MH\cdot MNH(R)BH_2N(R)MBH_3$ (**3**$\cdot$MH) as an intermediate as shown in reaction **A** in Scheme 1. Rapid deprotonation of **3** by MH would liberate H_2 and give **2** (reaction **B**). Since **2** was not observed in the MAS ^{11}B NMR spectra of LAB heated at 90(5) °C (Figure 3) nor in the products of thermolysis of SAB, (Figure 4), intermediate **2** decomposes rapidly giving H_2 and **1** (reaction **C**) as the observed product. The decomposition of **2** to give **1** likely proceeds by a similar mechanism as **A/B** but in an intramolecular fashion as **2** decomposition is faster than intermolecular reaction of LAB.

Although the mechanism shown in Scheme 1 is consistent with the computationally derived mechanism proposed previously for LAB dehydrogenation, the calculated activation barriers do not agree with the KIE results.[19,20] The KIE studies suggest that **3**$\cdot$MH is formed irreversibly, and reaction **B** has a lower barrier than reaction **A** in Scheme 1. However, calculations place the activation barrier for reaction **B** 7.3[20] or 4.59[19] kcal/mol above reaction **A**. This discrepancy may indicate that energies in the gas phase may not be the same as in the solid state for the dehydrogenation of LAB.

The mechanism of hydrogen release from MAB, *metal ion assisted hydride transfer*, involves the scission of a metal$-$nitrogen and a boron$-$hydride bond resulting in the formation of a metal$-$hydride bond, (Scheme 1, reaction A). As the ionic character of the metal cation increases, $Li^+ < Na^+ < K^+$, the strength of the corresponding metal$-$hydride bond

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(25) Dietrich, B. L.; Goldberg, K. I.; Heinekey, D. M.; Autrey, T.; Linehan, J. C. *Inorg. Chem.* **2008**, *47*, 8583.

(26) Miller, A. J. M.; Bercaw, J. E. *Chem. Commun.* **2010**, *46*, 1709.

(27) Spielmann, J.; Jansen, G.; Bandmann, H.; Harder, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6290.

decreases, and the strength of the metal—nitrogen bond decreases as well. A lower barrier for M—N bond scission, $K^+ < Na^+ < Li^+$ is consistent with the observed reactivity trend in MAB decomposition. Furthermore, the KIE studies suggest that scission of the B−H bond is involved in the rate limiting step. It is reasonable to expect that the nature of the metal cation may have an effect on the B−H bond strength in the corresponding MAB. This is observed in the BH stretching frequencies in the IR spectra of the compounds investigated. Specifically, the BH stretch in PMAB is red-shifted compared to SMAB and that the BH stretch in SAB is red-shifted compared to indicating a weakening of the BH bond. Increasing the ionic character of the metal cation in the series $K^+ > Na^+ > Li^+$ will result in an increasing negative charge on the nitrogen anion. This increase in ionic bonding character in MAB will in turn increase the N−B dative bond strength and provide a corresponding weakening of the B−H bond, which is consistent with the observed trend in reaction rates for the MAB compounds.

A comparison of the reactivity trends for hydrogen release from MABs with reactivity trends for hydrogen release from alkali metal borohydrides, MBH_4 ($M = K^+, Na^+, Li^+$), which have been study extensively,[1] provides a surprising result. For the same series of alkali metal cations the trend in the rate of MAB decomposition, $K^+ > Na^+ > Li^+$, is opposite to the trend in the rate of MBH_4 decomposition, which is $Li^+ > Na^+ > K^+$. A correlation between the decomposition temperature of MBH_4 and the Pauling electronegativity of the corresponding metal has been previously noted; however, it is appealing to discuss this trend in terms of chemical reactivity to put the decomposition of MBH_4 in context with the decomposition of MAB. While a M—N bond is not broken in the transition state leading to MBH_4 decomposition as is the case for MAB, it is chemically reasonable that a metal—hydride bond is formed in the decomposition of MBH_4, $MBH_4 \rightarrow MH + BH_3$, in analogy with MAB decomposition, $2\ MAB \rightarrow MH + MNH_2BH_2{-}NH_2BH_3$. The formation of MH from the decomposition reaction of MBH_4 is not unreasonable given the reports that the reverse reaction, $MH + BH_3 \rightarrow MBH_4$, is fast.[28] Research efforts to understand the reaction pathways involved in the initial stages of MBH_4 decomposition are underway.

In recent experimental studies on the thermolysis of SAB formed by ball milling, a significant quantity of NH_3, 0.18 mol NH_3/mol H_2 based on combustion analysis of the product, was observed as a side product.[16] However, the quantity of NH_3 formed during the thermolysis of LAB and SAB prepared in a THF solution is below the detection limits of the Drägar tube (10 ppm). Although the mechanism that leads to NH_3 formation during the thermolysis of MAB compounds is not known, one possibility is from small amounts of unreacted AB left during the synthesis of MAB compounds. In this case, the NH_3 would be liberated by S_n2 replacement of NH_3 in AB by $[NH_2BH_3]^-$. The larger quantity of NH_3 formed during the thermolysis of SAB synthesized by ball milling is likely due to a larger quantity of AB as ball milling is not expected to mix the reagents as well as solution phase synthesis. However, absorption of NH_3 by the tubing or reaction of NH_3 with the MAB thermolysis product may also contribute to the much lower NH_3 yields in our system.

The reactivity of MAB compounds is notably different than the reactivity of AB. AB has a significant induction period that has been attributed to the disruption of dihydrogen bonds and slow formation of $[NH_3BH_2NH_3]^+[BH_4]^-$ (DADB), which was proposed to be a key reactive species leading to H_2 liberation in AB.[3,29] In contrast, pure LAB, SAB, SMAB, and PMAB show no induction period at the temperatures studied and show no products that contain BH_4 groups by ^{11}B NMR spectroscopy at the temperatures studied. The difference in reaction mechanism is not surprising considering the structure of solid LAB differs significantly from that of AB. The BH---HN distance is much longer in LAB (2.249 Å) compared to that in AB [2.02(3) Å],[10,30] suggesting that the dihydrogen bonding network present in AB is not discernible for LAB. Instead there is a notable interaction between the metal cation, M^+, and the hydridic BH_3 groups on adjacent MAB molecules (Li−B distance = 2.50−2.69 Å).

Conclusion

The rates H_2 liberation and the products formed in the decomposition of a series of alkali metal amidoboranes were studied. On the basis of the observed trends in reaction rates of H > Me > ^{t}Bu, K > Na > Li, and the KIE, the mechanism of hydrogen release from MAB compounds was found to proceed through a bimolecular mechanism involving the intermediacy of a MH (M = Li, Na, or K). Also, the rate of H_2 release was shown to have large temperature dependence, which is a desired property in hydrogen storage materials. They must be thermally stable at 60 °C yet release H_2 at high rates near the operating temperature (85 °C) of a Polymer Electrolyte Membrane (PEM) fuel cell.[31] High rates of hydrogen release, while maintaining stability, may be accomplished by the judicious selection of an optimized cation and alkyl group pair on the nitrogen in metal amido boranes. The results presented here are expected to aid the rational development of a new generation of hydrogen storage materials.

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(28) Schlesinger, H. I.; Brown, H. C.; Hoekstra, H. R.; Rapp, L. R. *J. Am. Chem. Soc.* **1953**, *75*, 199.

(29) Shaw, W. J.; Karkamkar, A.; Howard, C. J.; Heldebrant, D. J.; Bowden, M.; Hess, N. J.; Linehan, J. C.; Autrey, T. *Energy Environ. Sci.* **2010**, *3*. DOI: 10.1039/b914338f.

(30) Klooster, W. T.; Koetzle, T. F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 6337.

(31) Rassat, S. D.; Aardahl, C.; Autrey, T.; Smith, R. S. *Energy Fuels* **2010**, *24*. DOI: 10.1021/ef901430a.