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Interaction of lithium hydride and ammonia borane in THF†

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The two-step reaction between LiH and NH_3BH_3 in THF leads to the production of more than 14 wt% of hydrogen at 40 °C.

The demand for high capacity on-board hydrogen storage systems for hydrogen fuel cell vehicles has stimulated tremendous efforts in materials research and development. Recent research efforts have focused on materials that are composed of hydrogen bound to light elements including borohydrides,[1] MOFs,[2] amide–hydride combination systems,[3–5] and ammonia borane.[6–9] With a hydrogen capacity of 19.6 wt%, ammonia borane (NH_3BH_3, AB for short) shows promise for hydrogen storage; however, decomposition gives a volatile side product, borazine, that will poison PEM fuel cells.[10] In addition, the desorption of hydrogen from this chemical hydride has a sufficient barrier to render the kinetics too slow at temperatures below 80 °C.[6] Our recent effort to modify the kinetics and thermodynamics of H_2 release from AB by replacing one H with an alkali metal, *i.e.*, alkali amidoboranes (MNH_2BH_3, M = Li and Na) provided some improvement.[11] These amidoboranes release large amount of hydrogen (exp. 10.9 wt%) with no measurable borazine formation, however, the kinetics for H_2 desorption are still insufficient. Previous investigations on hydrogen release from complex hydrides revealed that mass transport or mobility of the reacting species is one of the kinetic controlling factors.[12] The mobility of the species can be enhanced substantially upon dissolution in a solvent. In the present study we investigate the reactivity of AB dissolved in tetrahydrofuran (THF) with a suspension of LiH and observe the formation of $LiNH_2BH_3$ and enhanced reaction kinetics with an interesting dependence on AB concentration. More than 2.8 equiv. of hydrogen can be released in two steps at a temperature as low as 40 °C.

LiH and AB were purchased from Sigma-Aldrich with stated purities of 95% and 90%, respectively, and were used without further purification. THF was a Tedia product with a purity of 99.9%. Typically, a suspension was prepared by blending LiH (67.4 mg, 0.008 mol) and a solution of AB (275.6 mg, 0.008 mol) in THF (30 ml). A commercial Stirred Tank Reactor (STR) combined with a mass spectrometer was employed to evaluate hydrogen evolution from samples. Gaseous products were conducted to the mass spectrometer for analysis. Liquid NMR characterizations were performed on a Bruker AMX (500 MHz) Fourier transform NMR spectrometer. High-field solid NMR was conducted on a Varian Unity Inova console operating at 900 MHz ^1H frequency. Structural identifications were performed on a Bruker X-ray diffractometer equipped with an *in situ* cell.

Fig. 1 shows the time dependence of hydrogen release from the LiH–AB THF suspension (LiH/AB molar ratio is 1 : 1) at 40, 50 and 55 °C, respectively. Gas evolution from the suspension is a two-step process; each step has an induction period which can be effectively shortened through temperature increase. Hydrogen, the only detectable gaseous product, was calculated by the ideal equation of state and found to be *ca.* 1.0 and 1.8 equiv. for the first and second steps, respectively. Therefore, a total of *ca.* 2.8 equiv., or 14.3 wt% of hydrogen based upon added AB and LiH, were evolved at temperatures as low as 40 °C. Compared with the solid-state

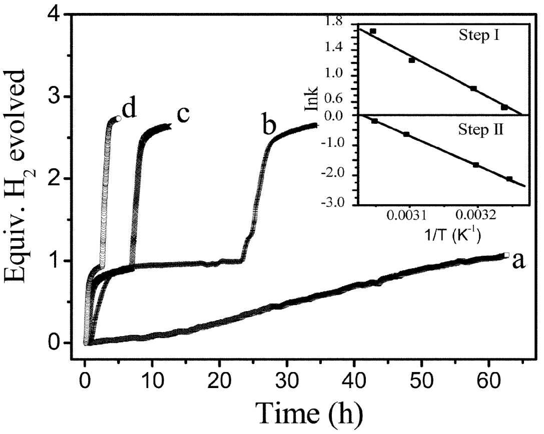

Fig. 1 Time dependence of hydrogen release from (a) AB–THF solution (0.27 M) at 55 °C and from the LiH–AB THF suspension (AB concentration is 0.27 M at temperatures of (b) 40 °C, (c) 50 °C, (d) 55 °C, respectively. The induction period for the first step ranges from 10 minutes to an hour depending on the operation temperatures. The inset shows the plot of ln*k versus* 1/*T* for Steps I and II. The slopes of the best-fit lines were used to determine activation energies by applying the Arrhenius equation.

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dehydrogenation of lithium amidoborane (the intermediate product of LiH + AB)[11] the THF-mediated dehydrogenation takes place at lower temperatures and with increased rates. The kinetic analyses of the dehydrogenation steps revealed that the first step follows a first-order rate law, with an apparent activation energy of 46.6 kJ mol^{-1} (Fig. 1). Increasing the amounts of AB and LiH resulted in an enhanced reaction rate (Fig. 2). In the second step, a nearly linear increase of hydrogen pressure was observed, indicating that the corresponding reaction followed a zero-order law in reactant ($LiNH_2BH_3$, see below) concentration, which is further supported by the observation of the independence of the reaction rate with the concentration of reactant (Fig. 2). Although further in-depth analyses are needed, it indicates that hydrogen release in the second step may not be directly from the initial reactant ($LiNH_2BH_3$). The rate constant measured at different temperatures gives apparent activation energy of 83.2 kJ mol^{-1} (Fig. 1). Decomposition of AB in THF alone was monitored at 55 °C for comparison. It is notable that only negligible amounts of hydrogen was liberated even after 15 h of reaction at the same concentrations.

Fig. 3 shows the ^{11}B NMR spectra of the pristine AB–THF and LiH–AB THF samples collected at different reaction intervals. The BH_2 resonance (at −11.0 ppm) of cyclotriborazane (CTB, $[NH_2BH_2]_3$), the BH resonance of borazine ($[NHBH]_3$, at 30.6 ppm) and the BH_3 (−24.3 ppm), BH_2 (−11.3 ppm) and BH (−5.4 ppm) resonances of *B*-(cyclodiborazanyl)aminoborohydride (BCDB)[13] were detected after heating the AB–THF solution at 55 °C, respectively. AB (BH_3 at −22.1 ppm) is still the dominant species after 63 hours of reaction. In contrast, when LiH was introduced to the AB–THF solution, BH, BH_2, BH_3, and BH_4 resonances with chemical shifts of −3.8, −8.3, −23.5 and −41.7 ppm, respectively, were developed in the first induction period. The peak at −41.7 ppm is close to where $LiBH_4$ is observed but the BH, BH_2, and BH_3 peaks at −3.8, −8.3 and −23.5 ppm are interesting new species that may arise from a minor side reaction(s). From Fig. 3A, we know that one of the decomposition products of AB in THF is *B*-(cyclodiborazanyl)-aminoborohydride (BCDB). If this species is formed in competition with $LiNH_2BH_3$ then a subsequent reaction with LiH to give lithium substitution on the NH_2 in the BCDB ring will result in the observed downfield chemical shift, *i.e.*, the BH (−5.4 to −3.8 ppm), the BH_2 (−11.3 to −8.3 ppm) and the BH_3 (−24.3 to −23.5 ppm). To confirm this, we added LiH to a solution of AB that was partially decomposed to BCDB and observed the corresponding chemical shifts (Fig. S1). After completion of the first dehydrogenation step, the solution contains no visible solid residue and the dominant ^{11}B signal shifts from −22.1 ppm (pristine AB) to −21.9 ppm (Fig. 3B). The ^{7}Li resonance also appears to shift from −0.1 ppm to 0.4 ppm (Fig. S2).

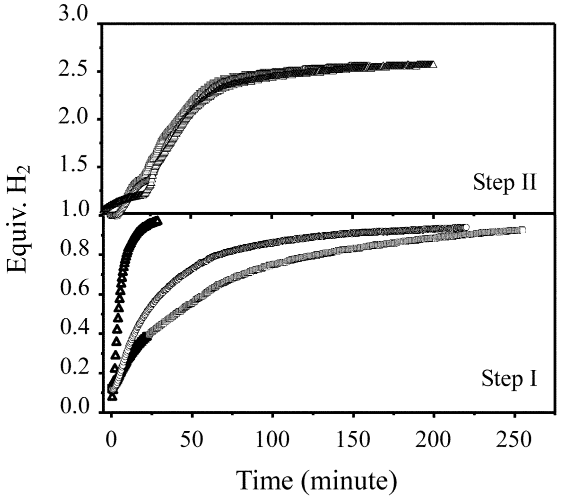

Fig. 2 Dependence of concentration on hydrogen release from the LiH–AB (1 : 1 molar ratio) THF suspension in Step I and Step II, respectively, at 50 °C. ☐ −0.4 M, ○ −0.53 M, △ −0.67 M.

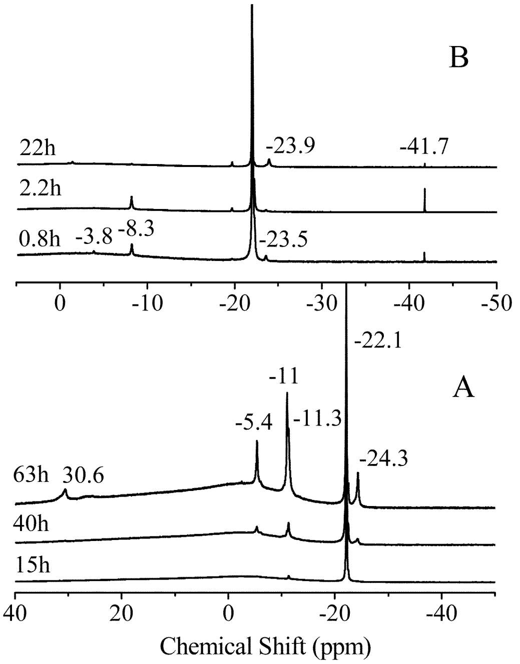

Fig. 3 ^{11}B NMR spectra of (A) NH_3BH_3 THF solution reacted at 55 °C and (B) LiH–NH_3BH_3 THF suspension at 40 °C collected at the indicated reaction times.

Removing the THF solvent at this point yields a polycrystalline white solid with a XRD pattern (Fig. S3) identical to lithium amidoborane, $LiNH_2BH_3$, synthesized by mechanical ball milling of AB and LiH (molar ratio 1 : 1).[12] This observation supports the chemical transformation as shown in eqn (1).

$$NH_3BH_3 + LiH \rightarrow LiNH_2BH_3 + H_2 \qquad (1)$$

One of the driving forces for this reaction pathway may come from an interaction between the $H^{\delta+}$ in NH_3 and $H^{\delta-}$ in LiH to form H_2.

To follow the hydrogen release in the second dehydrogenation step, the *in situ* ^{11}B NMR spectra of $LiNH_2BH_3$ in THF were monitored at 50 °C, as shown in Fig. 4. The linear decrease of BH_3 at −21.9 ppm (Fig. S4) corresponds directly with the linear increase of hydrogen pressure observed in the initial experiments shown for the second step in Fig. 1. The boron species at −23.9 ppm is present through the course of

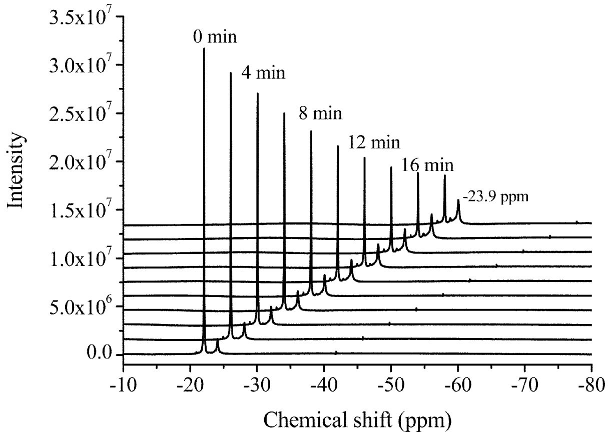

Fig. 4 *In situ* ^{11}B NMR spectra of $LiNH_2BH_3$ in THF recorded at 50 °C at intervals of 2 minutes.

the dehydrogenation; however, the intensity does not appear to change much with time while that of the $LiNH_2BH_3$ species is clearly decreasing. Although there is no authentic compound to identify this minor species, a quartet in the ^1H undecoupled spectra, it is likely the terminal BH_3 in a partially dehydrogenated dimerized $LiNH_2BH_3$, such as $Li_2[NHBHNHBH_3]$.[14] It also does not appear to release hydrogen. Further investigations are in progress to identify this species.

A white solid product(s) was precipitated from the solution, which is amorphous in nature. It is clear from the decrease in intensity of $LiNH_2BH_3$ that, as this species releases hydrogen, it converts to a THF-insoluble product. The difference in the weight of the starting material ($LiNH_2BH_3$) and the weight of the solid residue corresponds to the weight loss expected for the quantity of observed hydrogen (*ca.* 1.8 equiv. H_2). High field ^{11}B NMR measurements show that the major B species in the solid product has a planar $-B(N_2H)$ environment in addition to some residual BH_3 and BH_4 species (Fig. S5). Taking into consideration the purity of the starting materials and possible side reaction(s), the full 2.0 equiv. H_2 released from $LiNH_2BH_3$ can be represented by eqn (2).

$$LiNH_2BH_3 \rightarrow [LiBNH] + 2H_2 \qquad (2)$$

It is interesting to note that there are no BH_2 resonances observed in either the *in situ* NMR experiments or the residual solids, indicating that the 2nd equivalent of hydrogen is released concurrently with the release of the 1st equivalent of hydrogen. This observation is important as it suggests the presence of lithium in the PAB-like products is destabilizing, resulting in a low barrier pathway for release of the 2nd equivalent of hydrogen. This is very different from the observations for pristine AB, where several BH_2 species are observed and there is a higher barrier for release of the 2nd equivalent of H_2 from the resulting polyaminoborane (PAB) products.

The overall reaction of LiH and AB in THF can be expressed by eqn (3).

$$NH_3BH_3 + LiH \rightarrow LiNH_2BH_3 + H_2 \rightarrow [LiBNH] + 3H_2 \quad (3)$$

The THF-mediated reaction of AB in a suspension of LiH yields 2.8 equiv. or 14.3 wt% of H_2 from the mixture of LiH + AB. The high H_2 capacity and low temperatures for activation suggest that new approaches should be further investigated for this hydrogen storage complex. Although the solvent contributes extra weight to the system, an appropriate system design will minimize this side effect. From a scientific point of view, the overall dehydrogenation is rich in chemistry. Further investigations are needed to identify intermediates formed in the induction periods and to understand the dehydrogenation mechanism.

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