

Interaction between Lithium Amide and Lithium Hydride

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Pure lithium amide (LiNH_2) decomposes to lithium imide and ammonia at temperatures above 300 °C. Lithium hydride, on the other hand, liberates hydrogen at temperatures above 550 °C. By thoroughly mixing these two substances and conducting temperature-programmed desorption (TPD), we noticed that hydrogen was produced at temperatures around 150 °C. Combined thermogravimetric (TG), X-ray diffraction (XRD), and infrared (IR) analysis revealed that lithium amide would react with lithium hydride and convert to hydrogen and lithium imide (or Li-rich imide). The reaction mechanism was investigated by isotopic exchange.

Introduction

Amides of alkali metals have been extensively used in organic synthesis. Lithium amide (LiNH_2), which was first synthesized and identified in 1894,¹ was found to be a strong base and a powerful deprotonation reagent.^{2,3} In the alkylation of amines and condensation of esters, it even possesses superior performances to sodium amide.^{4,5} The monomer LiNH_2 has been proved theoretically and experimentally to be planar even through NH_3 is pyramidal.^{6,7} In LiNH_2 molecules, lithium atoms have much larger positive charges than the corresponding hydrogen atoms and the Coulombic repulsions involving Li are stronger; thus, the Li–N–H bond angle is wider than that of H–N–H.⁸ It should, however, be noted that the Li–N bond is not 100% ionic. As calculated by Würthwein et al.,⁹ the low-lying vacant Li p-orbitals can accept π -electrons fed back from N. The charge density in Li is calculated to be +0.458, which is considerably less than that in ionic Li. The overlap between Li p-orbital and N lone-pair p-orbital contributes significantly to the molecular geometry, i.e., inducing planarity in LiNH_2 and its oligomers.⁹ Such overlap is enhanced when more H is substituted by Li. Hinchliffe et al. pointed out that the Li–N bond in Li_2NH and Li_3N molecules should be far from being ideally ionic,¹⁰ as the Li charge density is even less in these molecules. So far only limited investigations have been done on the chemistry of LiNH_2 . LiNH_2 is very sensitive to moisture, it will convert to LiOH and NH_3 when it reacts with H_2O , and on heating in a vacuum, it will decompose to Li_2NH and NH_3 , etc.¹¹ The other substance concerned in this paper is lithium hydride (LiH), the simplest lithium compound with face-centered-cubic crystal structure. In contrast to the Li–N bond in LiNH_2 molecules, the Li–H bond is calculated to be highly ionic.¹² Li is positively charged and H is negatively charged. Besides BeH_2 , LiH possesses the highest H density (14.4 wt %) among other metal hydrides, and has been used as a H-generator.¹⁴ The Li–H bond is very strong so that its thermodissociation requires temperatures above 550 °C.¹³

In this paper, we report our recent investigations on the interaction between the above-mentioned compounds, i.e., LiNH_2 and LiH . Such an interaction was observed during our exploration of Li_3N as a new H_2 storage material.¹⁵ We noticed

that hydrogen can be reversibly stored in lithium nitride. The hydrogenated lithium nitride sample was found to be composed of lithium amide and hydride. This suggested that some chemical processes must be responsible for such a phenomenon. The results presented here are the first to appear in the literature, and it is hoped that they can provide new insight into the chemistry of metal amides and hydrides.

Experiments

Lithium amide, lithium hydride, and lithium deuteride are commercially available. Two LiNH_2 – LiH samples with LiNH_2/LiH molar ratios of 1/1 and 1/2 were prepared by thoroughly mixing corresponding amounts of LiNH_2 and LiH under inert atmosphere. The mixture of LiNH_2 and LiD was also prepared in the same manner. The temperature dependence of desorption/decomposition in Li–N–H samples was monitored by a homemade temperature-programmed-desorption (TPD), with purified Ar as a carrier gas) system with on-line mass spectrometer (MS) and gas chromatography (GC) attached. Approximately 300 mg of sample was loaded and tested each time. The temperature was increased at an interval of 1.0 °C/min. As ammonia was likely to be formed, the outlet gas was conducted into an ammonia reagent (which changed color when it came into contact with NH_3) to detect traces of NH_3 . Weight variation within desorption/decomposition processes was monitored by an intelligent gravimetric analyzer (IGA) provided by Hiden. The temperature was detected by a thermocouple placed slightly above the sample. Approximately 200 mg of sample was tested. The sample chamber was evacuated to 10^{-5} mbar, and the temperature was gradually increased to 195 °C and then kept constant until weight loss was almost undetectable. After this, the sample temperature was further increased to 430 °C. A Bruker D8-advance X-ray diffractometer (XRD) with Cu K α radiation was used to identify structural/compositional changes. The vibrations of the N–H bond in Li–N–H and Li–N–H(D) samples, before and after TPD treatments, were monitored by a Perkin Elmer FTIR-3000. As lithium amide and hydride are very sensitive to moisture, oxygen, and carbon dioxide, all sample preparation and loading (except in XRD and IGA measurements) were conducted within a glovebox.

Results and Discussion

Three samples, i.e., pure LiNH_2 , LiNH_2 – LiH (molar ratio of $\text{LiNH}_2/\text{LiH} = 1/1$), and LiNH_2 – 2LiH (1/2), were prepared

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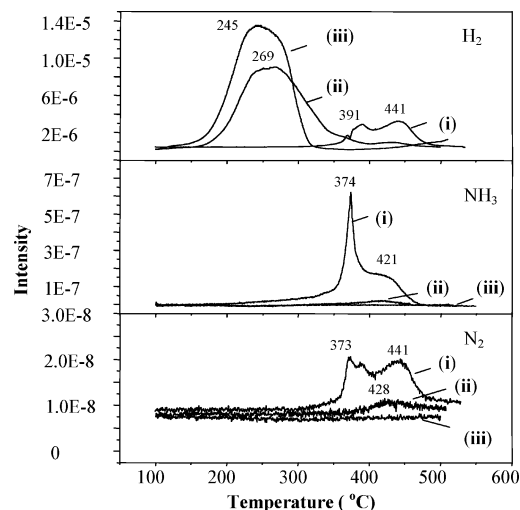


Figure 1. MS signals of H_2 , NH_3 , and N_2 . (i) Pure LiNH_2 sample; (ii) $\text{LiNH}_2\text{-LiH}$ sample; (iii) $\text{LiNH}_2\text{-2LiH}$ sample.

for TPD investigations. To identify all possible gaseous products, survey scans in the mass range of 1–80 amu were recorded over the above three samples in their TPD processes (temperature range from 100 to 500 °C) by an on-line mass spectrometer. The results revealed that H_2 , N_2 , and NH_3 were the possible gaseous products formed. Figure 1 shows H_2 , NH_3 , and N_2 signals detected in the TPD process. It can be seen that the decomposition of pure LiNH_2 begins around 200 °C; the decomposed product is ammonia, where the ammonia characteristic peak is around 374 °C (the melting point of LiNH_2) and has a shoulder around 421 °C (Figure 1(i)). At higher temperatures N_2 and H_2 appear and are enhanced (compared to NH_3), probably resulting from the subsequent decomposition of NH_3 which is favored at higher temperatures. When LiNH_2 is mixed with an equivalent amount of LiH , its TPD profile changes completely (Figure 1(ii)). H_2 instead of NH_3 appears around 150 °C which is ~ 150 °C lower than the onset temperature of LiNH_2 decomposition. Vigorous H_2 release starts out at temperatures above 170 °C and peaks around 270 °C. Only when the temperature rises above 350 °C can a very weak ammonia signal be detected. We noticed that if the temperature was kept long enough below 300 °C ammonia emission could be greatly minimized, indicating that the small amount of ammonia released might be mainly due to the decomposition of unreacted LiNH_2 . A much improved TPD profile for H release was observed in $\text{LiNH}_2\text{-2LiH}$ sample (Figure 1(iii)). H_2 signal shifts to a low-temperature region, its intensity enhanced (note that the same amount of LiNH_2 was used in the above three samples). No ammonia was detected in the whole period under investigation. In addition, after the end of the intensive H_2 release, a slow but continuous H signal started to appear at temperatures higher than 350 °C. Pure LiH , as mentioned in the Introduction, is hard to decompose: we could only observe a hydrogen signal at temperatures above 550 °C. As pure LiNH_2 decomposes to NH_3 at temperatures above 300 °C and the dissociation of LiH requires an even higher temperature, hydrogen released from $\text{LiNH}_2\text{-LiH}$ and $\text{LiNH}_2\text{-2LiH}$ samples should be due to the interaction between these two substances.

To quantitatively describe such an interaction, we measured the weight loss of the above three samples during their TPD treatment by IGA. As NH_3 is much heavier than H_2 , it is predicted that the weight loss from pure LiNH_2 sample should be greater than that from $\text{LiNH}_2\text{-LiH}$ and $\text{LiNH}_2\text{-2LiH}$

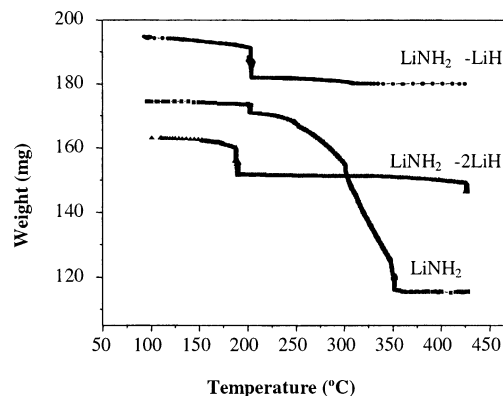


Figure 2. Weight loss from samples of pure LiNH_2 , $\text{LiNH}_2\text{-LiH}$, and $\text{LiNH}_2\text{-2LiH}$. Temperature was gradually increased to and kept at ~ 200 °C until chamber pressure dropped below 10^{-5} mbar, followed by a further increase to 430 °C.

samples. As the IGA measurements were performed under high vacuum, the reaction temperatures were lower than those under TPD conditions. Also, the temperature was deliberately kept at a given point for a certain period of time in the operation procedure to allow the completion of reaction. The temperature dependence of the weight loss may not match exactly with that in TPD. Slow weight loss from pure LiNH_2 began around 200 °C (Figure 2). Only 1.5 wt % loss was achieved after the sample was kept at 200 °C overnight. Quick loss was observed at temperatures above 250 °C. The total weight loss reached ~ 36 wt % after the decomposition stopped at 350 °C. The weight loss from $\text{LiNH}_2\text{-LiH}$ sample began around 100 °C and accelerated at temperatures above 150 °C. When the temperature was deliberately kept at 200 °C until the sample chamber pressure dropped below 10^{-5} mbar, ~ 6.0 wt % loss was noted. When the temperature was further increased to above 250 °C, additional 1.0 wt % loss was detected, which was probably due to the decomposition of unreacted or overmixed LiNH_2 . As the temperature further increased to 430 °C, no additional weight loss was observed. Following the same procedure, ~ 6.5 wt % loss in $\text{LiNH}_2\text{-2LiH}$ sample at temperatures around 190 °C was observed. However, further increase of the temperature to 300 °C did not result in additional weight loss. At temperatures above 320 °C, however, slow weight loss was detected. The total weight loss reached 9.6% after the sample was maintained at 430 °C until the chamber pressure dropped below 10^{-5} mbar.

Samples before and after TPD treatments were collected for XRD measurements. It was found that tetragonal LiNH_2 shifted to face-centered-cubic Li_2NH after being decomposed at 500 °C (Figure 3). This finding agrees well with that reported by Juza et al.¹¹ For $\text{LiNH}_2\text{-LiH}$ sample, the individual LiNH_2 and LiH phases disappeared after TPD treatment; the same structure, i.e., Li_2NH , has formed. As regards the $\text{LiNH}_2\text{-2LiH}$ sample, after undergoing TPD treatment at 320 °C, it was found that the LiNH_2 phase was completely vanished, and the residue was composed of greatly weakened LiH phase and a newly developed structure. This newly formed structure, inferred from its diffraction pattern, closely resembled that of Li_2NH , but all the diffraction peaks shifted slightly to higher positions, indicating a shrunken lattice (d spacing reduced from 2.92 to 2.89 Å). We tentatively assign this structure as $\text{Li}_x\text{NH}_{3-x}$, where $x > 2$. The further desorption of $\text{LiNH}_2\text{-2LiH}$ at 430 °C results in the appearance of a red-brown substance with strong diffraction peaks situated at 22.9° , 28.2° , 46.9° , and 49.9° . No LiH survived. By pattern matching, this red-brown substance is hexagonal Li_3N , which is usually formed by heating Li metal in N_2 atmosphere. Both Li_2NH and Li_3N would convert to

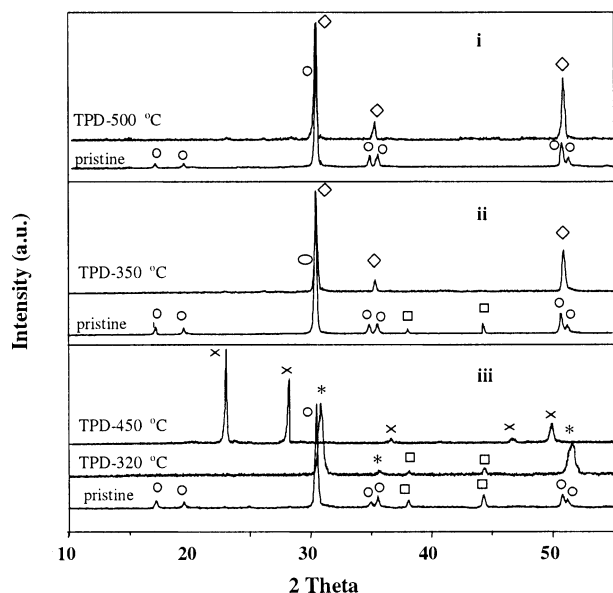


Figure 3. XRD patterns of samples before and after TPD treatments. (i) Pure LiNH₂ sample; (ii) LiNH₂-LiH sample; (iii) LiNH₂-2LiH sample. Peaks marked with ○ belong to LiNH₂; □, LiH; ◇, Li₂NH; ×, Li₃N; *, Li_xNH_{3-x}.

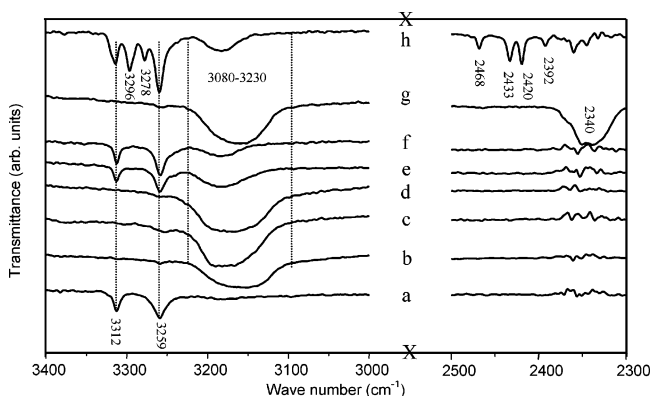


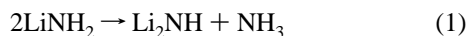
Figure 4. FTIR spectra of (a) pristine LiNH₂, (b) decomposed LiNH₂ sample, (c) dehydrogenated LiNH₂ + LiH, (d) dehydrogenated LiNH₂-2LiH sample, (e) partially hydrogenated Li₂NH sample, (f) further hydrogenated Li₂NH sample, (g) dehydrogenated LiNH₂-2LiD sample, and (h) rehydrogenated Li₂NH(D) sample.

LiNH₂ and LiH again after they reacted with hydrogen at temperatures above 150 °C.¹⁵

The composition of solid products was further analyzed by FTIR. Results show that (Figure 4a-d) the pristine LiNH₂ has two peaks at 3312 and 3259 cm⁻¹, corresponding to asymmetric and symmetric stretching of N-H bonds in LiNH₂ molecules.¹⁶ After decomposition at 500 °C, these two peaks are almost undetectable and a broad peak centered around 3160 cm⁻¹ develops. Similar features were also observed from the dehydrogenated LiNH₂-LiH and LiNH₂-2LiH (desorbed to 320 °C) samples. To confirm the nature of this broad peak, we subsequently hydrogenated the corresponding sample and noted the gradual weakening of the broad peak and regeneration of peaks at 3312 and 3259 cm⁻¹ with the enhancement of hydrogenation. We deduced that this broad peak should be ascribed to the N-H stretching in Li₂NH or Li_xNH_{3-x} molecules. As can be seen in the text below, the designed isotopic experiments further confirm that assignment. The broadening of IR peak may be related to some unknown chemical/structural

environments within Li-N-H crystal, which requires further investigation.

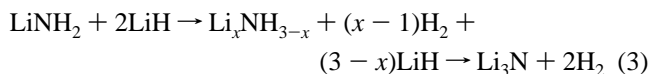
There are a limited number of known Li-N-H compounds. Those that could sustain high temperature (above 200 °C) are Li₂NH, LiNH₂, Li₃N, and Li₄NH. Li₄NH is a white substance with a unique lattice structure. It is synthesized by calcination of the mixture of Li₃N and LiH at 490 °C;¹⁷ thus, it is unlikely formed under present reaction conditions. The remaining Li₂NH and Li₃N have been well identified by XRD and FTIR. Together with the gaseous products, we could figure out the interaction between lithium amide and hydride (Table 1). Pure lithium amide mainly evolves NH₃ at elevated temperatures following the reaction of



The reaction heat ΔH is around 83.68 kJ/mol. The calculated weight loss from reaction 1 is about 37%, which agrees very well with that measured by IGA. However, when LiNH₂ is in contact with LiH, the reaction path changes completely. When 1 equiv of LiH is used, H₂ is released at a much lower temperature and imide is formed:



The reaction heat ΔH is around 45 kJ/mol. In this case, weight loss was calculated to be 6.5%, quite close to that measured by IGA. When 2 equiv of LiH was used, H₂ and imide-like structure formed at temperatures below 320 °C and H₂ and Li₃N formed at higher temperatures:

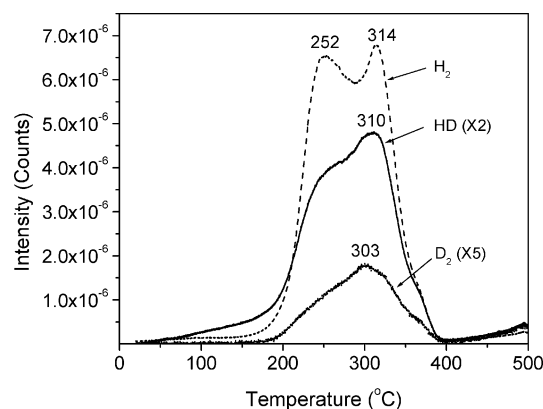


The reaction heat of the first stage is estimated to be much less than 83 kJ/mol; the overall reaction heat is around 161 kJ/mol. Again, the total weight loss calculated is close to that measured by IGA. This further supports the suggested reaction path. At temperatures below 320 °C, 6.5 wt % H₂ was released, which equals the theoretical value of 7.0 wt %. Thus, the intermediate structure Li_xNH_{3-x} has the formula Li_{2.2}NH_{0.8}. It might be treated as Li-rich imide. More detailed investigations are presently being carried out for the verification of that structure.

Compared with LiNH₂ decomposition, the reaction heat of the interaction of LiNH₂ and LiH is less; thus it takes place at relatively low temperatures. As mentioned in the Introduction, H in LiNH₂ is partially positively charged, but in LiH it is negatively charged. The redox of H^{δ+} and H^{δ-} to H₂ and simultaneously combination of N^{δ-} and Li^{δ+} (in LiH) are understandable. In this context, HD should be the main gaseous product if LiD is used instead of LiH in this interaction. To test this idea, we prepared LiNH₂-2LiD sample for TPD measurement. To our surprise, the desorbed gas is a mixture of H₂, HD, and D₂ (see Figure 5). The H₂ signal is very sensitive to temperature changes. Each gas has its own temperature dependence. As can be seen from Figure 5, selectivity to H₂ is higher at temperatures below 300 °C. Although it is hard to quantify the amount of H₂, HD, and D₂ released, it is quite certain that some of the deuterium atoms are retained in the Li-N-H structure. FTIR measurements show that, after desorption, LiNH₂ + 2LiD sample presents two broad peaks around 3160 and ~2340 cm⁻¹, respectively. Taking into account that the broad peak around 3160 cm⁻¹ is due to N-H stretching, then the approximately calculated value of N-D stretching of

TABLE 1: Summary of TPD, TG, and XRD Results

sample	peak max temp (°C)	gaseous products	solid products	TG weight loss (%)	calcd weight loss (%)
LiNH ₂	374	NH ₃ , N ₂ , H ₂	Li ₂ NH	~36	37
LiNH ₂ –LiH	269	H ₂	Li ₂ NH	~6.0	6.5
LiNH ₂ –2LiH	245	H ₂	Li _{2.2} NH _{0.8} /Li ₃ N ^a	6.5/9.6 ^a	7.0/10.3 ^a

^a After heating to 430 °C.**Figure 5.** MS signals of H₂, HD, and D₂ detected in TPD measurements over LiNH₂–2LiD sample.

the isotopomer Li₂ND is $\sim 2310\text{ cm}^{-1}$, corresponding well with that observed. This result not only confirms that there is deuterium retained in the Li–N–H structure, but also verifies that the broad peak centered at 3160 cm^{-1} could be assigned to N–H stretching in Li₂NH or Li_xNH_{3–x} molecules.

The prominent H₂ content in the gaseous phase and the large peak area of N–D stretching reveal the overwhelming D retention in the Li–N–H structure. Successive hydrogenation of Li₂NH(D) by normal H₂ results in the development of peaks at 3312, 3296, 3278, 3259, 2468, 2433, 2420, and 2392 cm^{-1} , respectively. Peaks at 3160 and 2340 cm^{-1} were greatly weakened. As mentioned above, peaks at 3312 and 3259 cm^{-1} belong to the asymmetric and symmetric N–H stretching in LiNH₂. Peaks at 3296 and 3278 cm^{-1} are due to N–H stretching in LiNHD molecules, where H occupies two different crystallographic sites.¹⁵ Also, N–D stretching in LiNHD molecules appears at 2433 and 2420 cm^{-1} . The interesting phenomenon is the appearance of peaks situated at 2468 and 2392 cm^{-1} , which account for N–D stretching in LiND₂ molecules. As normal H₂ was used as reaction gas, the formation of LiND₂ is unexpected. Together with the retention of D in Li–N–H

structure, H–D exchange seems involved. It should be noted that, in the interaction of LiNH₂ and LiD, D in LiD is negatively charged; the direct combination of D^{δ–} with N^{δ–} seems energetically unfavorable. Even if the heat of formation for Li₂–ND is greater than that for Li₂NH, a certain energy barrier should be overcome. Thus, we suggest that more investigations are needed for the mechanistic understanding.

In summary, LiNH₂ reacts with LiH at temperatures around 150 °C with hydrogen released. The solid products could be Li₂NH, Li-rich imide, and lithium nitride depending on the temperature and the molar ratio of LiNH₂/LiH.

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