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Regeneration of Lithium Aluminum Hydride

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Abstract: Lithium aluminum hydride ($LiAlH_4$) is a promising compound for hydrogen storage, with a high gravimetric and volumetric hydrogen density and a low decomposition temperature. Similar to other metastable hydrides, $LiAlH_4$ does not form by direct hydrogenation at reasonable hydrogen pressures; therefore, there is considerable interest in developing new routes to regenerate the material from the dehydrogenated products LiH and Al. Here we demonstrate a low-energy route to regenerate $LiAlH_4$ from LiH and Ti-catalyzed Al. The initial hydrogenation occurs in a tetrahydrofuran slurry and forms the adduct $LiAlH_4 \cdot 4THF$. The thermodynamics of this reversible reaction were investigated by measuring pressure−composition isotherms, and the free energy was found to be small and slightly negative ($\Delta G = -1.1$ kJ/mol H_2), suggesting an equilibrium hydrogen pressure of just under 1 bar at 300 K. We also demonstrate that the adduct $LiAlH_4 \cdot 4THF$ can be desolvated at low temperature to yield crystalline $LiAlH_4$.

Introduction

A cornerstone of the hydrogen economy is the hydrogen-powered vehicle that uses a compact, lightweight, and inexpensive hydrogen fuel cell system. One of the key challenges with using hydrogen for mobile applications is the poor volumetric energy density of conventional hydrogen storage media. Solid-state storage in metal hydrides or complex hydrides offers enhanced volumetric hydrogen densities, but these media often have poor gravimetric capacity (<4 wt %), due to the additional weight of the host, or release hydrogen at impractically high temperatures (>600 K). A class of metastable (kinetically stabilized) hydrides (e.g., AlH_3, $LiAlH_4$, $Mg(AlH_4)_2$) offers some new hope with high volumetric (>80 g of H_2/L) and gravimetric (≥8 wt %) energy densities and low decomposition temperatures (<423 K).[1] However, these materials typically have very high hydrogenation pressures (>1 kbar) and are generally prepared from costly organometallic reactions. Therefore, there is considerable interest in developing new, low-cost methods to regenerate these hydrides from the spent (hydrogen-depleted) material and hydrogen gas.

Lithium alanate does not form directly from LiH, Al, and H_2 in the solid state but is typically produced through an ethereal reaction between $AlCl_3$ and LiH.[2] This is a costly process since the majority (75%) of the lithium becomes trapped in a deep thermodynamic well as LiCl. Early attempts at producing a solvated form of $LiAlH_4$ directly were made by Classen[3] and Ashby[4] in diethyl ether (Et_2O), tetrahydrofuran (THF), and diglyme. Classen observed some conversion from LiH and activated Al in THF to form solvated $LiAlH_4$ at low pressure (30 bar) and temperature (308 K). Ashby demonstrated the formation of $LiAlH_4 \cdot 4THF$ at H_2 pressures of 350 bar and 393 K.[4] More recently, Wang et al. produced crystalline $LiAlH_4$ from LiH and Al using high-pressure ball milling followed by desolvation.[5]

In this effort we demonstrate a low-energy route to regenerate $LiAlH_4$ at low pressure without the need for mechanical milling. We employ a two-step regeneration process, which involves initially forming the hydride as a stabilized intermediate (e.g., hydride adduct), followed by adduct separation and hydride recovery. This procedure is similar to the regeneration procedure proposed for AlH_3, which involves the direct formation of an alane amine (AlH_3-NR_3), where alane is stabilized by a nitrogen bond, followed by decomposition and AlH_3 recovery.[6] Here the metastable $LiAlH_4$ is stabilized (using an oxygen bond) as a THF adduct ($LiAlH_4 \cdot 4THF$). The initial hydrogenation step was found to be reversible in the presence of a Ti catalyst,

$$LiH + Al + 3/2H_2 \overset{THF}{\rightleftharpoons} LiAlH_4 \cdot 4THF \qquad (1)$$

and the thermodynamics of this reaction were determined from pressure−composition isotherms. The full regeneration procedure involves direct hydrogenation (reaction 1), followed by a low-temperature desolvation step to recover crystalline $LiAlH_4$. We note that this two-step regeneration procedure may be broadly applicable to other metastable hydrides (e.g., $Mg(AlH_4)_2$).

Materials and Methods

The following materials were obtained from Aldrich: THF (99.9% anhydrous), Et_2O (99.7%), $AlCl_3$ (99.999%), $LiAlH_4$ (reagent grade 95%), LiH (99.4%), and $TiCl_3$ (99.999%). The hydrogen gas was obtained form Praxair (99.95%).

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A sample of 2 mol % Ti-catalyzed lithium alanate was prepared by mixing $LiAlH_4$ and $TiCl_3$ in THF in the reactor immediately before the cycling experiment. The Ti-catalyzed Al (henceforth denoted as Al*) was prepared by first synthesizing AlH_3 in an ethereal reaction between $LiAlH_4$ and $AlCl_3$.[7] The $TiCl_3$ catalyst was added to the diethyl ether solution and filtered to remove the LiCl precipitate. The filtrate (AlH_3 + Ti + Et_2O) was dried and decomposed under vacuum at 373 K for 1 h to remove the ether and decompose the hydride. The addition of Ti significantly destabilized the hydride (AlH_3), and decomposition occurred readily at room temperature using a concentration of 2 mol % (Ti/Al). Powder X-ray diffraction (XRD) of the dried and decomposed material showed no evidence of the hydride phase and confirmed that the final product was pure Al*. The uncatalyzed Al powder (for the control experiment) was prepared in exactly the same way, except no $TiCl_3$ was included in the synthesis and the decomposition was performed at a slightly higher temperature (413 K for 1.5 h).

Pressure−composition−temperature (PCT) measurements were performed in a 300 mL stainless steel pressure vessel (Parr Instruments) with a magnetic stirrer. The reactor vessel was equipped with a 70 bar pressure transducer and an internal thermocouple to monitor the temperature of the slurry. Samples were loaded into the reactor under an inert Ar atmosphere. In this study, two different hydrogen PCT experiments were performed, one initiated in the hydrogenated state ($LiAlH_4$) and the other in the dehydrogenated state (LiH + Al*). For experiments initiated in the hydrogenated state, the reactor was loaded with 1.0 g of $LiAlH_4$ (2.6×10^{-2} mol), 0.21 g of LiH (2.6×10^{-2} mol), and 0.081 g of $TiCl_3$ (5.3×10^{-4} mol). For experiments initiated in the dehydrongeated state, the reactor was loaded with 0.59 g of LiH (7.4×10^{-2} mol) and 1.0 g of Al* (3.7×10^{-2} mol). A similar experiment (starting in the dehydrogenated state) was performed with the same quantity of materials, but using uncatalyzed Al. An excess amount of LiH (2×) was used in all reactions. The starting materials were combined in the reactor along with 90 of mL THF, and the reactor was then sealed under Ar and attached to a gas-vacuum manifold. The reactor was flushed with H_2 gas three times to remove the blanket of inert gas. In the absence of any agitation, the solids remain on the bottom (not in suspension) and very little H_2 is dissolved into the liquid slurry. Therefore, the magnetic stirrer can be used as a switch to start and stop the hydrogenation reaction. Once the appropriate hydrogen pressure and reactor temperature were established, the reaction was initiated by agitating the system at a stirring rate of approximately 300 rpm.

Due to the high vapor pressure of THF ($P_{THF} = 1$ bar at $T =$ 339 K), it is difficult to add or remove H_2 from the reactor at the cycling temperature (>350 K). Therefore, H_2 aliquots were added (or removed) from the reactor at room temperature to avoid loss of THF vapor to the manifold. A typical cycle started with adding or removing an aliquot of H_2 at room temperature. The vessel was then closed to the manifold and heated back to the cycling temperature, and the reaction was initiated by agitating the slurry. After a constant pressure was reached (equilibrium), the reactor was cooled back to room temperature and the pressure was recorded. The H_2 uptake (or release) was determined by the room-temperature pressure difference between the start of the reaction (immediately after H_2 was introduced or removed) and the end of the reaction (after the reactor returned to equilibrium). In each step, the solubility of H_2 in THF was taken into account in determining the hydrogen concentration.

Fourier transform infrared (FTIR) spectroscopy was performed in transmission mode on a Perkin-Elmer Spectrum One spectrometer. The FTIR sample holders, which consisted of calcium fluoride (CaF_2) windows with a 0.1 mm Teflon spacer, were loaded and sealed in an Ar glovebox. A background spectrum from an empty cell was acquired (along with the sample) as a blank and subtracted from the sample spectrum to eliminate window artifacts. Powder XRD patterns were acquired with a Philips X-ray diffractometer using Cu Kα radiation. Powder XRD samples were mixed with silicon grease and sealed under Ar using a Kapton window.

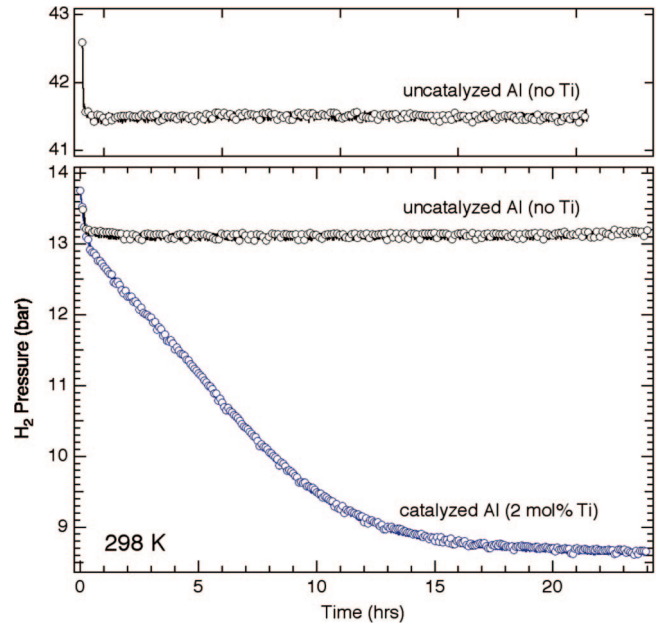

Figure 1. Room-temperature hydrogenation of LiH + Al* in THF (second cycle) immediately after introduction of hydrogen at ∼13 bar (lower plot). Attempted hydrogenation of a similar system using uncatalyzed Al at pressures of 13 (middle) and ∼42 bar (top) at 298 K. The pressure drop that occurs with the catalyzed Al* (bottom) is due to the formation of $LiAlH_4$·4THF and is complete after ∼15 h. The pressure is constant with uncatalyzed Al, indicating no hydrogenation even at high pressure (42 bar).

Results

The direct hydrogenation of LiH and Al in THF was attempted with pure Al and Ti-catalyzed Al* at room temperature (298 K). Figure 1 shows the reactor pressure plotted vs time at pressures of 13 and 42 bar for the uncatalyzed material and 13 bar for the catalyzed material (second cycle). Both samples exhibit a rapid pressure drop with the onset of agitation due to the dissolution of hydrogen in the solvent, which is complete after a few minutes. The uncatalyzed Al showed no evidence of hydrogenation at 13 bar (Figure , bottom) and 42 bar (Figure 1, top), while the catalyzed Al* exhibited a clear, continuous pressure drop (Figure 1, bottom), indicating hydrogen uptake by the slurry. The hydrogenation reaction was complete after ∼15 h, resulting in a total hydrogen uptake of about 70% (H/Al ≈ 2) of the theoretical value. Subsequent experiments at higher pressures and temperatures resulted in capacities closer to 90% (H/Al ≈ 2.7) of theoretical (H/Al = 3.0).

The hydrogenation reaction (1) is completely reversible in THF. The data shown in Figure 1 were obtained on the second cycle due to a long induction period (∼10 h) during the initial hydrogenation, which may be attributed to catalyst activation. Preliminary observations suggest that this induction period is shorter and possibly absent at elevated temperatures (≥363 K).

Upon reaching equilibrium ($\Delta P \rightarrow 0$) after hydrogenation, the reaction products (liquids and solids) were removed from the reactor and separated by filtration. X-ray diffraction of the solid products revealed some unreacted Al and LiH. The high

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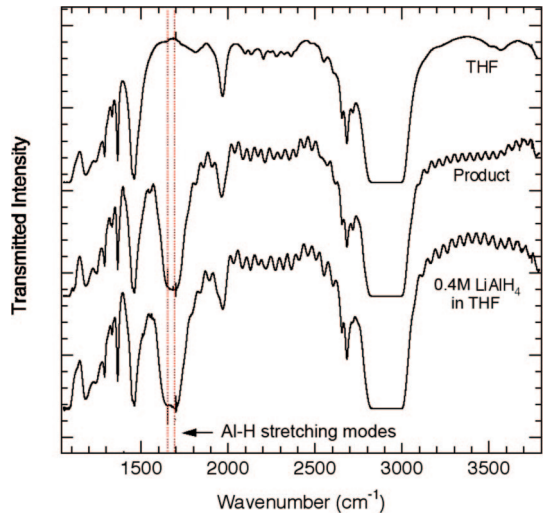

Figure 2. Fourier transform infrared spectra from 0.4 M $LiAlH_4$ in THF (standard solution), THF + reaction product, and pure THF. The peaks at 1693 and 1652 cm^{-1}, which correspond to the Al−H stretching modes, are clearly evident in the reaction product, suggesting the formation of alane or alanate species.

solubility of $LiAlH_4$ in THF (13 g per 100 g of THF[8]) ensures that the hydrogenated product remains in solution. Complete conversion of the Al to the alanate yields an expected 0.4 M solution of $LiAlH_4$ in THF. The liquid product was analyzed with FTIR and compared with spectra from pure THF and a standard solution of 0.4 M $LiAlH_4$ in THF (Figure 2). In THF-solvated $LiAlH_4$, the Al−H stretching modes[9] appear at 1693 and 1652 cm^{-1} and are clearly evident in the reaction product. The positions of the Al−H peaks are nearly identical to those that appear in the $LiAlH_4$ control sample. Since there are no THF peaks between 1500 and 1900 cm^{-1}, these peaks are solely attributed to the formation of an alane or alanate species in solution. The integrated intensity of the Al−H stretching modes indicates that the concentration of $LiAlH_4$ in the reaction product is ~0.4 M, suggesting that most of the Al was consumed.

A complete set of (de)hydrogenation PCT isotherms were performed at 353 and 363 K and are shown in Figure 3. The isotherms at 363 K were initiated in the dehydrogenated state (LiH + Al*), while the 353 K isotherms were initiated in the hydrogenated state ($LiAlH_4$). Since the composition of the starting material is well known, the dehydrogenation isotherm in Figure 3 is extrapolated (dashed line) back to the stoichiometric value (H/Al = 3.0). The pressures shown represent the actual equilibrium pressures measured in the reactor and include contributions from H_2 gas and the THF vapor pressure (1.56 bar at 353 K and 2.08 bar at 363 K). Equilibrium times varied somewhat but were typically around 1 day per point. The hydrogen concentrations were determined from the pressure change at each step (measured at room temperature), and corrections were made for the dissolution of H_2 in THF on the basis of Henry's law and the data of Gibanel et al.[10] It is interesting to note that a large hysteresis is observed on both cycles, which is 3−8 bar at a composition of H/Al ≈ 1.5.

Hydrogenation isotherms collected at 298, 353, and 363 K were used to construct a van't Hoff plot (Figure 4) using

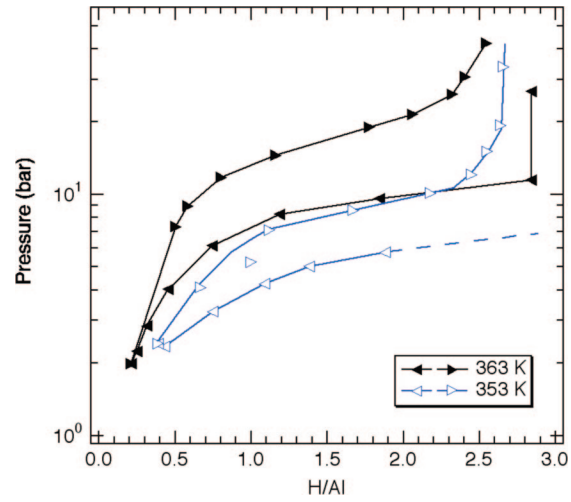

Figure 3. Equilibrium pressure−composition isotherms for reaction 1 in THF at 353 and 363 K. The markers indicated the reaction direction for hydrogenation (right-pointing symbols) and dehydrogenation (left-pointing symbols). The H_2 solubility in the solvent was taken into account when determining the H content (H/Al). The equilibrium pressures represent the actual pressure in the reactor and include contributions from H_2 and the THF vapor pressure.

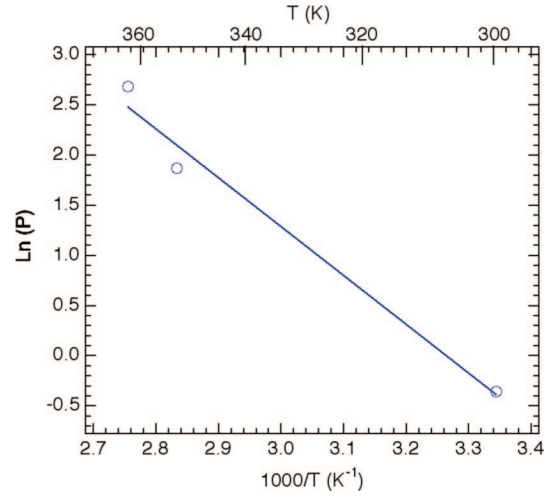

Figure 4. van't Hoff plot from hydrogenation isotherms. The isosteric formation enthalpy (ΔH_f = −40.4 kJ/mol) and entropy (ΔS_f = −132 J/mol·K) were determined from the slope and *y*-intercept, respectively.

equilibrium pressure values taken at the midpoint of hydrogenation (H/Al = 1.5). The thermodynamic parameters for the formation of $LiAlH_4$·4THF were determined from the van't Hoff equation:

$$\ln P(H_2) = (\Delta H_f/RT) - \Delta S/R \qquad (2)$$

Using this equation and the linear fit to the equilibrium pressures (Figure 4), the formation enthalpy was determined from the slope ($\Delta H_f = -40.4 \pm 5.7$ kJ/mol H_2) and the formation entropy was determined from the *y*-intercept ($\Delta S_f = -132 \pm 17$ J/mol H_2·K). Similar to metal hydride reactions, the entropy change is nearly equivalent to the entropy of the hydrogen gas (S_{H_2} = 131 J/mol·K). Using the thermodynamic equation $\Delta G = \Delta H - T\Delta S$, the free energy for this reaction is $\Delta G = -1.1$ kJ/mol H_2.

In addition to the PCT cycling measurements, experiments were also performed to prepare pure crystalline $LiAlH_4$ directly from LiH and Al by hydrogenation in THF followed by

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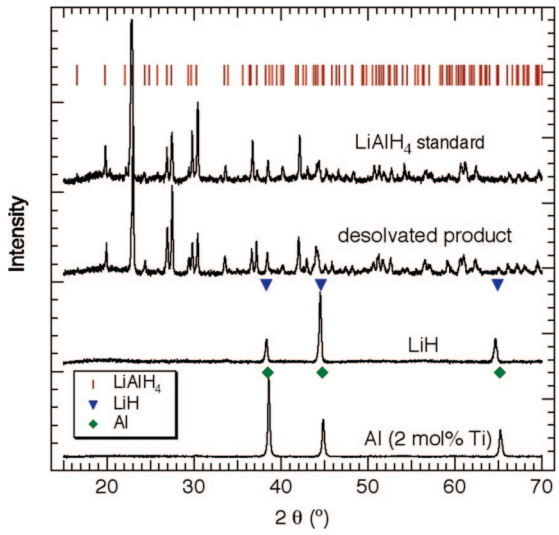

Figure 5. Powder X-ray diffraction patterns from the reactants, catalyzed Al* and LiH, the desolvated product and a standard of $LiAlH_4$.

desolvation. In this experiment, the reactor was prepared with LiH and Al* similar to the PCT measurements, starting in the dehydrogenated state. After direct hydrogenation in THF, the liquid $LiAlH_4$/THF solution was filtered to remove any residual LiH and unreacted Al*. The $LiAlH_4$/THF solution was initially dried in a flask under vacuum at room temperature to remove excess THF. The remaining $LiAlH_4$/THF solvate was transferred to a rotary furnace and desolvated by heating to 333 K for approximately 4 h under vacuum. It is important to note that $LiAlH_4$ is destabilized in the presence of a transition metal catalyst, and some residual Ti may remain in the hydrogenated product after filtration. Therefore, the desolvation temperature was kept low ($\leq$333 K) to avoid decomposition of the alanate.

The final desolvated product consisted of a dark gray powder, which was characterized by powder XRD. Figure 5 shows a complete set of powder XRD patterns from the reactants LiH and Al*, the desolvated reaction product, and a standard of $LiAlH_4$. The XRD profile from the desolvated product is nearly identical to that of the $LiAlH_4$ standard, with no indication of the reaction precursors (LiH and Al) and no evidence of any decomposition products (Li_3AlH_6, LiH, and Al). This suggests that the desolvation was successful in removing much of the THF with little or no loss of hydrogen from the alanate.

Discussion

Solid-state decomposition of the tetrahydride $LiAlH_4$ is known to occur in a two-step process, going first to the hexahydride and then to the binary hydride as shown in the following reactions:

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \rightarrow 3LiH + 3Al + 9/2\,H_2 \qquad (3)$$

It has been suggested that the (de)hydrogenation reactions of $LiAlH_4$ in THF follow a different pathway and bypass the hexahydride (Li_3AlH_6) phase.[11] Since Li_3AlH_6 is completely insoluble in THF, any of this phase formed should immediately precipitate out of solution. Based on the reactant concentrations used in these experiments (2LiH + Al) and the amount of hydrogen uptake, the hexahydride phase should be the dominant solid reaction product after hydrogenation if the formation of this phase occurs in THF. However, XRD analysis of the reaction products at both ends of the (de)hydrogenation cycle and after partial hydrogenation revealed no evidence of the Li_3AlH_6 phase. Therefore, we conclude that the reversible (de)hydrogenation reaction cycles between LiH + Al and $LiAlH_4$, as shown in reaction 1. The strong heat of solvation, which makes the direct formation of $LiALH_4$ possible at low pressure (in THF), is much greater than the small thermodynamic driving force to form crystalline Li_3AlH_6.[11]

The (de)hydrogenation isotherms of Figure 3 were acquired near equilibrium, but unlike those of most metal hydrides[12] and some organic−metal hydride systems,[6] the isotherms exhibit a large hysteresis and sloping plateau. These characteristics may be attributed to the slow rate of hydrogen solubility in the THF solvent, especially at pressures near equilibrium, where the driving force for hydrogen dissolution is extremely low. In addition, since LiH hydride is nearly insoluble in THF and hydrogenation (reaction 1) requires the interaction between two solids (LiH and Al*), a liquid (THF), and a gas (H_2), the slow reaction kinetics are not surprising.

What is the nature of $LiAlH_4$ in the THF solution, and why does the alanate form in THF but not in Et_2O? Ebulloscopic and conductometric studies by Ashby et al.[13,14] and Shirk and Shriver[15] have shown that the state of the cation (Li^+) and the anion (AlH_4^-) in the polar THF solvent is concentration dependent, consisting of solvent-separated ion pairs and free ions at low concentrations (<0.1 M) and larger aggregates at high concentrations, with primarily triple ions at concentrations >0.4 M. The oxygen in THF binds strongly with the lithium ion, forming a cage of four THF molecules surrounding a single lithium ion.[13] A more recent study from Bikiel et al. found that the four-fold coordinated lithium picture was valid with Li−Al distances greater than 3.5 Å.[16] Unlike the concentration-dependent solvent-separated ions in THF, the ions in a $LiAlH_4$/Et_2O solution are concentration independent and form only contact ions.[14] This is an important distinction, because there is an estimated 32 kJ/mol difference in the formation enthalpy for solvent-separated ions (in THF) over contact ions (in Et_2O)[5,13] due to the reduced interaction of the oxygen with the lithium ion. The large enthalpy difference makes the direct hydrogenation of LiH and Al (reaction 4) in THF much more favorable and explains why the conversion of LiH to $LiAlH_4$ in diethyl ether occurs in only small quantities (~10%).[4]

The PCT isotherms (Figure 3) and the van't Hoff plot (Figure 4) yield a free energy of formation of $\Delta G = -1.1$ kJ/mol H_2 (−1.65 kJ/mol $LiAlH_4$) for $LiAlH_4 \cdot 4THF$ (reaction 1), suggesting that the equilibrium pressure is just under 1 bar at room temperature. This implies that hydrogenation will occur at H_2 pressures >1 bar at 300 K and, equivalently, dehydrogenation will occur at temperatures just above 300 K at 1 bar pressure. As a comparison, the free energy to form unsolvated $LiAlH_4$ directly from LiH, Al, and H_2 gas (no THF) can be approximated from the decompositon energy, $\Delta G_{decomp} = 23$ kJ/mol H_2 (34 kJ/mol $LiAlH_4$),[17] giving an equilibrium pressure of around 10.9 kbar at 300 K. If we consider the direct formation of $LiAlH_4$ starting from the hexahydride phase (Li_3AlH_6 rather than LiH),

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the estimated free energy is somewhat lower, $\Delta G_{decomp} = 19$ kJ/mol H_2 (28 kJ/mol $LiAlH_4$),[17] but the equilibrium pressure is still extremely high, 2.2 kbar at 300 K. Regardless of the reaction precursors (LiH or Li_3AlH_6), the direct formation of $LiAlH_4$ in the solid state requires kilobars of H_2 pressure, whereas direct hydrogenation in THF requires ~1 bar pressure at room temperature.

The pure crystalline $LiAlH_4$ is metastable at ambient pressure and temperature (similar to AlH_3),[18] whereas the THF-solvated phase is stable. The results of our thermodynamic study suggest that the difference in free energy between $LiAlH_4$ and $LiAlH_4 \cdot 4THF$ is approximately 35 kJ/mol $LiAlH_4$. It is interesting to note that this difference in free energy is approximately equal to the enthalpy difference between solvent-separated ions and contact ions (32 kJ/mol $LiAlH_4$).[5] It should also be noted that the direct formation of $LiAlH_4$ also occurs in diglyme,[4] which forms an even stronger solvate with $LiAlH_4$ and therefore may form at even lower pressures.

Hydrogen Storage Applications

The direct formation of $LiAlH_4$ from LiH and Al in THF has broad implications in organic synthesis but may be especially important for hydrogen storage applications. $LiAlH_4$ is a metastable hydride (similar to AlH_3 and $Mg(AlH_4)_2$)[1] with an extremely high useful gravimetric and volumetric hydrogen density (7.9 wt % and 78 g of H_2/L) and a low decomposition temperature (393 K).[19] Since these hydrides typically require impractically high pressures to re-form from the spent material, there is considerable interest in the development of low-energy regeneration methods. The direct hydrogenation of LiH and Al in THF is a potentially useful regeneration step for $LiAlH_4$ if the energy costs are kept low and the solvent can be easily removed from the hydride. A similar regeneration approach by Wang et al. demonstrated this concept in a process using high-pressure, high-energy ball milling.[5] In the approach discussed here, the hydrogenation reaction requires minimal agitation (stirring at 300 rpm) and occurs at low pressure.

It is likely that the challenge of removing the THF from the alanate can also be accomplished with minimal energy cost. In fact, Ashby et al. have demonstrated that 95−97% of the THF can be removed from $LiAlH_4 \cdot THF$.[4] Although some energy is required to separate the solvate species, this process occurs at low temperature (333 K), and therefore only low-grade heat is required. The full procedure for regenerating $LiAlH_4$ from LiH and Al consists of a solution-based hydrogenation followed by desolvation, as shown below:

$$LiH + Al^* + 3/2\,H_2 \xrightarrow{THF} LiAlH_4 \cdot 4THF \xrightarrow[vacuum]{333\ K} LiAlH_4 + 4THF\uparrow \quad (4)$$

Replacing THF with another solvent is unlikely to improve this process, since a weakly bound solvent like Et_2O produces very low yields (~10%) and a strongly bound solvent like diglyme[4] is likely to be much more difficult to separate than $LiAlH_4 \cdot 4THF$.

The amount of Ti in the regenerated product is expected to be small but has not been well characterized. The Ti concentration is of concern for the desolvation process since any residual Ti will likely destabilize the alanate, making it more difficult to remove the THF without losing H_2. A simple filtration step, where the solids are separated from the $LiAlH_4$/THF solution, may not be sufficient to remove all of the Ti. Although this study clearly demonstrates that $LiAlH_4$ can be recovered from the solvent, possibly with some residual Ti, a better understanding of the concentration and character of the Ti catalyst before, during, and after hydrogenation is necessary.

The formation of $LiAlH_4$ in THF may also be a useful step in the regeneration of other Al-based kinetically stabilized hydrides, such as the high capacity hydride AlH_3. Although this is the subject of an ongoing effort, the regeneration concept is simply an extension of what is presented here for $LiAlH_4$. Recent efforts to regenerate AlH_3 have focused on forming amine alanes from an amine (NR_3) and Al* powder in solution.[6] Although the direct formation of the amine alane works well with amines that form a strong Al−N bond (e.g., $AlH_3 \cdot TEA$), it may be possible to form a less-stable amine alane by a reaction with $LiAlH_4$, as shown below:

$$3LiAlH_4 + 2NR_3 \rightarrow 2NR_3 \cdot AlH_3 + Li_3AlH_6 \quad (5)$$

Amine alanes with a weak Al−N bond are desirable because they are easily separated to recover pure AlH_3. When coupled with the regeneration reaction of $LiAlH_4$, the complete regeneration scheme for AlH_3 can be envisioned as shown below:

$$LiH + Al + 3/2\,H_2 \rightarrow LiAlH_4 \cdot 4THF + 2NR_3 \rightarrow 2NR_3 \cdot AlH_3 + Li_3AlH_6\downarrow \rightarrow AlH_3 + 2NR_3\uparrow \quad (6)$$

where NR_3 represents an amine that forms a weak Al−N bond, such as triethylamine (NEt_3). It is likely that other metstable alanates (e.g., $Mg(AlH_4)_2$) may also form at low pressures in solution. The challenge is finding a solvent with a heat of solvation strong enough to form the solvated alanate at low pressure but weak enough that it can be separated without decomposing the hydride. This will be especially challenging for $Mg(AlH_4)_2$ and $Ca(AlH_4)_2$ since these compounds are much less stable (more positive ΔG) than $LiAlH_4$.

Conclusion

A simple, low-energy procedure to regenerate $LiAlH_4$ from LiH and Al* powder was demonstrated in THF at low pressures and temperatures. The formation of the $LiAlH_4 \cdot 4THF$ is completely reversible in the presence of a Ti catalyst, with a formation energy of $\Delta G = -1.1$ kJ/mol H_2 and an equilibrium pressure of just under 1 bar at room temperature. Desolvation of the adduct $LiAlH_4 \cdot 4THF$ occurs under mild conditions (333 K for 3−5 h) to yield crystalline $LiAlH_4$. We demonstrate that the procedure of forming a stable intermediate adduct ($LiAlH_4 \cdot 4THF$) followed by adduct breakup (desolvation) can be used to regenerate lithium alanate. A similar procedure may be useful to regenerate other kinetically stabilized hydrides, or $LiAlH_4$ regeneration may be a single step in other, more complex reactions to regenerate other metastable, high-capacity hydrides, such as AlH_3.

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