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The reversible synthesis of bis(quinuclidine) alane

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ABSTRACT

Aluminum hydride is a material that is well known for its high gravimetric and volumetric hydrogen densities and thus is an attractive hydrogen storage compound; however, it is thermodynamically unstable at room temperature requiring 7×10^3 bar pressure to reform the hydride from Al and H_2. An alternate method of AlH_3 formation is possible using a reversible organometallic synthesis employing catalyzed Al powder, H_2, and quinuclidine, or another tertiary amine, as an intermediate step. Additionally, many tertiary amines are known to react directly with AlH_3 to form adducts. Previous work indicates that two polymorphs of quinuclidine alane exist, formed using an irreversible process that requires expensive starting materials (e.g. $LiAlH_4$). The conditions of reversible adduct formation are detailed herein, as well as an analysis of quinuclidine alane by Fourier transform infrared spectroscopy and X-ray diffraction.

1. Introduction

Metal hydrides with high gravimetric and volumetric hydrogen densities are potentially useful compounds in fuel cell applications and the hydrogenation of organic compounds. One of the more promising options for solid-state hydrogen storage is AlH_3, which is a metal hydride with 10.1 wt.% hydrogen, a density of 1.48 g/ml, that decomposes at <100 °C. Since AlH_3 is thermodynamically unstable at room temperature [1,2], its primary limitation is the high pressure (7×10^3 bar at 300 K) required to form the hydride from Al and H_2 [3].

Following the pioneering work of Ashby [4], AlH_3 adducts of the tertiary amines were recently prepared using triethylenediamine (TEDA) [5] and dimethylethylamine (DMEA) [6] via direct reaction with catalyzed Al (hereafter written as Al*) in a THF slurry at room temperature under moderate hydrogen pressure. The direct synthesis of alanates and alane adducts from activated or catalyzed aluminum powder and hydrogen gas (under pressure) was originally performed by Ashby [4,7] and Clasen [8] and more recently by Bogdanovic and Schwickardi [9]. This is part of a continuing effort to regenerate aluminum hydride using a simple regeneration procedure that involves the formation of a ligand-stabilized adduct followed by separation. This process was also used to regenerate $LiAlH_4$ from LiH, Al*, and H_2 using a THF ligand [10,11], and AlH_3 from dimethylethylamine alane [6]. Here we describe the synthesis and characterization of bis(quinuclidine) alane via the direct and reversible reaction [1], shown below:

$$Al* + 2(N(CH_2CH_2)_3CH) + 3/2H_2 \leftrightarrow AlH_3(N(CH_2CH_2)_3CH)_2 \quad (1)$$

The theoretical, reversible hydrogen capacity of bis(quinuclidine) alane is 1.19 wt.% (H/Al = 3.0).

Quinuclidine alane is known to form both a 1:1 complex (quinuclidine/AlH_3) and 2:1 (2 quinuclidine/AlH_3) bis complex. Greenwood and Thomas used $LiAlH_4$ to prepare both adducts, and noted that the formation of a particular complex was dependent upon the ratio of Al to quinuclidine in the precursors [12]. We prepared standards of both complexes (1:1 and 2:1) by a direct reaction of quinuclidine with AlH_3 in THF. A depiction of each complex is shown in Fig. 1.

2. Experimental methods and materials

Hydrogen (99.95% pure) was purchased from Praxair Corporation and the following materials were obtained from Sigma–Aldrich: THF (tetrahydrofuran 99.9% anhydrous), diethyl ether (99.7% anhydrous), toluene (99.8% anhydrous), quinuclidine, $C_7H_{14}N$ (97% pure), $LiAlH_4$ (reagent grade 95%) and $TiCl_3$ (99.995%). The catalyzed aluminum, Al*, contains <2 mol% titanium and its preparation was described in detail previously [5]. Powder X-ray diffraction was performed with a Philips X-ray diffractometer using Cu Kα radiation. Fourier Transform Infrared (FTIR) spectra of liquid and solid phases were acquired on a Perkin–Elmer Spectrum One Spectrometer.

The synthesis of bis(quinuclidine) alane via direct hydrogenation of catalyzed aluminum was carried out in a stirred 300 ml stainless steel reactor from Parr Instruments. The amount of reacted hydrogen was determined from the pressure change in the reactor after correcting for the dissolution of H_2 in the solvent. The reactor was charged with 5 g (4.5×10^{-2} mol) of quinuclidine, 1 g (3.7×10^{-2} mol) of Al* (quinuclidine to Al mol ratio of 1.24), and 100 ml of THF, and then sealed in an argon-filled glove box. The reactor was removed from the box, attached to a gas/vacuum man-

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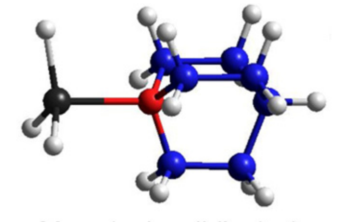
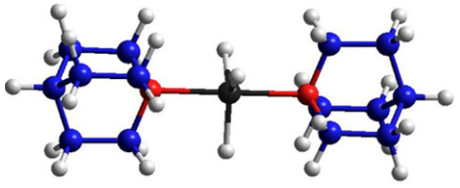


Mono(quinuclidine) alane



Bis(quinuclidine) alane

Fig. 1. Depiction of the molecular structure of the mono and bis complexes of quinuclidine alane.

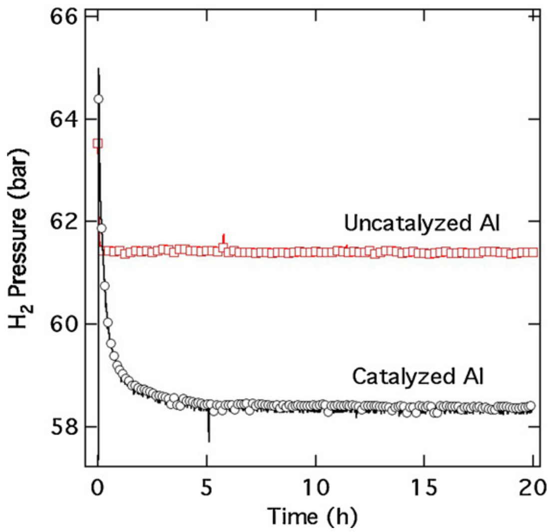


Fig. 2. Reactor pressure during hydrogenation of catalyzed Al^* and quinuclidine to form quinuclidine alane. A similar experiment using uncatalyzed Al showed no decrease in pressure indicating no hydrogenation.

ifold, and evacuated. Hydrogen gas was added to the reactor at pressures ranging from 60 to 70 bar after which stirring was initiated to ensure the aluminum was kept in suspension and well mixed with the amine. The stirring is also essential for H_2 dissolution since the diffusion of the H_2 molecule in the still liquid is slow [13,14].

The hydrogenated product, bis(quinuclidine) alane, is soluble in THF and was recovered from solution by first decanting the reactor contents in the glove box and then filtering off the unreacted Al^* using a 0.7 μm glass fiber filter combined with a diatomite filter aid. The filtrate was a slightly yellow, bright transparent liquid. The solvent was removed by slow evacuation at room temperature in a Buchi rotary furnace in the glove box. The dried product was a free flowing white powder. The final hydrogen content was determined from the pressure change during the reaction.

Standards of both mono and bis(quinuclidine) alane were synthesized by a direct reaction between quinuclidine and α-AlH_3 in THF. The reactions may be written as follows,

$$AlH_3 + 2N(CH_2CH_2)_3CH \rightarrow AlH_3(N(CH_2CH_2)_3CH)_2 \quad (2)$$

$$AlH_3 + N(CH_2CH_2)_3CH \rightarrow AlH_3(N(CH_2CH_2)_3CH) \quad (3)$$

The mono compound was produced by adding 1.5 g (1.35×10^{-2} mol) of pure quinuclidine to 50 ml of THF and stirring with a magnetic stirrer until all material had dissolved. 0.5 g (1.6×10^{-2} mol) of α-AlH_3 was added to the solution and stirred for several hours. The unreacted material was filtered from the THF and the soluble quinuclidine alane was recovered under dynamic vacuum at room temperature. The bis(quinuclidine) alane complex was prepared using the same procedure as the mono complex, except using 4 g (3.6×10^{-2} mol) of quinuclidine.

3. Results

Fig. 2 shows the uptake of hydrogen by a slurry of Al^*, quinuclidine, and THF. The initial H_2 pressure was 65 bar, which immediately dropped to 62.5 bar when the stirrer was activated due to the dissolution of H_2 in the THF. The hydrogenation of quinuclidine and aluminum to form quinuclidine alane proceeds immediately after H_2 dissolution as indicated by the continuous decrease in pressure down to a 58.4 bar. Based upon the total amount of H_2 uptake, the yield of AlH_3 was 2.13×10^{-2} mol, or 58% of the initial Al charge. The amount of quinuclidine consumed in the reaction was 93% of the initial quinuclidine charge for a 2:1 compound. The yield determined from the amount of hydrogen evolved during the decomposition reaction gave a similar result.

Although the pressure drop was continuous during this experiment, previous experiments on similar materials showed an induction period of up to ∼10 h after H_2 dissolution, but before hydrogenation of the quinuclidine and Al^*. The induction period and its duration are likely dependent upon the thickness of a passivation layer on the surface of the Al^* (e.g., oxide), which inhibits the reaction until it is slowly broken apart. Previous experiments have also indicated that the induction period disappears after the first cycle suggesting that the passivation layer does not reform after the initial hydrogenation.

The results from a “blank” experiment using uncatalyzed aluminum (Fig. 2) show no pressure change after the initial dissolution of H_2 in THF indicating no hydrogen uptake. No alane was detected by FTIR or XRD and the weight of the unreacted Al recovered from the reactor was the same as the weight of the original Al charge confirming that no alane was formed in the absence of the titanium catalyst. These results highlight the importance of the Ti catalyst for hydrogenation of aluminum and are similar to those obtained for the formation of TEDA–AlH_3 [5] and $LiAlH_4$–THF [10].

FTIR spectra from the THF solution of the reaction product and pure quinuclidine are shown in Fig. 3a. The peak at 1690 cm^{-1}, also visible in the spectrum from solid bis(quinuclidine) alane recovered from the solvent, corresponds to the Al–H atomic bond stretching modes (typically 1650–1850 cm^{-1}) indicating the formation of alane. Neither pure quinuclidine nor the solvent (THF) exhibit peaks within this range. The XRD patterns from the bis and mono standards of quinuclidine alane are illustrated in Fig. 3b. The calculated peak positions of the bis (2:1) and mono (1:1) forms of quinuclidine alane were calculated from the data of Harlan et al. [15] and Atwood et al. [16] respectively, and are in good agreement with observed peaks. The XRD pattern from the alane adduct prepared by direct hydrogenation (Fig. 3b) closely resembles the pattern from the bis(quinuclidine) alane standard and calculated peak positions, indicating the sample is predominantly the bis (2:1) polymorph. The small peak at 17.2° suggests a small amount of unreacted quinuclidine is also present in the reaction product. The diffraction pattern shows no trace of unreacted Al^* which was removed by filtration.

To test the reversibility of the bis(quinuclidine) alane product formed by direct hydrogenation, the alane was decomposed and then reformed in the reactor as shown in Fig. 4. On the second cycle, quinuclidine alane begins to form immediately (at a rate similar to the initial hydrogenation). The plot in the inset of Fig. 4 shows the decomposition of the initial product upon heating to 100 °C. No decomposition of the amine ligand (quinuclidine) or the THF

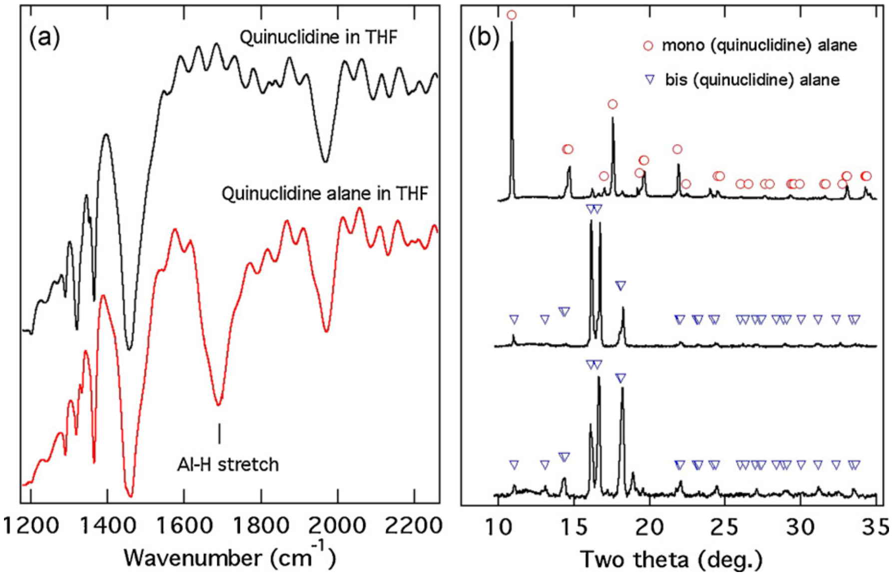


Fig. 3. (a) FTIR spectra showing for quinuclidine alane product dissolved in THF along with a standard of pure quinuclidine in THF showing Al–H stretch modes at 1690 cm^{-1}. (b) XRD patterns from hydrogenation product (bottom) and standards of bis(quinuclidine) alane (middle) and mono(quinuclidine) alane (top) along with the calculated peak positions.

solvent was observed at this temperature. Before releasing the H_2 to the manifold, the system was cooled (no stirring) to 25 °C to prevent excess release of THF into the manifold. The hydrogen gas was vented to bring the reactor down to atmospheric pressure. The reactor was again heated back to ~100 °C and the system released an additional ~1.8 bar of H_2. The total change in H_2 pressure was ~3.2 bar (0.0229 mol H_2), indicating that most of the AlH_3 adduct (95% of initial hydrogenation) decomposed. The final product and solvent were decanted and filtered in the glove box to recover the unreacted Al*. Based on the weight of the unreacted Al* the yield of quinuclidine alane was 54% with respect to the initial Al*. Solid quinuclidine alane was recovered by drying under vacuum and was again identified as the bis (2:1) adduct, i.e. $AlH_3(N(CH_2CH_2)_3CH)_2$ using XRD.

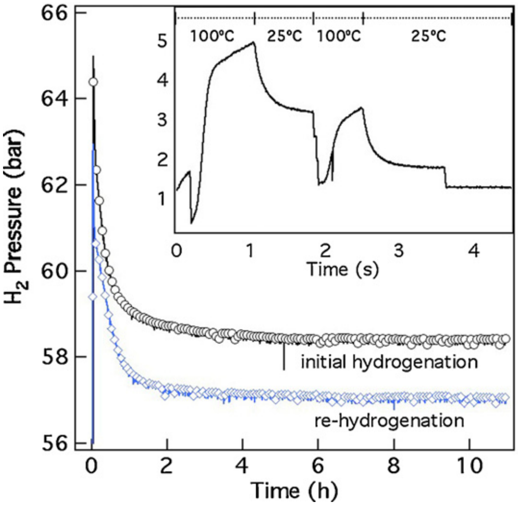


Fig. 4. Reactor pressure during the initial hydrogenation (◯) and subsequent re-hydrogenation (◊) of Al* and quinuclidine. The inset shows the reactor pressure during decomposition with the top axis showing the liquid temperature at each stage of decomposition.

4. Discussion

A number of factors likely play a role in determining the reactivity of Al* and H_2 with any particular amine. In our studies, we have only been successful in synthesizing two non-cyclic AlH_3 adducts of tertiary amines by direct hydrogenation, namely trimethylamine (TMA) and dimethylethylamine (DMEA). Despite numerous attempts at various temperatures and hydrogen pressures, triethylamine (TEA) does not react with Al* and hydrogen to form triethylamine alane; nor have we found any more complex non-cyclic tertiary amine to react directly with Al* and H_2. In this connection, an early paper by Brown and Susjishi [17,18] presciently discuss the steric effects of TMA, TEA, and quinuclidine in relation to forming addition compounds with trimethylborane. It was noted that, of the methylborane adducts, the order of increasing stability was $(CH)_3B$:TMA < $(CH)_3B$:TEA < $(CH)_3B$:quinuclidine. They concluded that the cyclic nature of the quinuclidine molecule anchored the ethyl groups at both the N atom and the bridgehead C atom, which allowed a closer approach of the boron atom to the electron pair of the N atom. Despite many attempts, we have not been able to prepare adducts of non-cyclic tertiary amines with alkyl side chains more complex than TMA and DMEA. Steric hindrance also becomes an important factor with amine alanes when alkyl groups attached only to the tertiary amine become large and inhibit the close approach of the AlH_3 species to the Lewis base electron pair on the N atom. Thus it is likely that future work to prepare new alane adducts will involve, with few exceptions, only tertiary, heterocyclic amines.

A primary objective of this effort was to readily regenerate AlH_3 from spent Al* using quinuclidine to stabilize the complex. Although the formation of bis(quinuclidine) alane occurs at low temperature, this complex is difficult to separate and decomposes at high temperatures where the AlH_3 is unstable. Although some amine alanes can be converted into less stable adducts by a transamination reaction (e.g., with triethylamine [19]) as previously demonstrated for DMEA [6] and trimethylamine [20]), stable adducts formed with solid amines, such as quinuclidine alane or TEDA alane, are unlikely to be effective for AlH_3 regeneration. However, bis(quinuclidine) alane may be useful for other applications, such as the reduction of organic functional groups

[21]. For instance, a reaction involving the direct hydrogenation of Al using an unidentified stabilizing ligand L (to form AlH_3-L) was recently demonstrated in the preparation of $NaBH_4$ from $NaBO_2$, a key step in the regeneration of ammonia borane (NH_3BH_3) [22].

5. Conclusions

The formation of bis(quinuclidine) alane occurs readily via direct reaction between Al*, H_2, and quinuclidine in a THF slurry at moderate pressures (<68 bar) with a yield of 58%. X-ray diffraction of the recovered product and standards of mono and bis(quinuclidine) alane indicate the material formed by direct hydrogenation was primarily bis(quinuclidine) alane. The reversibility of the hydrogenation reaction was demonstrated, and a separate experiment with uncatalyzed aluminum (no Ti) showed no reaction indicating that Ti is essential for hydrogenation. Although quinuclidine alane may not be ideal for the regeneration of AlH_3, reversible amine alanes may be useful as reducing agents or in the regeneration of other chemical hydrides, such as NH_3BH_3.

Acknowledgements

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