Dehydrogenation of ammonia-borane by Shvo's catalyst[†]

Brian L. Conley and Travis J. Williams*

Received 15th February 2010, Accepted 8th May 2010 First published as an Advance Article on the web 27th May 2010 DOI: 10.1039/c003157g

Shvo's cyclopentadienone-ligated ruthenium complex is an efficient catalyst for the liberation of exactly two molar equivalents of hydrogen from ammonia-borane, a prospective hydrogen storage medium. The mechanism for the dehydrogenation features a ruthenium hydride resting state from which dihydrogen loss is the rate-determining step.

The utility of hydrogen as a transportation fuel is limited by safety and practicality concerns involving pressurized gas in a mobile vehicle.¹ Thus, a practical hydrogen storage system paired with an efficient fuel cell can enable hydrogen as an alternative to liquid transportation fuels. One conceptual solution is to store hydrogen in a small molecule like MgH_{2} ,² methanol,³ a hydrocarbon,⁴ or a boron-nitrogen compound.⁵ Particularly, ammonia-borane (AB, NH₃BH₃) is a promising material due to its high hydrogen content (19.6 wt%) and capacity to dehydrogenate under mild conditions. Accordingly, several reports of transition metal catalyzed AB dehydrogenation have recently appeared. These involve rhodium,⁶ iridium,⁷ ruthenium,⁸ and nickel⁹ catalysts, among others. Among homogeneous systems, only Baker's Ni(NHC)₂ catalysts⁹ have achieved both high productivity (>2.5 equivalents H_2) and a useful rate (> 10^{-3} s⁻¹ at 60 °C).¹⁰

Studies of these systems indicate that coordination of aminoborane (NH_2BH_2) , the first dehydrogenation product of AB, to the catalyst limits productivity to 1 equivalent of H₂ because NH₂BH₂ coordination promotes formation of insoluble oligomers, $[NH_2BH_2]_n$, that leave the reaction solution.¹¹ We believe that AB's dual functionality (hydride plus proton) enables a bifunctional catalytic mechanism for its dehydrogenation⁹ that complements the polar nature of Shvo's cyclopentadienone-ligated catalyst (1).¹² This approach is similar to Noyori-type bifunctional catalysts studied previously by Schneider and Fagnou^{8,13} as well as "frustrated Lewis-pair" chemistry reported by Zou and Bercaw while this manuscript was in preparation.¹⁴ We believe an added benefit of 1 is its coordinative saturation, which might force solely outer-sphere oxidation mechanisms¹⁵ and disfavor NH₂BH₂ coordination to the catalyst, thus enabling further dehydrogenation of resulting intermediates in solution.

We report here that Shvo's catalyst (1, Scheme 1) enables liberation of 2.0 equivalents of H_2 from AB. Under certain

University of Southern California, 837 Bloom Walk,

Los Angeles CA 90089-1661, USA. E-mail: bconley@usc.edu, travisw@usc.edu; Fax: +1 213 740 6679; Tel: +1 213 740 5966, +1 213 740 5961



Scheme 1 Dehydrogenation of AB with Shvo's catalyst, 1.

conditions, this reaction is complete in 2 hours at 70 °C. Equally interesting as this reactivity are the mechanistic data for the reaction. These indicate a kinetic regime previously unseen for 1 and are consistent with a bifunctional mechanism featuring release of NH_2BH_2 and dehydrogenation of the resulting intermediate(s).

Catalytic reactivity of **1** with AB in a 2 : 1 diglyme/benzene solution in a sealed reactor proceeds at 70 °C. The solution changes color from bright orange to yellow/brown and evolves hydrogen pressure in the reaction vessel. Hydrogen gas evolution (quantified by eudiometer) and ¹H or ¹¹B NMR are effective tools to monitor the reaction. Under optimized conditions the reaction of 5.0 mol% **1** and 2.0 mol% ethanol (*vide infra*) with AB (0.42 M) liberated 1.0 equivalent hydrogen in 30 minutes and reached full conversion after 120 min to yield 2.0 equivalents hydrogen gas (Fig. 1, top) when run in a reaction vessel open to a eudiometer. The presence of elemental mercury did not influence conversion for the reaction. The ¹¹B NMR spectrum of this solution at completion revealed borazine as the exclusive boron product. This indicates that cross-linking to form polyborazylene is not efficient under these conditions.

We investigated the mechanisms involved in AB dehydrogenation using ¹H and ¹¹B NMR spectroscopy. We began by studying the reaction of 5.0 mol% 1 with AB in diglyme/ benzene- d_6 . Surprisingly, over several hours at room temperature we observed disappearance of the metal µ-hydride resonance of 1 (-18 ppm) and appearance of a signal at -10 ppm, which is consistent with the formation of ruthenium hydride 2^{16} This rapid rate of dimer dissociation is notable, given the reported barrier to dissociation of 28.8 kcal mol⁻¹ in toluene.¹⁵ Analysis of the ¹¹B spectrum several hours after the disappearance of 1 was complete did not reveal catalytic conversion of AB. However, upon heating to 70 °C, the disappearance of AB is observed along with formation of several boroncontaining species, including cyclic trimer 5¹⁷ and borazine in the ¹¹B spectrum. Notably, ¹¹B NMR analysis at early times (through ca. 30% conversion) reveals that the most prominent boron containing species is borazine. At the same time, we also

Department of Chemistry and Loker Hydrocarbon Institute,

[†] Electronic supplementary information (ESI) available: Experimental procedures, kinetics data, and graphical spectra. See DOI: 10.1039/ c003157g



Fig. 1 (top) Eudiometer data showing production of hydrogen gas in the presence of 5.0 mol% **1** and 2.0 mol% ethanol in 2 : 1 diglyme/ benzene at 70 °C. (bottom) ¹¹B NMR data showing consumption of AB in the presence of 2.5 mol% **1** in a sealed J. Young NMR tube.

observed a smaller resonance at -11 ppm. This overlaps with the $-BH_2$ group of 5 as it grows into solution and is most likely 5's unbranched isomer, cyclotriborazane.¹⁰

A kinetic profile for AB consumption was generated by plotting [AB] against time (Fig. 1, bottom). The data feature three rate regimes: 1. a brief initiation period (*ca.* 2% conversion), 2. a fast linear regime (through *ca.* 30% conversion), and 3. a slower regime that fits to first order exponential decay.¹⁸†

The kinetics of the initiation period (regime 1) were studied by ¹H NMR and are consistent with dissociation of 1 to 2 and 3 followed by rapid reduction of 3 to 2 by AB. Interestingly, there is zero order in [AB] for this process while [1] is first order, which suggests that dissociation of the dimer is rate limiting in catalyst initiation and that AB is uninvolved in the rate determining step.

Regime 2 was of particular interest because the plot of [AB] vs. time was linear with a sharp slope and eudiometer measurements at corresponding times showed rapid H₂ evolution.

Indeed, our calculations suggest that the rate of hydrogen production in regime 2 (eudiometry) is comparable to AB loss (¹¹B NMR integration) with rates of 6.1×10^{-8} mol s⁻¹ and 7.9×10^{-8} mol s⁻¹, respectively. Varying the catalyst concentration allowed for the comparison of regime 2 rate values determined from the slope of this linear region. A ln (rate)/ln [1] plot reveals a linear relationship with a slope of 0.96, which indicates a first order dependence on [Ru].[†] This contrasts cases of 1-catalyzed aldehyde hydrogenation¹³ and alcohol oxidation^{12,19} which have half-order dependence on [Ru].²⁰ In AB dehydrogenation, this regime is changed by the very rapid reduction of 3 to 2, which makes dehydrogenation of 2 ratedetermining. Our kinetics and NMR data support the presence of a persistent ruthenium hydride throughout the reaction and indicate that a monomeric hydride (such as 2 or a closely related species) is the resting state of the catalyst. Interestingly, as the reaction proceeds into regime 3, the hydride region of the ¹H NMR spectrum contains at least three distinct resonances within 0.5 ppm of the originally derived hydride compound at -10 ppm. This indicates conversion of 2 to related compounds as the concentration of dehydrogenated products increases, potentially accounting for the observed loss in rate.

We observed that the reaction was significantly faster in deoxygenated, benchtop grade diglyme than under anhydrous conditions. Along these lines, we found that adding ethanol to anhydrous diglyme/benzene increased the reaction rate: we repeated our kinetics experiment in the presence of various catalytic quantities of ethanol in rigorously anhydrous reaction solutions containing AB and 5.0 mol% 1. We observed a linear dependence of k_{obs} on concentration from 0 to 17.0 mole percent,[†] which is consistent with Casey's finding that added alcohol catalyzes the release of hydrogen from a tolyl-analogue of **2** by shuttling the ligand hydroxyl proton to the Ru–H to form a labile dihydrogen complex (**4**, Scheme 2).²¹

Although we cannot exclude the possibility of stepwise mechanisms involving oxidative addition of the B–H bond to **3** or successive deprotonation/hydride transfer, we currently favor a concerted, outer sphere pathway for proton and hydride transfer to **3**. Unfortunately, the rapid rate of k_3 relative to dihydrogen loss from **2** (k_1) precludes measurement of kinetic isotope effects for k_3 under catalytic conditions.²²

We believe that the third regime in the ¹¹B NMR kinetics arises due to the buildup of products other than H_2 that slow



Scheme 2 Proposed mechanism for catalysis in regime 2. Rate = $2k_1[1][EtOH]$.†

catalysis. In a reaction run under D_2 pressure (50 psig, 3.4 atm) deuterium is not incorporated into AB or the dehydrogenated products as monitored by ²H NMR. Further, the kinetic profile of this reaction matches the reaction run under 1 atm N₂. These observations indicate that dehydrogenation is irreversible under these conditions and that rate inhibition is not related to increased H2 pressure. However, a reaction run with 1 equivalent added borazine shows significant differences in its kinetic profile. Under these conditions, there is also a short initiation period followed by slow catalysis that fits a first order exponential decay model.[†] Thus, we propose that the catalysis slows gradually in the presence of borazine. However, when more AB is added to spent reaction solutions, we observed an increase in rate of AB loss through 3 successive catalytic runs, even as the borazine concentration builds in the sealed NMR tube. The increased rate coincides with a change in product distribution. We are currently investigating the extent of reusability for this system and identifying the nature of the active catalytic species as well as the boron intermediates.

In sum, we have described an efficient system for catalytic dehydrogenation of ammonia-borane that liberates two equivalents of hydrogen and gives borazine as the by-product. This is the second example of a homogeneous transition metal catalyst that liberates more than one equivalent of hydrogen gas from AB itself.²³ Our data and literature precedent lead us to the mechanistic proposal in Scheme 2 for regime 2, the initial mechanism of ammonia-borane dehydrogenation with 1. Precatalyst 1 undergoes first order dissociation (k_{init} , [AB] order is zero) to give 2 and 3; the latter is rapidly reduced to 2 by AB. 2 is the resting state of the cycle; ethanol-catalyzed dihydrogen loss from 2 (k_1) is rate determining, where k_1 is first order in [Ru] and dependent on [ROH]. This presumably proceeds through the intermediacy of a ruthenium dihydrogen complex (4) to give the postulated oxidizing species 3 as Casey has shown.¹⁸ The situation that k_1 is rate-determining in a catalytic system is a previously unobserved regime for 1. We predict a concerted, bifunctional transition state for B-H and N-H transfer in the conversion of 3 to 2, but this remains speculative. Ongoing studies in our laboratory are focusing on the mechanism of regime 3, N-H and B-H bond cleavage steps for AB and its intermediate oxidation products, conditions for cross-linking borazine, reversibility of AB dehydrogenation, and extension of bifunctional dehydrogenation to Shvo congeners and other motifs.24

We thank the University of Southern California, Loker Hydrocarbon Research Institute, and the Hydrocarbon Research Foundation for research support and the NSF (DBI-0821671) and NIH (S10-RR25432) for NMR spectrometers. We are grateful to Profs. A. Weller and R. T. Baker, and our reviewers for insightful comments and discussions. We dedicate this paper to the memory of Prof. Keith Fagnou, a respected member of the community whose contributions will be missed greatly.

View Article Online

Notes and references

- 1 United States Dept. of Energy, *Hydrogen Fuel Cells and Infra*structure Technology Program. Multi-Year Research Development and Demonstration Plan, Sect. 3.3, GPO, Washington, 2009.
- 2 B. Bogdanović, Angew. Chem., Int. Ed. Engl., 1985, 24, 262–273.
- 3 G. A. Olah, A. Goeppert and G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy*, Wiley: VCH, Weinheim, 2nd edn, 2009.
- 4 M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska and C. M. Jensen, *Chem. Commun.*, 1996, 2083–2084; W. Xu, G. P. Rosini, M. Gupta, C. M. Jensen, W. C. Kaska, K. Krogh-Jespersen and A. S. Goldman, *Chem. Commun.*, 1997, 2273–2274.
- 5 E. Fakioglu, Y. Yurum and N. Veziroglu, Int. J. Hydrogen Energy, 2004, 29, 1371–1376.
- 6 C. A. Jaska, K. Temple, A. J. Lough and I. Manners, J. Am. Chem. Soc., 2003, **125**, 9424–9434; C. A. Jaska and I. Manners, J. Am. Chem. Soc., 2004, **126**, 1334–1335.
- 7 M. C. Denney, V. Pons, T. J. Hebden, M. Heinekey and K. I. Goldberg, J. Am. Chem. Soc., 2006, **128**, 12048–12049.
- 8 N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black and K. Fagnou, J. Am. Chem. Soc., 2008, **130**, 14034–14035; M. Käβ, A. Friedrich, M. Drees and S. Schneider, Angew. Chem., Int. Ed., 2009, **48**, 905–907.
- 9 R. J. Keaton, J. M. Blacquiere and R. T. Baker, J. Am. Chem. Soc., 2007, 129, 1844–1845.
- F. H. Stephens, V. Pons and R. T. Baker, *Dalton Trans.*, 2007, 2613–2626;
 T. B. Marder, *Angew. Chem., Int. Ed.*, 2007, 46, 8116–8118;
 C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, 38, 279–293, and references therein.
- 11 V. Pons, R. T. Baker, N. K. Szymczak, D. J. Hildebrant, J. C. Linehan, M. H. Matus, D. J. Grant and D. A. Dixon, *Chem. Commun.*, 2008, 6597–6599.
- 12 B. L. Conley, M. K. Pennington-Boggio, E. Boz and T. J. Williams, *Chem. Rev.*, 2010, **110**, 2294–2312.
- 13 A. Friedrich, M. Drees, J. S. auf der Günne and S. Schneider, J. Am. Chem. Soc., 2009, 131, 17552–17553.
- 14 Y. Guo, X. He, Z. Li and Z. Zou, *Inorg. Chem.*, 2010, 49, 3419–3423; A. J. M. Miller and J. E. Bercaw, *Chem. Commun.*, 2010, 46, 1709.
- 15 J. B. Johnson and J.-E. Bäckvall, J. Org. Chem., 2003, 68, 7681–7684; C. P. Casey, S. E. Beetner and J. B. Johnson, J. Am. Chem. Soc., 2008, 130, 2285–2295; M. K. Thorson, K. L. Klinkel, J. Wang and T. J. Williams, Eur. J. Inorg. Chem., 2009, 295–302.
- 16 Y. Blum and Y. Shvo, J. Organomet. Chem., 1985, 282, C7–C10; Y. Shvo, D. Czarkie and Y. Rahamim, J. Am. Chem. Soc., 1986, 108, 7400–7402.
- 17 V. Pons, R. T. Baker, N. K. Szymczak, D. J. Heldebrant, J. C. Linehan, M. H. Matus, D. J. Grant and D. A. Dixon, *Chem. Commun.*, 2008, 6597–6599.
- 18 At low catalyst loadings the thermal background must be considered when fitting kinetics curves. Kinetics in regime 2 are *ca*. 10^2 more rapid than thermal dehydrogenation at all [1] studied. Some distortion of the e^x fit of regime 3 at low catalyst loadings is observed when a natural log [AB] treatment is employed and may be attributed to a competitive background rate that is only *ca*. 6-fold slower than catalysis. This effect is not seen at higher [1].
- 19 J. B. Johnson and J.-E. Bäckvall, J. Org. Chem., 2003, 68, 7681-7684.
- 20 J. Espenson, Chemical Kinetics and Reaction Mechanisms, McGraw-Hill, 2nd edn, 2002, pp. 77–82.
- 21 C. P. Casey, J. B. Johnson, S. W. Singer and Q. Cui, J. Am. Chem. Soc., 2005, **127**, 3100–3109.
- 22 Such a measurement is expected to report the KIE for the ratedetermining step, hydrogen loss from 2.
- 23 The first example of a transition metal catalyzed process (heterogeneous Rh nanoparticles) that released >1 equivalent of H_2 from AB is described in ref. 7.
- 24 B. L. Conley and T. J. Williams, J. Am. Chem. Soc., 2010, 132, 1764–1765.