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Hydrogen Storage in Ionic Liquids

The Role of Ionic Liquids in Hydrogen Storage

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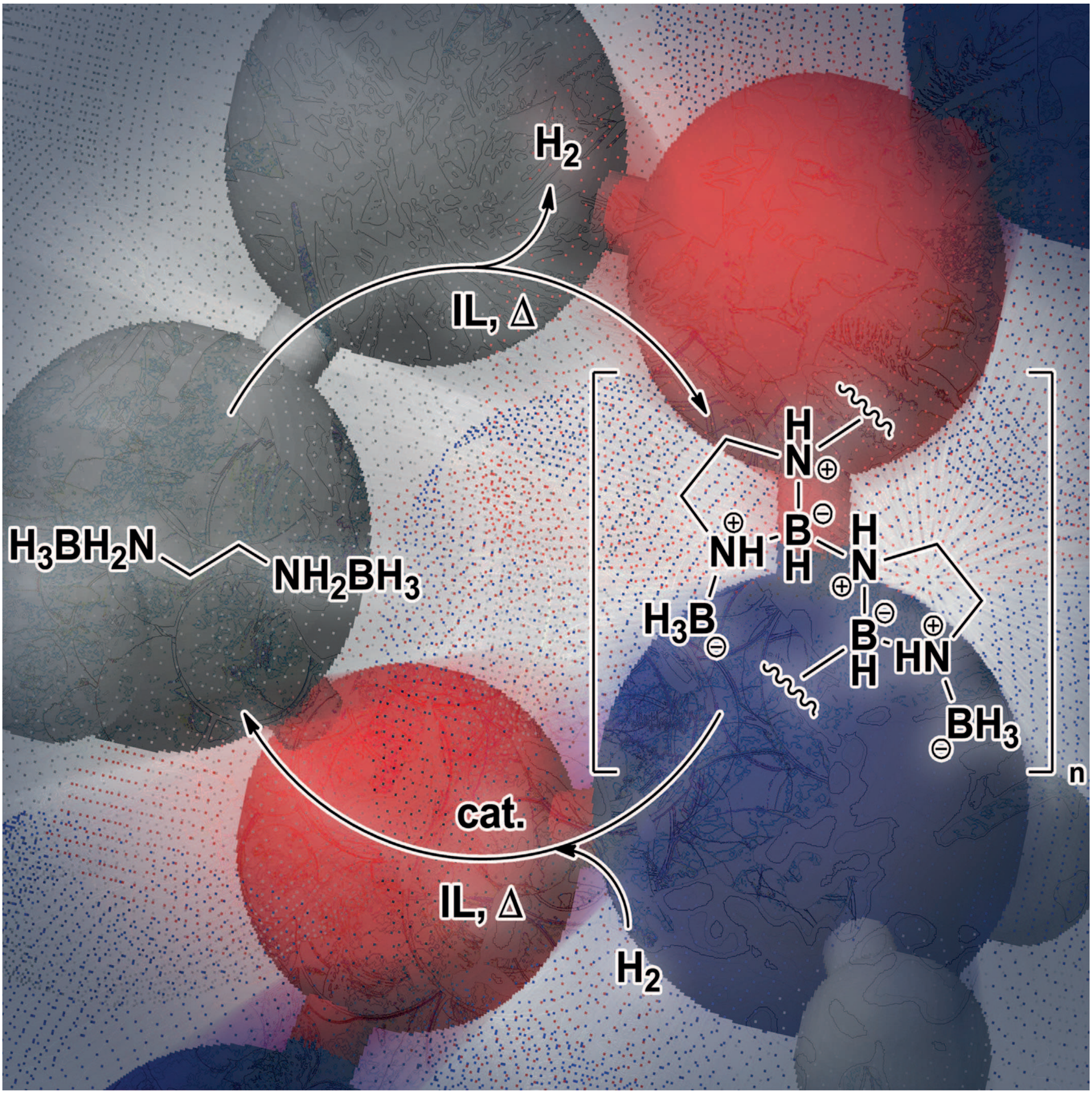

Abstract: Ionic liquid (IL) based H_2 storage for H_2 generation from NH_3BH_3 derivatives is shown. These systems promote H_2 generation at low temperature, with good reaction rates and high total H_2 yields. The effects of ILs and the H_2 yield in correlation with the basicity, the cations of the ILs, and the role of carbenes are discussed. Furthermore, mechanistic findings on the dehydrogenation are described. IL material blends are competitive with conventional H_2 storage materials with experimental efficiencies of at least 6.5 wt% H_2.

Introduction

The extensive use of energy in our society is based on a stable and comfortable power grid. Applications premised on mobile energy mainly rely on fossil fuels derived from oil. Since the depletion of the natural reserves is forecast for the current century, scientists have started developing alternate energy supply strategies for mobile applications. One considerable energy storage medium is hydrogen. The wide availability and ease of production by electrolysis from water make it very appealing. However, for its wide implementation certain obstacles have to be overcome, and efficient storage in particular is a major hurdle demanding research. Molecular hydrogen is gaseous under atmospheric pressure at room temperature, condensing at $-252\,^{\circ}C$. In the condensed form, hydrogen has a reasonable density sufficient for energy storage. Due to handling and technical issues as well as loss in dwell times (boil-off), liquid hydrogen is not considered for implementation in widespread energy storage anymore. The state-of-the-art benchmark is hydrogen storage in a high-pressure vessel operating at pressures of up to 70 MPa.[1] The requirement for the high-pressure vessel corresponds to a gravimetric storage efficiency of only 4.8%. The hydrogen content of several substances lies well above this value, provoking extensive research in the field of chemical hydrogen storage solutions.[1,2] One appealing group of substances in this context is the storage in amine boranes. This substance class combines high hydrogen content with relatively mild conditions for release. Many amine boranes release a substantial amount of hydrogen at temperatures below 200 °C.[2b,3] The best investigated compound of this class is ammonia borane (AB), which is appealing due to its hydrogen content of 19.6 wt.%.[2b] The dehydrogenation mechanism in the solid state proceeds via an ionic intermediate species (see Figure 1): diammoniate of diborane (DADB, $[BH_2(NH_3)_2][BH_4]$). The formation of this intermediate causes an induction time, before extensive hydrogen formation is observed.[4] Certain ionic liquids have been shown to remove the induction period. This effect is supposed to be caused by stabilization of an ionic intermediate, possibly DADB.[5]

After the initial formation of DADB, dehydrogenation to linear, branched, and (poly)cyclic oligo- and polymers is possible. The formation of poly(aminoborane)s as well as poly(iminoborane)s (polyborazylene) is usually observed, as well as the volatile iminoborane trimer borazine.[2b] The formation of volatile borazine is critical since it constitutes a risk towards fuel cells.[6] The formation of boron nitride, the product of complete dehydrogenation, is only observed when the reaction is conducted at temperatures as high as 450 °C.[7] Due to its chemical inertness and problems associated with the regeneration of the spent fuel, boron nitride formation is avoided.

The regeneration of spent fuel from AB dehydrogenation has recently been addressed by Sutton and co-workers, using hydrazine in liquid ammonia.[8] Earlier attempts employed HCl, alkyl amines, and H_2.[9] HBr or benzenedithiol digestion and subsequent reduction with an organotin compound were also shown as possible pathways.[10]

Instead of ammonia borane, substituted amine boranes can be used. These have lower hydrogen content, but entail fewer problems in the course of the reaction, since the formation of volatile borazine is avoided. As examples methyl amine borane (MeAB), *sec*-butyl amine borane (SBAB), and ethylene diamine bisborane (EDB) are worthy of mention. The corresponding trimeric borazine derivatives are substantially less volatile. Notably, in the case of SBAB dehydrogenation, the trimer forms selectively under certain conditions.[3b] The mechanism of EDB dehydrogenation and the formation of the corresponding products still require more detailed studies to completely understand the reactions; two reaction pathways have been suggested.[11]

Whereas the dehydrogenation of neat AB is delayed by an induction phase, EDB dehydrogenates instantly when heated. This indicates a different mechanism of EDB dehydrogenation (Figure 2). In contrast to AB, EDB can initially undergo an intramolecular reaction, forming the ionic species **1** (Figure 2) and subsequently under hydrogen release the neutral species **2**. Alternatively EDB might dimerize in an ionic manner to form **3**.[11]

Ionic liquids (ILs) are often referred to as solvents with unique solubilization properties that are chemically inert.[12] In the last decade, the application of ILs in various fields of chemistry, especially catalysis, has drastically increased.[12,13] The presence of an ionic intermediate in amine borane dehydrogenations might explain the catalytic effect observed with some ionic liquids (ILs). A stabilizing effect on the ionic intermediates might be the reason for the strong enhancement of

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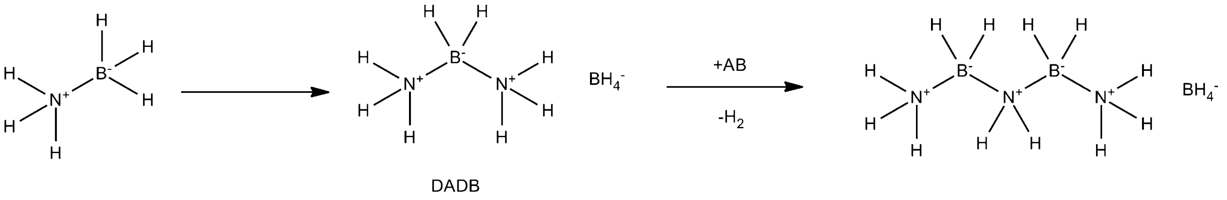

Figure 1. Ionic ammonia borane dehydrogenation mechanism.[2b]

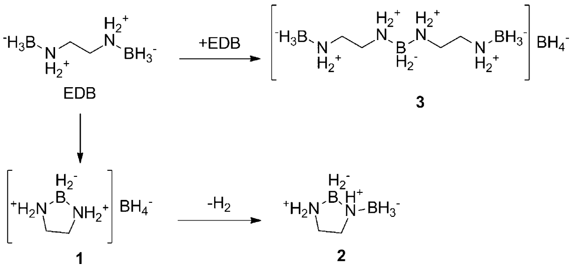

Figure 2. Possible dehydrogenation mechanisms of EDB.[11]

hydrogen release, as well as for the suppression of the induction time by addition of ionic liquids.

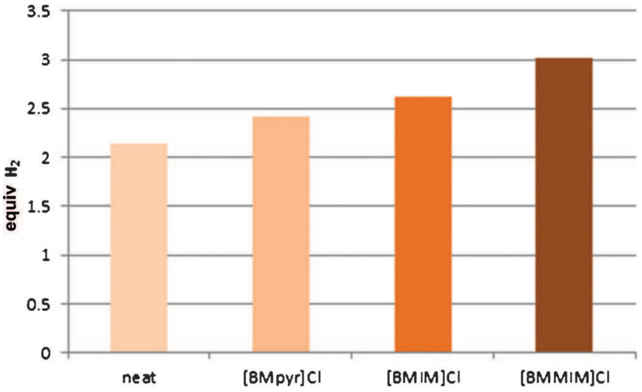

Figure 3. Dehydrogenation of EDB in the presence of different chloride-containing ILs at 120 °C for about 100 min.

Results and Discussion

In our ongoing research we are focusing on the investigation of amine borane derivatives blended with ILs with the aim of developing regenerative hydrogen storage materials. As discussed in previous work from our group,[14] the choice of IL is decisive for a reasonable effect on the dehydrogenation of EDB. Besides the choice of IL, there is a distinct effect of the IL/EDB ratio on the hydrogen yield. In the investigated case of 1-butyl-2,3-dimethylimidazolium chloride ([BMMIM]Cl), the yield passes through a maximum at an IL/EDB ratio of 0.25 to 1.0 (mass/mass) depending on the temperature.

Effect of ion choice

The choice of cation was found to be important when comparing the dehydrogenation of EDB in the presence of different chloride ILs (see Figure 3).[14]

Dehydrogenation in the presence of chloride ILs enhances yield (neat EDB: 2.14 equiv) moderately. Whereas the presence of butyl methyl pyrrolidinium chloride ([BMpyr]Cl) raises the yield to 2.42 equivalents, [BMIM]Cl addition results in 2.62 equivalents, and admixed [BMMIM]Cl in release of 3.02 equivalents of hydrogen. Imidazolium ILs perform remarkably in comparison to other ILs[14] indicating a mechanism associated with the imidazolium core of the cation. Since imidazolium ions are able to form carbenes in certain cases,[15] intermediate carbene formation might be involved in a mechanism of imidazolium ILs supporting EDB dehydrogenation. As depicted in Figure 5, carbene formation might play a role as well (vide infra).

Furthermore imidazolium cations exert a strong effect on the hydrogen yield, when combined with basic anions.[14] This effect was not be observed when there was no imidazolium cation present. Basic anions might facilitate the formation of intermediate carbene species.

Besides the cation, we observed that also the nature of the anion plays a role regarding the efficiency, in particular with respect to the reaction rate and total hydrogen yield. The basicity (associated with the anion) of the IL is quantified by the (empirical) β-value of the Kamlet–Taft parameters.[16] A correlation was found between the hydrogen yield from EDB dehydrogenation and the mean β-values (exact β-values were not available) of the employed imidazolium IL's anions (see Table 1). Notably, repeated experiments of EDB dehydrogenation with [BMMIM]Cl under strict exclusion of water and air yielded comparable amounts of hydrogen. Since hygroscopic ILs might open the pathway to concurrent hydrolysis, we investigated the water content of the employed ILs by Karl-Fischer titration. It was calculated that if the complete water content of the IL took part in the hydrolysis reaction, no more than 1.74% of the additional hydrogen yield is caused by the hydrolysis. Therefore, the thermolysis pathway is the dominant one which is supported by certain ILs. However, experiments

Table 1. Relation of hydrogen yield in EDB dehydrogenation to mean β-values of the anion of employed imidazolium ILs.[14]

Anion	mean β-value	Equiv H_2
NTf_2^-	0.24	2.04
PF_6^-	0.29	2.18
BF_4^-	0.36	2.56
Cl^-	0.93	3.02
OAc^-	0.99	3.67

on EDB dehydrogenation with [BMIM]OAc amazingly did not yield any hydrogen at all and no foaming was observed. This implies that water acts as an initiator for the dehydrogenation. Further information on the water content of the ILs can be found in the Supporting Information.

In situ carbene formation?

The possibility of intermediate carbene formation in imidazolium ILs was further investigated by isotopic labeling experiments. Owing to the inherent C–H acidity of the imidazolium protons, deuteration of [BMIM]Cl and [BMMIM]Cl is straightforward.[17]

The mass spectrometric investigation of EDB dehydrogenation in the presence of [D_5]-[BMMIM]Cl shows a distinct evolution of HD besides H_2 (Figure 4a). An intermediate formation of carbenes from [D_5]-[BMMIM]Cl seems to provide an explanation for the HD evolution. Further investigations on the origin of HD showed that upon strict exclusion of water (or D_2O) traces (these experiments were conducted under glovebox/Schlenk technique conditions with extensive drying of the ILs), no HD evolution is observable (Figure 4b), the signal for HD shows only background noise. Thus, intermediate carbene formation cannot be deduced from the observed HD evolution. Moisture or residual D_2O traces might explain the minor HD evolution from EDB/[D_5]-[BMMIM]Cl mixtures under air. The formation of carbenes in the C-2 position is favored over formation at the C-4 and C-5 positions (Figure 5). Since the C-2 position is blocked in [D_5]-[BMMIM]Cl by a methyl group, the experiment was repeated employing [D_3]-[BMIM]Cl, which is able to form a carbene species in the C-2 position. In this case, the formation of HD traces can be observed, indicating intermediate carbene formation in this case. The control experiments with defined addition of different amounts of D_2O showed a strong correlation between D_2O content and HD formation in the case of both ILs.

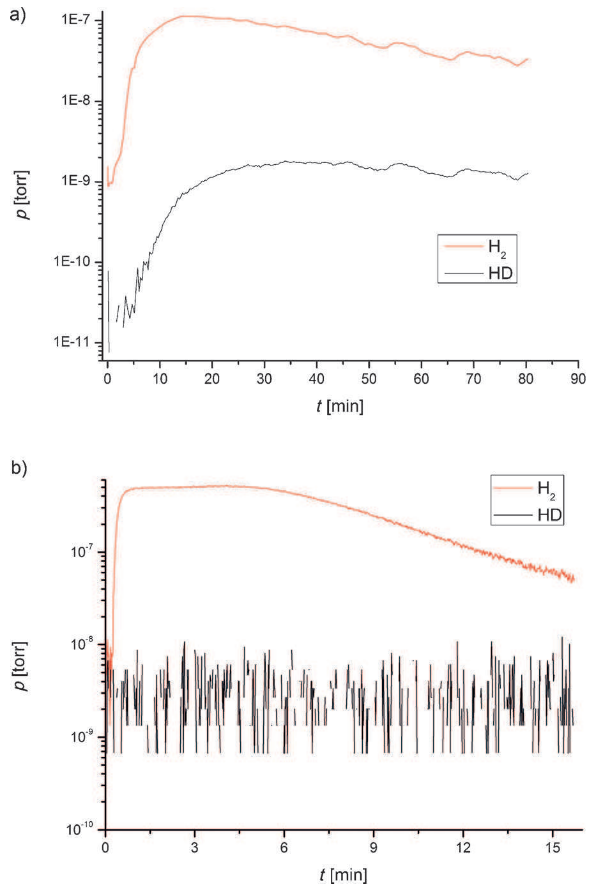

Figure 4. Mass spectrometric evaluation of released gas from EDB dehydrogenation in the presence of [D_5]-[BMMIM]Cl a) under air and b) under inert conditions.

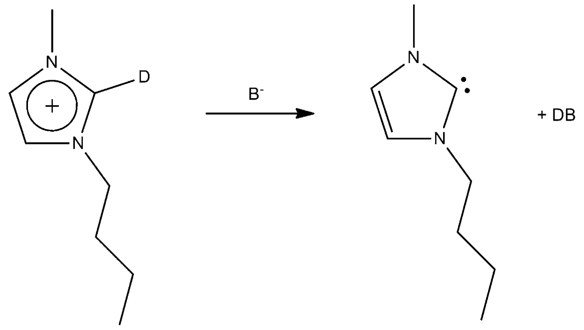

Figure 5. Carbene formation in the C-2 position of [D_1]-[BMIM]Cl under basic conditions.

Both ILs were subjected to the same drying process to remove water/D_2O traces (4 days under high vacuum at 60 °C). Despite these precautions, it cannot be completely excluded that HD formation is a result of water or D_2O traces in the reaction mixture with [D_3]-[BMIM]Cl. Since both ILs catalyze the dehydrogenation to a similar extent, carbene formation is unlikely the reason for the observed catalytic effect, though carbene formation is indicated by the observed HD release in the case of EDB dehydrogenation in the presence of [D_3]-[BMIM]Cl. If the formation of intermediate carbenes were the reason for catalytic activity of imidazolium ILs, the addition of preformed carbenes, in the form of Arduengo carbenes (see Figure 6), should support dehydrogenation of EDB in a similar manner.

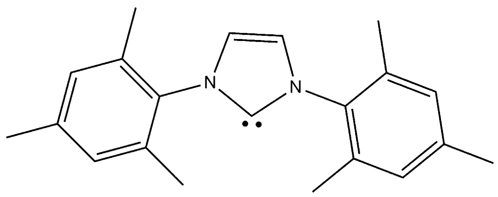

Figure 6. Structure of the employed Arduengo carbene.

Organocatalysis with the Arduengo-carbene IMes?

Whereas decomposition of neat EDB releases about two equivalents of hydrogen in 30 min (Figure 7, green curve), the addition of one mass equivalent of Arduengo carbene reduces the amount of released hydrogen to 1.6 equivalents (black curve).

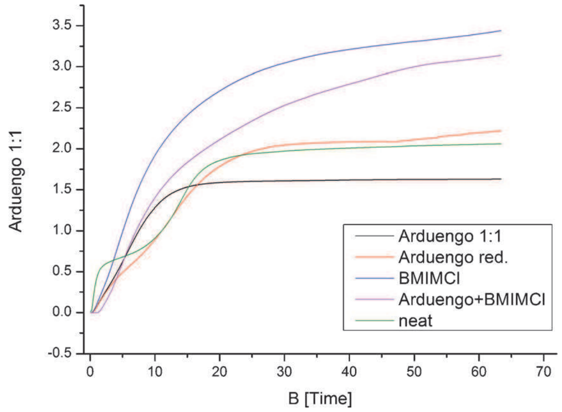

Figure 7. Dehydrogenation of EDB in the presence of Arduengo carbene.

A reduced amount (16.4 wt.%) of Arduengo carbene added to EDB has a minor effect on the hydrogen release (red curve). In comparison to EDB decomposition with [BMIM]Cl (blue curve), which releases more than three equivalents of hydrogen, all experiments including Arduengo carbene result in lower hydrogen yields. The absence of a catalytic effect of Arduengo carbene addition indicates that the intermediate carbene formation of imidazolium ILs is not the source of the promoting effect on the dehydrogenation of AB and EDB. All experiments employing Arduengo carbenes were conducted under strict exclusion of water and air.

Mechanistic investigations

EDB polymerization is proposed to proceed via an intra- or intermolecular mechanism (compare Figure 2).[11] In both cases an ionic as well as a neutral species might form initially. The polymer is hardly soluble in common organic solvents, which limits the analytical possibilities. Additionally, the amorphous structure and polymeric nature of the products limit analysis by XRD or MAS-NMR spectroscopy, as also described elsewhere.[11] A small amount of polymer could be subjected to MALDI-TOF and high-resolution ESI-MS and revealed valuable information about the polymer. Due to the sample preparation, polymers might have been altered from the original dehydrogenation product. This implies that the oligomers found are a lower limit, for example, in terms of the degree of polymerization, which is supported by the fact that the amount of released hydrogen cannot be explained by the degree of polymerization.

The ESI mass spectrum of the polymer (see Figure 10) shows several equidistant signals, corresponding to oligomers formed in the dehydrogenation. The signals consist of sets due to the natural isotope distribution of ^{11}B and ^{10}B (about 4:1). The found polymers are mainly the single-bond species (**P$_1$**$=[C_{2n}N_{2n}B_{2n-1}H_{10n}]$), only for $n=1$–5 further dehydrogenated species were identified (**P$_2$**$=[C_{2n}N_{2n}B_{2n-1}H_{10n-2}]$) that contain one additional double bond equivalent (Figure 8). For $n=1$–7, species containing an additional borane group were found (**P$_3$**$=[C_{2n}N_{2n}B_{2n}H_{10n+2}]$). It remains unclear why there is no **P$_3$** for $n>7$, but one explanation is that all **P$_3$** species are fragments from higher polymers. The reason for **P$_2$** only being found for $n<6$ is also unclear, though solubility might play the key role here. Another explanation might be another intramolecular cyclization reaction forming a bicyclic compound.

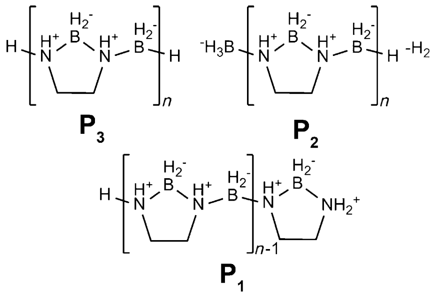

Figure 8. Suggested linear polymers.

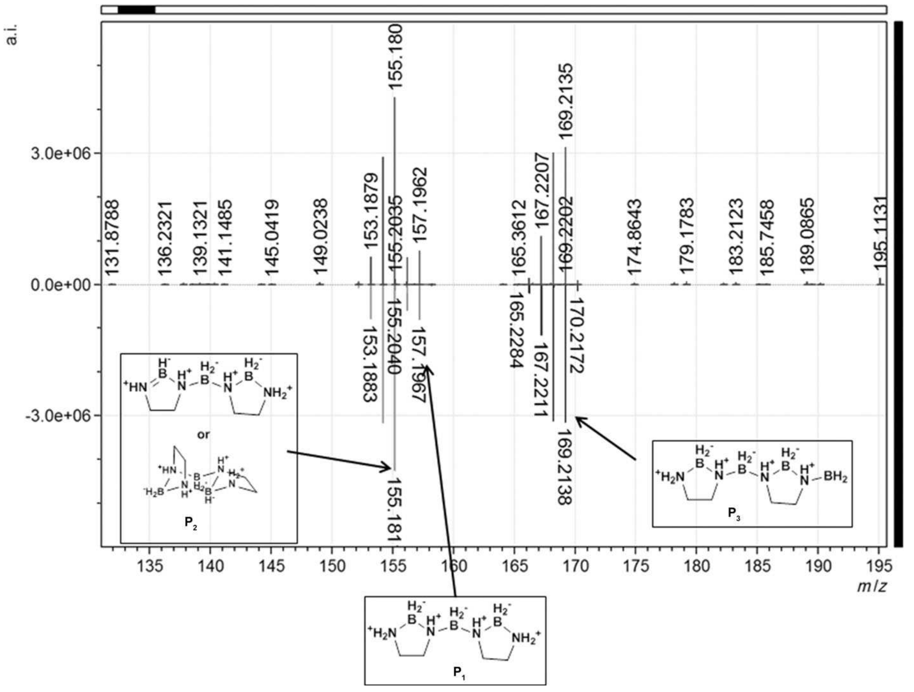

Figure 9. ESI-HR-MS signal set around 155 [*m/z*] with simulated data (down) and possible chemical structures for $n=2$.

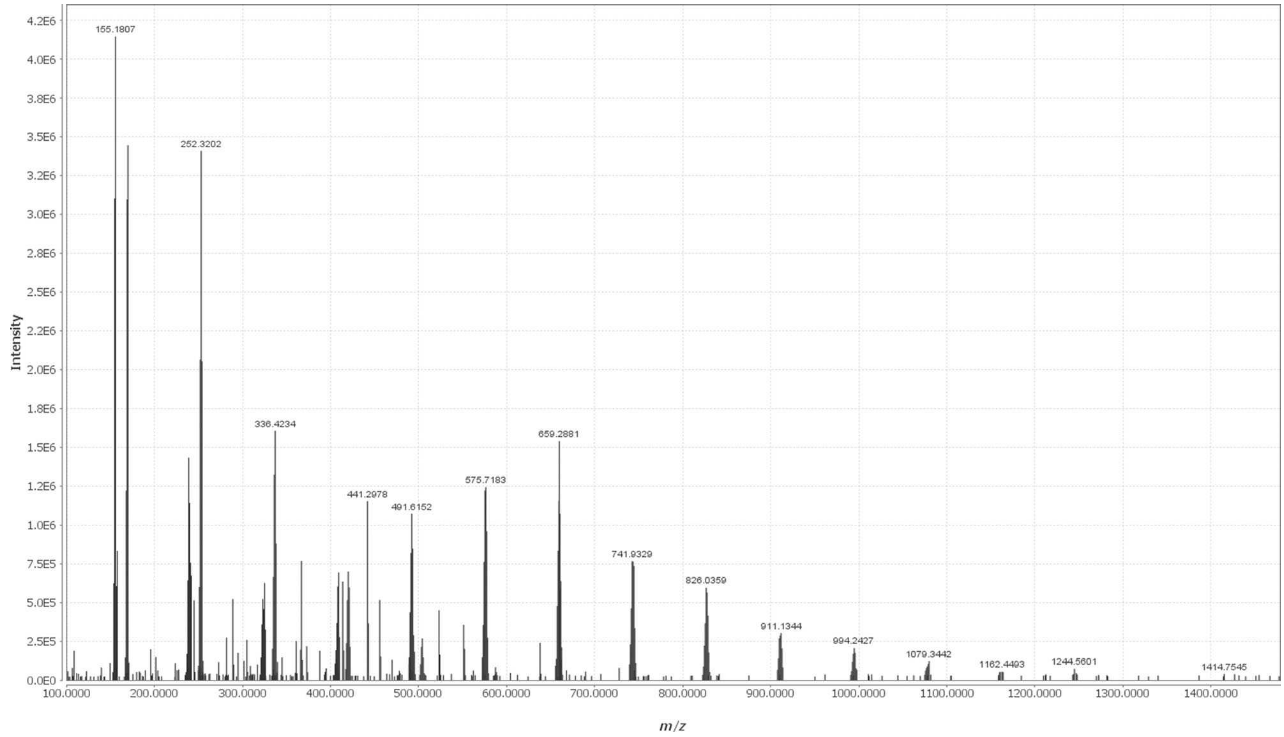

Figure 10. High-resolution ESI-MS of the EDB dehydrogenation product.

The structures of the possible formed compounds for $n=2$ are depicted in Figure 9. The found signal sets are in good agreement with the simulated spectra, which are shown as downward peaks. The simulated spectra are in good agreement with the major peaks found in the ESI-MS up to 1161 (see Figure 10 and the Supporting Information for further information).

The observed species at low *m/z* values might provide additional information about the initial dehydrogenation mechanism of EDB, from which some possible pathways are depicted in Figure 2. Whereas the species at *m/z* 61.06 can be identified as an ethylenediamine fragment, it is unclear if the found species at *m/z* 71.066, *m/z* 73.081, and *m/z* 85.101 correspond to preformed EDB dehydrogenation products, possibly **1** for *m/z* 73.066 and **2** (Figure 2) for *m/z* 85.101 ([**2**-H$^-$]$^+$), or are fragments resulting from higher polymers. The species **3** could not be found, leading to the assumption that this species is not a major one, or, if formed, readily cyclizes to form $\mathbf{P_1}$ with $n=2$. Besides the MS identification, the BH_4^- ion was identified in the extract of the dehydrogenation product (see the Supporting Information for further information).

Metal-catalyzed dehydrogenation

It was shown in several publications that the hydrogen yield from amine boranes at low temperatures can be drastically improved by the addition of ionic liquids.[5b,7,14,18] The yield and reaction rate of EDB/IL mixtures is furthermore improved considerably at low temperatures by addition of some metal salts (see Figure 11).

Dehydrogenation of EDB in the presence of 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM]EtSO$_4$) yields only around one equivalent of H_2 at temperatures of 85 °C and 100 °C. At

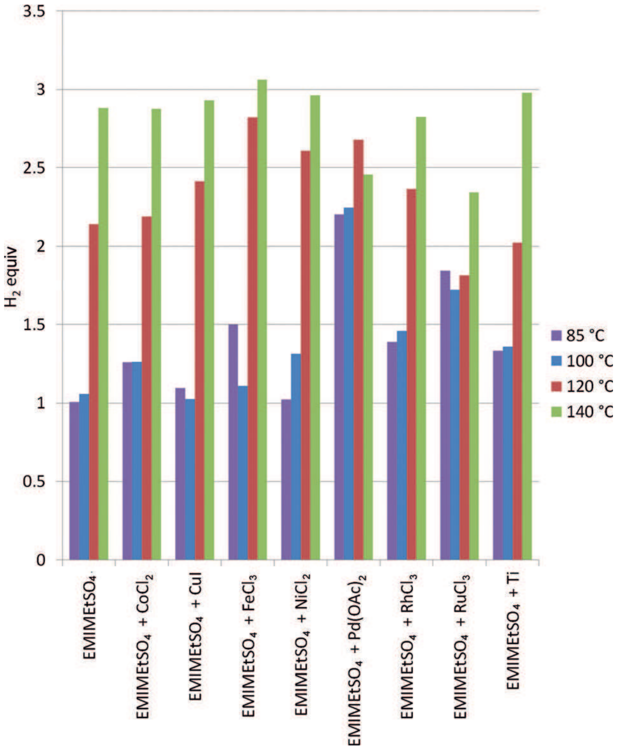

Figure 11. Metal-catalyzed dehydrogenation of EDB in presence of [EMIM]EtSO$_4$.

120 °C the yield rises to 2.14 equivalents, which is comparable to that from neat EDB dehydrogenation, that is, [EMIM]EtSO$_4$ does not improve EDB dehydrogenation. When a temperature of 140 °C is applied, nearly 2.9 equivalents can be obtained. We employed [EMIM]EtSO$_4$ since we wanted to investigate the influence of metal salt additions in the presence of an IL, without the IL severely affecting the yield. For the following experiments the amount of 10 wt% metal salt with respect to EDB was added to the mixture before heating. In direct comparison, the addition of Pd(OAc)$_2$ results in comparable yields at 120 °C and 140 °C, but at temperatures of 85 °C and 100 °C the hydrogen yield more than doubles to 2.2 and 2.25 equivalents, respectively. Notably, Pd(OAc)$_2$ addition resulted in hydrogen evolution already at room temperature. Another noteworthy feature is the performance of RuCl$_3$ at low temperatures (1.85 equiv at 85 °C and 1.72 equiv at 100 °C), though at the higher temperatures the yield drops in comparison to that obtained in the control experiment with neat EDB. The addition of FeCl$_3$ leads to a decent improvement at 85 °C and this reaction performs best at 120 °C (2.82 equiv). Most other metal additives lead to a slight gain in yield at lower temperatures, whereas at higher temperatures the change in yield is negligible. The reason for the decrease in yield from 85 °C to 100 °C in the measurements of CuI, FeCl$_3$, and RuCl$_3$ is unknown, but might be connected to hydrogen consumption by reduction of the salt. In all experiments a dark foam indicated metal(0) formation.

Besides a distinct improvement in yield a strikingly improved reaction rate was observed. The hydrogen evolution from EDB in the presence of [EMIM]EtSO$_4$ proceeds slowly, and only after about 50 min is the reaction complete. In comparison, the same reaction with the addition of Pd(OAc)$_2$ nears completion after only 5 min (see Figure 12).

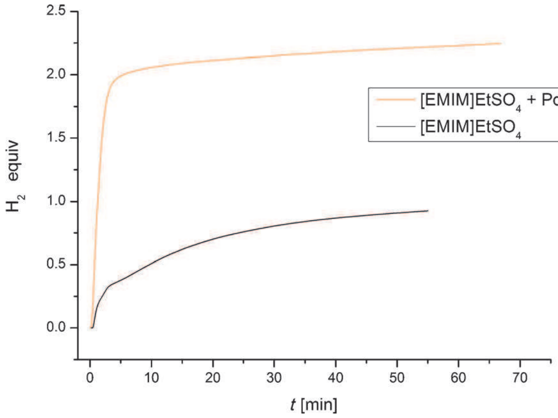

Figure 12. Pd(OAc)$_2$ supported hydrogen evolution from EDB in presence of [EMIM]EtSO$_4$.

Summary and Outlook

The storage of hydrogen in polar amine borane adducts is a promising field of research. With their unique solubilization properties and their supporting effects in dehydrogenation reactions, ILs are promising candidates for useful additives. The water content of hygroscopic ILs was found not to be crucial for enhanced hydrogen yield. The addition of metal salts to the mixture has shown encouraging results and led to a further increase in efficiency at low temperatures. Detailed analysis of the catalytically active species as well as optimization of the catalyst concentration and temperatures are further steps towards the employment of EDB as a hydrogen storage material in accordance with the Department of Energy targets.

Experimental Section

All reactants were obtained from Sigma–Aldrich, Acros, or Deutero and used as received. EDB was prepared as described by Autrey and co-workers,[11] and recrystallized from H_2O at 60 °C to yield a colorless crystalline substance, which was dried in vacuo. ILs were prepared by employing published methods.[19] Deuterated ILs were prepared by using an adapted method from Giernoth and co-workers.[17] Mass spectrometric investigations in the gas phase were conducted with a HPR20 gas analysis system by Hiden Analytical. The samples for mass spectrometry were prepared from freshly dehydrogenated EDB samples (120 °C). The dehydrogenated foamy solid was stirred with acetonitrile (ca. 3 mL). The suspension was centrifuged and decanted twice and analyzed by exact ion mass determination on a Thermo LTQ Orbitrap XL - FTMS Analyzer operating in positive-ion mode with a resolution of 30000. Sample ionization was conducted by ESI. Karl-Fischer Titration was performed on a 831 KF coulometer by metrohm with Hydranal® anolyte by Fluka. Detailed results can be found in the Supporting Information. Mass spectra were simulated by using the software mMass 5.5.0.[20]

All dehydrogenation reactions were carried out without precautions against moisture or oxygen unless otherwise stated. For the dehydrogenation experiments, in general 25 mg EDB was mixed with 25 mg of the respective IL in a glass reactor, connected to a mass flow meter and set into an aluminum block that was preheated to 120 °C (unless otherwise stated). For the dehydrogenation experiments employing metal salts, Arduengo carbene, or D_2O, the respective substance was added directly before heating. All Arduengo carbene and D_2O experiments were prepared in an argon glove box under exclusion of water and oxygen. The experiments employing metal salts were conducted with an addition of 10 wt% metal salt with respect to EDB. All dehydrogenation data were corrected by taking into account the data for empty glass reactors at the set temperature to compensate for thermal expansion. The amount of released hydrogen was determined with a mass flow meter from mks connected via an analogue connection to a desktop computer. The data were recorded with the software RealView 3.0 from ABACOM. Data processing was conducted with OriginPro 8.5G from OriginLab.

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[1] U. Eberle, M. Felderhoff, F. Schuth, *Angew. Chem.* **2009**, *121*, 6732 – 6757; *Angew. Chem. Int. Ed.* **2009**, *48*, 6608 – 6630.

[2] a) L. Schlapbach, A. Zuttel, *Nature* **2001**, *414*, 353 – 358; b) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613 – 2626.

[3] a) G. E. Ryschkewitsch, J. W. Wiggins, *Inorg. Chem.* **1970**, *9*, 314 – 317; b) S. S. Mal, F. H. Stephens, R. T. Baker, *Chem. Commun.* **2011**, *47*, 2922 – 2924; c) M. E. Bowden, I. W. M. Brown, G. J. Gainsford, H. Wong, *Inorg. Chim. Acta* **2008**, *361*, 2147 – 2153.

[4] A. C. Stowe, W. J. Shaw, J. C. Linehan, B. Schmid, T. Autrey, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1831 – 1836.

[5] a) M. E. Bluhm, M. G. Bradley, R. Butterick, U. Kusari, L. G. Sneddon, *J. Am. Chem. Soc.* **2006**, *128*, 7748 – 7749; b) D. W. Himmelberger, L. R. Alden, M. E. Bluhm, L. G. Sneddon, *Inorg. Chem.* **2009**, *48*, 9883 – 9889; c) W. R. H. Wright, E. R. Berkeley, L. R. Alden, R. T. Baker, L. G. Sneddon, *Chem. Commun.* **2011**, *47*, 3177 – 3179.

[6] T. B. Marder, *Angew. Chem.* **2007**, *119*, 8262 – 8264; *Angew. Chem. Int. Ed.* **2007**, *46*, 8116 – 8118.

[7] R. K. Ahluwalia, J. K. Peng, T. Q. Hua, *Int. J. Hydrogen Energy* **2011**, *36*, 15689 – 15697.

[8] A. D. Sutton, A. K. Burrell, D. A. Dixon, E. B. Garner, J. C. Gordon, T. Nakagawa, K. C. Ott, P. Robinson, M. Vasiliu, *Science* **2011**, *331*, 1426 – 1429.

[9] C. Reller, F. O. R. L. Mertens, *Angew. Chem.* **2012**, *124*, 11901 – 11905; *Angew. Chem. Int. Ed.* **2012**, *51*, 11731 – 11735.

[10] a) B. L. Davis, D. A. Dixon, E. B. Garner, J. C. Gordon, M. H. Matus, B. Scott, F. H. Stephens, *Angew. Chem.* **2009**, *121*, 6944 – 6948; *Angew. Chem. Int. Ed.* **2009**, *48*, 6812 – 6816; b) S. Hausdorf, F. Baitalow, G. Wolf, F. O. R. L. Mertens, *Int. J. Hydrogen Energy* **2008**, *33*, 608 – 614; c) L. G. Sneddon, “Amineborane-Based Chemical Hydrogen Storage”, *DOE Chemical Hydrogen Storage Center of Excellence*, Report, **2008**.

[11] D. Neiner, A. Karkamkar, M. Bowden, Y. Joon Choi, A. Luedtke, J. Holladay, A. Fisher, N. Szymczak, T. Autrey, *Energy Environ. Sci.* **2011**, *4*, 4187 – 4193.

[12] a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071 – 2083; b) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667 – 3691.

[13] a) P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926 – 3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772 – 3789; b) R. Sheldon, *Chem. Commun.* **2001**, 2399 – 2407; c) D. B. Zhao, M. Wu, Y. Kou, E. Min, *Catal. Today* **2002**, *74*, 157 – 189; d) T. Welton, *Coord. Chem. Rev.* **2004**, *248*, 2459 – 2477; e) V. I. Parvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615 – 2665; f) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123 – 150; g) R. Giernoth, *Angew. Chem.* **2010**, *122*, 2896 – 2901; *Angew. Chem. Int. Ed.* **2010**, *49*, 2834 – 2839; h) X. Yuan, G. Sun, H. Asakura, T. Tanaka, X. Chen, Y. Yuan, G. Laurenczy, Y. Kou, P. J. Dyson, N. Yan, *Chem-Eur J* **2013**, *19*, 1227 – 1234.

[14] S. Sahler, H. Konnerth, N. Knoblauch, M. H. G. Prechtl, *Int. J. Hydrogen Energy* **2013**, *38*, 3283 – 3290.

[15] a) L. Xu, W. Chen, J. Xiao, *Organometallics* **2000**, *19*, 1123 – 1127; b) J. D. Scholten, G. Ebeling, J. Dupont, *Dalton Trans.* **2007**, 5554 – 5560.

[16] a) M. J. Kamlet, R. W. Taft, *J. Am. Chem. Soc.* **1976**, *98*, 377 – 383; b) P. G. Jessop, D. A. Jessop, D. B. Fu, L. Phan, *Green Chem.* **2012**, *14*, 1245 – 1259.

[17] R. Giernoth, D. Bankmann, *Tetrahedron Lett.* **2006**, *47*, 4293 – 4296.

[18] S. Basu, Y. Zheng, J. P. Gore, *J. Power Sources* **2011**, *196*, 734 – 740.

[19] a) S. Csihony, C. Fischmeister, C. Bruneau, I. T. Horvath, P. H. Dixneuf, *New J. Chem.* **2002**, *26*, 1667 – 1670; b) J. Jacquemin, P. Goodrich, W. Jiang, D. W. Rooney, C. Hardacre, *J. Phys. Chem. B* **2013**, *117*, 1938 – 1949.

[20] T. H. J. Niedermeyer, M. Strohalm, *Plos One* **2012**, *7*.

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