Recycle of tin thiolate compounds relevant to ammonia–borane regeneration†

Andrew D. Sutton,*[a] Benjamin L. Davis,[a] Koyel X. Bhattacharyya,[a] Bobby D. Ellis,[b] John C. Gordon*[a] and Philip P. Power*[b]

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The use of benzenedithiol as a digestant for ammonia–borane spent fuel has been shown to result in tin thiolate compounds which we demonstrate can be recycled, yielding Bu_3SnH and *ortho*-benzenedithiol for reintroduction to the ammonia–borane regeneration scheme.

A necessary target in realizing a hydrogen (H_2) based economy, especially for the transportation sector, is its storage for controlled delivery, presumably to an energy producing fuel cell.[1] Chemical hydrogen storage has been dominated by one appealing material, ammonia–borane ($H_3N–BH_3$, AB), due to its high gravimetric capacity of hydrogen (19.6 wt%) and low molecular weight (30.7 g mol^{-1}). In addition, AB has both hydridic and protic moieties, yielding a material from which H_2 can be readily released in contrast to the loss of H_2 from C_2H_6, which is substantially endothermic.[2] A number of publications have described H_2 release from amine boranes, yielding various rates depending on the method applied.[3–6] The viability of any chemical hydrogen storage system is critically dependent on efficient recyclability, but reports on the latter subject are sparse, invoke the use of high energy reducing agents, and suffer from low yields.[1,7–10]

We recently described an energy efficient regeneration process for polyborazylene (PB) spent fuel.[11] In this scheme, PB is digested with *ortho*-benzenedithiol to yield $[NH_4][B(C_6H_4S_2)_2]$ (**1**) and $(C_6H_4S_2)BH{\cdot}NH_3$ (**2**). **1** can then be converted into **2** using Bu_3SnH as a reductant with $C_6H_4SH(S–SnBu_3)$ (**3**) as a by-product, thus resulting in a single boron containing compound that can subsequently be converted to AB using a slight excess of Bu_2SnH_2.[11] Modification of this process due to the relative instability of Bu_2SnH_2 enables us to carry out the reduction chemistry with Bu_3SnH *via* an amine exchange step with Me_3N. In such a scheme, the use of Bu_3SnH as the reductant produces $C_6H_4(S–SnBu_3)_2$ (**4**) as a by-product. In order to maximize the overall efficiency of an AB regeneration process which utilizes the Sn–H moiety in a reduction step, recycle of the tin-containing by-products is essential, and herein we report a recycle scheme for the regeneration of both Bu_3SnH and the digesting reagent *ortho*-benzenedithiol from **3** and **4** (Fig. 1).

Our focus in this regard was centered on the conversion of **3** and **4**, *i.e.*, species containing Sn–SR bonds, to a species containing a formate moiety, ($Bu_3Sn–OC(O)H$), as this compound has been described as a precursor to Bu_3SnH *via* thermal decarboxylation.[12] Our initial investigations focused on a relatively simple system, *i.e.*, Bu_3SnSPh (**5**), which can be formed by refluxing $(Bu_3Sn)_2O$ and PhSH in a 1 : 2 molar ratio in toluene with a Dean–Stark apparatus (to collect the water generated). After refluxing for 12 h the toluene was removed *in vacuo* and the product distilled under reduced pressure to yield **5** in near quantitative yield. Direct reaction of **5** with formic acid does not result in a clean reaction, and although some evidence does exist for the production of $Bu_3Sn–OC(O)H$, an equilibrium appears to exist which predominantly favors

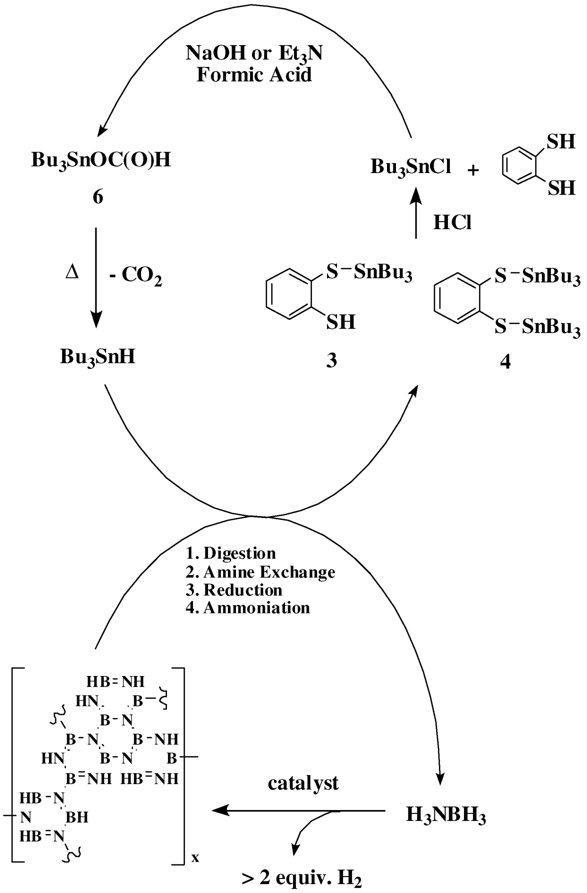

Fig. 1 Regeneration of AB with tin recycle and *ortho*-benzenedithiol recovery.

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[a] *Los Alamos National Laboratory, Los Alamos, NM 87545, USA. E-mail: adsutton@lanl.gov; Fax: (+1) 505 667 9905; Tel: (+1) 505 665 2931*
[b] *University of California, Davis, One Shield Ave, Davis, CA 96363, USA. E-mail: pppower@ucdavis.edu; Fax: (+1) 530 752 8995; Tel: (+1) 530 752 6913*

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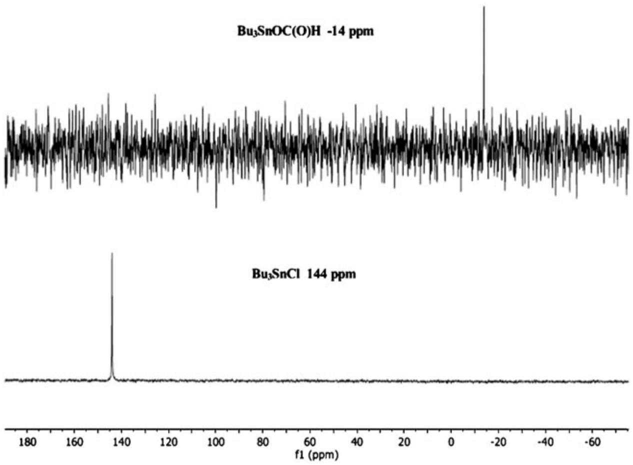

Fig. 2 ^{119}Sn {^{1}H} NMR spectra of Bu$_3$SnCl (bottom) conversion to Bu$_3$SnOC(O)H (top) following reaction with base and formic acid.

the presence of **5** at ambient temperature. No enhancement of Bu$_3$Sn–OC(O)H is observed by NMR spectroscopy at increased temperatures although a slight increase of **5** is observed with increasing concentrations of formic acid. In support of this fact is the observation that independently prepared Bu$_3$SnOC(O)H and PhSH react instantly to form **5** at room temperature, which indicates that the equilibrium lies heavily in favor of the Sn–SPh species.

However, when Bu$_3$SnSPh was dissolved in an ethereal solution of HCl (1.0 M, 0.5 mL), this resulted in clean conversion to Bu$_3$SnCl and PhSH. Upon removal of solvent and subsequent redissolution in deutero solvent, this gave an approximately 1 : 1 ratio of these two species according to ^{1}H NMR spectroscopy with no evidence for any residual **5**, indicating near quantitative conversion to the desired products.

After satisfactorily studying a model system, we then pursued the same conversion with the by-products of AB regeneration. Initial studies of $C_6H_4SH(S–SnBu_3)$[11] (**3**) in HCl–Et$_2$O in the above manner indeed yielded Bu$_3$SnCl and $C_6H_6S_2$ in a 1 : 1 ratio, as expected. On scale-up **3** can be converted to Bu$_3$SnCl (83% isolated yield) following washing and drying the resultant solid several times with Et$_2$O. **3** was not observed in either the ^{1}H or ^{11}B NMR on redissolution of the solid. Compound **4** can be readily synthesised *via* a salt metathesis route in THF from $[C_6H_4S_2][Na]_2$ and two equivalents of Bu$_3$SnCl in high yield (93%). Similarly to the model compound **3**, **4** can also be converted to Bu$_3$SnCl and *ortho*-benzenedithiol as expected with Bu$_3$SnCl being isolated (87% yield), again with no indication of residual **4** present. This shows that both the Sn–SR by-products of digestion, **3** and **4**, can be readily converted to Bu$_3$SnCl, which allows the following stages to be applied to either digestion scheme. The *ortho*-benzenedithiol can also be recovered by vacuum distillation at this stage under mild conditions (b.p. 119–120 °C, 17 torr). Attempts to achieve accurate isolated yields of *ortho*-benzenedithiol on removal of the solvent were hampered due to its volatility under dynamic vacuum and slight loss of the isolated compound following the rigorous washing and drying of the resultant Bu$_3$SnCl.

After the *ortho*-benzenedithiol has been removed, the resulting Bu$_3$SnCl that is subsequently formed can then be converted to Bu$_3$SnOC(O)H (**6**) *via* the reaction of Bu$_3$SnCl with formic acid in the presence of either NaOH or Et$_3$N which presumably proceeds *via* the formation of (Bu$_3$Sn)$_2$O. **6** is quantitatively formed as shown by ^{119}Sn NMR spectroscopy (Fig. 2) at room temperature. **6** has also been synthesised independently by refluxing a toluene solution of (Bu$_3$Sn)$_2$O with formic acid, followed by removal of solvent and distillation of the product giving 78% yield of **6**. The distillation of **6** through a column of 3 mm Raschig rings under reduced pressure (112 °C, 0.3 torr) afforded 60% isolated yield of Bu$_3$SnH, which can re-enter the AB regeneration process.

In conclusion, we have demonstrated that Bu$_3$SnH and *ortho*-benzenedithiol components can be recycled following their use in a scheme to recycle the tin reductant for AB regeneration which is a necessary component for a viable AB regeration scheme.

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