Hypergolicity

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Green Bipropellants: Hydrogen-Rich Ionic Liquids that Are Hypergolic with Hydrogen Peroxide**

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Researchers working in the area of rocket propulsion strive for environmental friendliness, low toxicity, and overall operability, as well as a performance level comparable with current propellant combinations such as hydrazine and N_2O_4. Maintaining high performance while lowering hazards is extremely difficult.

All rocket oxidizers are hazardous by their very nature, and so reduction of those hazards, even though the resulting materials might not be completely harmless, is at the heart of green initiatives in propulsion. The corrosivity of nitric acid is well known, and, although N_2O_4 is much less corrosive, it combines high toxicity with high vapor pressure. A significant step to a lower-toxicity bipropulsion system would be the demonstration of hypergolicity (spontaneous ignition) between an ionic liquid (IL), which is a paragon of low vapor toxicity, and a safer oxidizer. Apart from cryogens, hydrogen peroxide seems to be especially promising because of its high performance, less-toxic vapor and corrosivity, and its environmentally benign decomposition products,[1] which make handling this oxidizer considerably less difficult than N_2O_4 or nitric acid.

A high fuel performance can be fostered by light metals with large combustion energies and relatively light products. Elements with considerable performance advantages and nontoxic products are aluminum and boron. The need for light combustion products through the production of hydrogen gas and water vapor is fulfilled by a high hydrogen content. Aluminum and boron are well known for their ability to serve as hydrogen carriers in neutral and ionic molecules. Defense research in the 1960s focused extensively on the development of hydrogen-containing fuels with boron, aluminum, and other metals,[2] but was mainly concerned with neutral compounds that have high vapor toxicity. Their rich anionic chemistry combined with the design flexibility of ILs presage novel materials that have the potential to overcome problems that caused these promising propellants to be abandoned.

To date, no IL has been reported to be hypergolic with H_2O_2, and first-generation hypergolic ILs based on dicyanamide, nitrocyanamide, and azide anions lack high hydrogen content.[3] We tested ILs from each class with 90% and 98% H_2O_2, and all failed to ignite. This result is hardly surprising since fuels that are hypergolic with nitric acid vastly outnumber those that ignite with N_2O_4. For many years, hydrazine was the only fuel hypergolic with H_2O_2.[4]

Since solutions of lithium aluminum hydrides and $LiBH_4$ in ethers have demonstrated H_2O_2 hypergolicity,[5] the same behavior from ILs with metal hydride anions might be expected. However, the development of energetic room-temperature ILs (RTILs) with metal hydride anions involves a number of technical challenges. Simple metal hydride anions are poor liquefying agents. Furthermore, heterocyclic, unsaturated salts that feature imidazolium, triazolium, pyridinium, and other common IL cations are reduced by BH_4^- ions,[6] thus negatively affecting their thermal stability.

Saturated ammonium/heterocyclic cations therefore might be better candidates for RTIL metal hydrides; indeed there are two patents that feature quaternary ammonium aluminum hydrides.[7] Examples included trioctyl-*n*-propylammonium aluminum hydride (m.p. 65–66 °C) and trioctylmethylammonium aluminum hydride (viscous liquid). While these data are interesting, a cation that results in a stable, free-flowing RTIL with a simple metal hydride might not be easily found.

Another approach to liquefying metal hydrides is to replace hydrogen atoms with other groups. 1-Butyl-2,3-dimethylimidazolium cyanoborohydride (CBH) is reported to be a low-viscosity IL.[8] We prepared a variety of new CBH ILs,[9a] and Zhang and Shreeve prepared novel dicyanoborohydrides (DCBH) ILs.[9b] While all of these compounds are fast-igniting with nitric acid, our tests with CBH ILs and H_2O_2 revealed excessive ignition delays of several seconds. Since we also obtained negative results with 1-butyl-3-methylimidazolium tetracyanoborate, it is probable that DCBH ILs are equally unsuitable.

Another approach would be to combine an IL with aluminum borohydride (ABH) to form complex anions such as $Al(BH_4)_4^-$ (Scheme 1). Tetrabutylammonium (TBA)$Al(BH_4)_4^-$ has a melting point of 50 °C, which is 75 °C lower than the uncomplexed borohydride.[10] Noeth and Ehemann reported trioctyl-*n*-propylammonium $Al(BH_4)_4^-$ as a "viscous oil crystallizing very slowly".[11]

In view of the advantages of high hydrogen content, RTILs containing $Al(BH_4)_4^-$ ions may be viewed as a densified form of hydrogen stabilized by metal atoms. The volumetric hydrogen contents of tetraethylammonium

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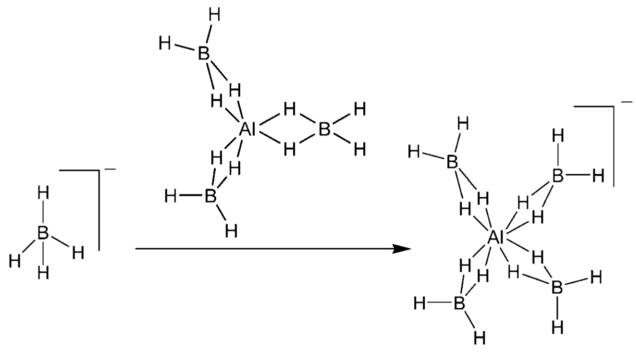


Scheme 1. Generic method for preparing ABH-containing ions.

(TEA)- and (TBA)$Al(BH_4)_4$[10] are 99% and 68% higher than that of liquid hydrogen.

Herein we report on our first efforts to prepare RTIL borohydrides with subsequent conversion to $Al(BH_4)_4^-$ RTILs and the reactivity of both toward oxidizers including hydrogen peroxide. We repeated a previously reported preparation of TEA $Al(BH_4)_4^-$,[10] a solid with a decomposition point of 150 °C, and obtained its X-ray crystal structure (Figure 1).

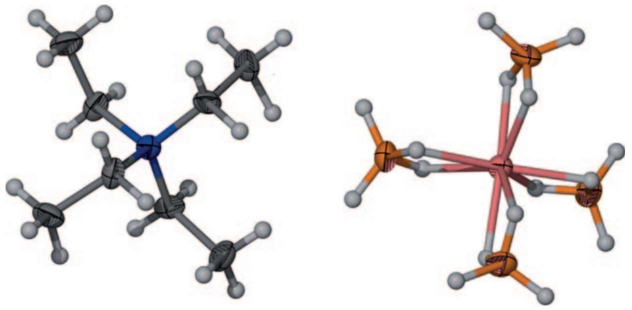
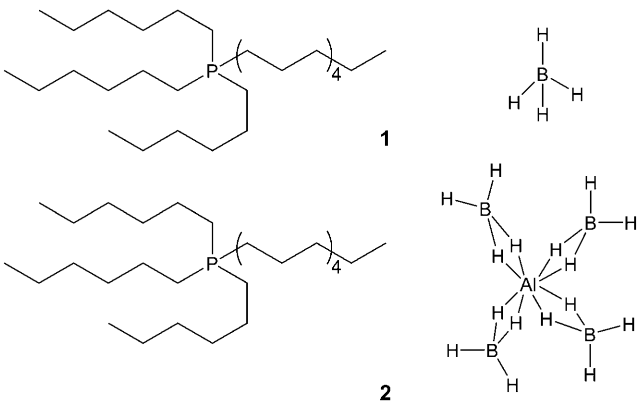


Figure 1. ORTEP diagram of the cation and anion of (TEA)$Al(BH_4)_4$ (disorder removed for clarity; thermal ellipsoids set at 50% probability). Al dark pink, B orange, C dark gray, H light gray, N blue.

The trihexyltetradecylphosphonium (THTDP) cation has been used to transform fullerenes into RTILs and forms liquids with BH_3Cl^-.[12,13] (THTDP)Cl is also soluble in most organic solvents, thus enabling facile, quantitative anion exchange of Cl^- for BH_4^- and making this cation an appealing component for our initial research. The new material (THTDP)BH_4 (**1**) is a viscous RTIL and was characterized by NMR and Raman spectroscopy. Subsequent reaction with a slight excess of ABH produced, in quantitative yield, the first RTIL **2** that incorporates a $Al(BH_4)_4^-$ ion (Scheme 2). Compound **2** is colorless and free-flowing (Figure 2) and was characterized by NMR and Raman spectroscopy, differential scanning calorimetery (DSC), and mass-balance and hydrogen analyses. A simple vacuum thermal stability test and isothermal thermogravimetric analysis (TGA) at 75 °C (48 h) revealed no mass loss. Vibrational spectroscopy proved especially useful as the cation and anion stretch vibrations do not overlap and the ν_{BH} signals of **1** are easily distinguished from those of **2** (Figure 3).



Scheme 2. Borohydride ILs **1** (top) and **2** (bottom).

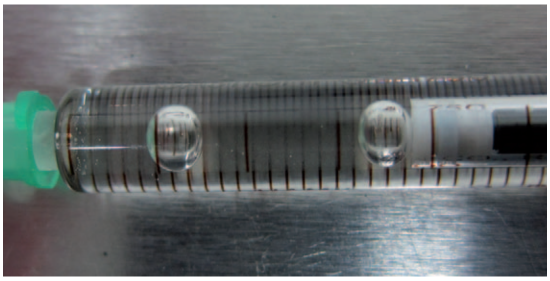


Figure 2. Image of a 250 μL syringe filled with **2** (note two air bubbles).

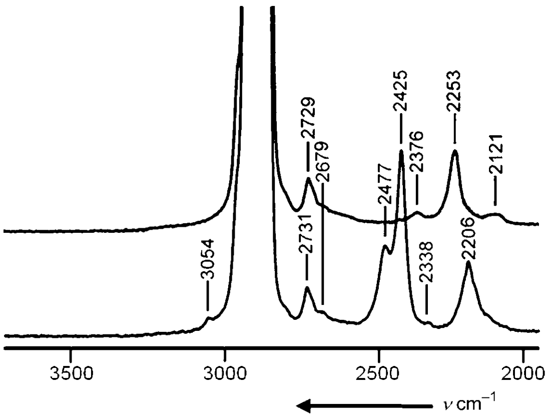


Figure 3. Raman spectra of **1** (upper) and **2** (lower; only the ν_{CH} and ν_{BH} region is shown).

The new materials were then subjected to drop tests to determine their reactivity with common propulsion oxidizers, including 90% and 98% H_2O_2 (Table 1). While **1** lights only 3 s after dropping onto H_2O_2, the ignition delay of **2** was quite short. The hypergolic dicyanamide ILs display changes in delay times (with white fuming nitric acid, WFNA) from 30 ms to 1000 ms[14] upon reversal of the order of addition of

Table 1: Drop test results of **2** on four oxidizers (N_2 atmosphere).[a]

	90% H_2O_2	98% H_2O_2	N_2O_4	WFNA
reactivity with **2**	ignition	ignition	ignition	explosion
ignition delay	< 30 ms	< 30 ms	–[b]	–

[a] See the Supporting Information for details. [b] IL ignited with N_2O_4 vapors before the liquids combined.

oxidizer and fuel. In contrast, the ignition of **2** is equally fast regardless of the order of addition.

These simple drop tests place only upper limits on the ignition delays because ignition may be initiated by hydrogen, which burns with an almost invisible flame. However, these tests do demonstrate that an RTIL with a complex ABH anion is universally reactive with traditional rocket oxidizers including lower hazard H_2O_2. Furthermore, this new class of ILs holds the potential for enabling high-performing, non-cryogenic, green bipropulsion for the first time.

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