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Hypergolic Ionic Liquids

Borohydride Ionic Liquids and Borane/Ionic-Liquid Solutions as Hypergolic Fuels with Superior Low Ignition-Delay Times**

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In memory of Malcolm MacKenzie Renfrew

Abstract: *In propellant systems, fuels of choice continue to be hydrazine and its derivatives, even though they comprise a class of acutely carcinogenic and toxic substances which exhibit rather high vapor pressures and require expensive handling procedures and costly safety precautions. Hypergolic ionic liquids tend to have low volatility and high thermal and chemical stability, and often exhibit wide liquid ranges, which could allow the use of these substances as bipropellant fuels under a variety of conditions. A new family of borohydride ionic liquids and borane–ionic-liquid solutions is described which meets nearly all of the desired important criteria for well-performing fuels. They exhibit ignition-delay times that are superior to that of any known hypergolic ionic liquid and may thus be legitimate replacements for hydrazine and its derivatives.*

Hypergolic fuels are chemical species that can be ignited under ambient conditions upon contact with an oxidant. Hypergolic liquid propellants are commonly used as fuels in rocket engines because of their high specific impulse, excellent ignition with a low ignition-delay (ID) time, and superior thrust control.[1,2] Combinations of hydrazine derivatives with dinitrogen tetroxide or white fuming nitric acid (WFNA) are currently employed as hypergolic liquid bipropellants. Unfortunately, the high vapor pressures of hydrazine derivatives in conjunction with their acute toxicity and carcinogenicity necessitate costly handling procedures and create difficulties during the manufacture, storage, transportation, and application of these compounds.[3–6] Nontoxic liquid hypergolic fuels with low vapor pressures, high energy densities, and short IDs are needed as safer, more cost effective alternatives.

Ionic liquids (ILs), designed and synthesized as a combination of different cationic and anionic components, have been studied as energetic materials in propellant applications.[7] The ability to modify both the cation and the anion of an IL chemically results in materials with tunable properties. Negligible vapor pressures (<1 Pa)[8] are one of the extraordinary properties of ILs and offer the possibility of employing these materials as substitutes for volatile hypergolic fuels (e.g., unsymmetrical dimethylhydrazine (UDMH)). Since the first report of a hypergolic IL in 2008,[9] growing interest in the development of new materials for use as propellants and fuels has resulted in research directed toward the design and synthesis of a variety of hypergolic ILs with low melting points, wide liquid ranges, high thermal stabilities, and short ignition-delay (ID) times.[10–16]

The ID time is one of the important parameters in evaluating the potential value of a hypergolic IL. A short ID is an important factor in effective combustion. Although the target ID of designed ILs was historically approximately 50 ms, current targets are significantly shorter—typically in the range of a few milliseconds, depending on the application. We earlier designed several new ILs with considerably reduced ID times.[10,12,16]

Our first success was the synthesis of ILs featuring 2,2-dimethyltriazanium (DMTA) cations $[(Me)_2N(NH_2)_2^+]$.[12] The ID of DMTA·DCA (DCA = dicyanamide) was approximately 22 ms, and that of the DMTA nitrate was 4 ms.[12] Discovered after the DMTA ILs, ILs that contain the dicyanoborate (DCB) anion $[BH_2(CN)_2^-]$ are another series of hypergolic ILs with remarkably short ID times; for example, the ID of 1-allyl-3-methylimidazolium dicyanoborate is 6 ms, and 4 ms was found for *N*-allyl-*N*,*N*-dimethylhydrazinium dicyanoborate.[10] Unfortunately, both of these types of ILs are plagued by some shortcomings that may preclude their practical application. For example, they are difficult to synthesize and formed in low yields; their synthesis requires the use of silver salts; and they have undesired properties, such as the high melting point (99 °C) of the DMTA nitrate. To overcome these shortcomings, we employed borane derivatives as additives to modify the IDs of hypergolic ILs.[17] The use of boranes as additives to common hypergolic ILs results in mixed fluids with ID times far shorter than those exhibited by neat ILs. The ID of hydrazine borane/1-butyl-3-methylimidazolium dicyanamide (BmimDCA) solution is 3 ms, whereas the ID time of pure BmimDCA is 47 ms.[8,17] Although boranes are effective in significantly decreasing ID times, they are typically solids and may have limited solubility in ILs.

As a suitable replacement for hydrazine or its derivatives, a hypergolic IL or IL–additive system should be readily

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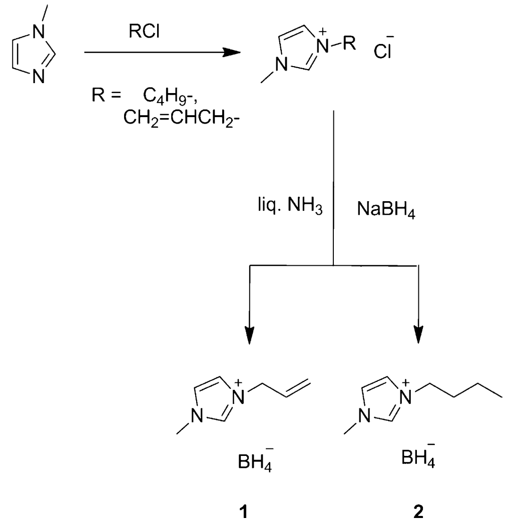
obtained. We reported previously that both sodium and potassium borohydride (BH_4^-) are hypergolic in the presence of WFNA or H_2O_2.[10] As described herein, borohydride-based ILs and ILs with borane additives have considerable potential in the field of hypergolic fluids because of short IDs. Commercially available, inexpensive materials, $NaBH_4$ and liquid triethylamine borane, were utilized in the synthesis of borohydride-based ILs or as additives in borane–IL solutions. These materials were then tested for their hypergolic properties with WFNA and were shown to have very short ID times.

The synthesis of BH_4-based ILs has been previously studied,[18] and liquid ammonia was found to be a reliable medium for their synthesis.[19] Now AmimBH$_4$ (**1**) and BmimBH$_4$ (**2**; Scheme 1) were prepared[19] and fully characterized (see the Supporting Information). Allyl substituents were selected because the functionalization of cations with allyl substituents is known to enhance the ignition properties of ILs.[9,14] The physicochemical properties of the ILs **1** and **2**, such as their phase-transition temperature (T_m or T_g), thermal-decomposition temperature (T_d, onset), viscosity, and density (ρ), were determined by differential scanning calorimetry (DSC), microviscometry, and gas pycnometry. The heat of formation and heat of combustion of **1** and **2** were calculated. Their ID times were obtained by droplet tests (Table 1).



Scheme 1. Synthesis of borohydride-based ILs.

One of the desirable properties of propellants used in liquid-fuel rocket engines is that they are liquids in the operating temperature range of −40 to +60 °C.[20] The T_d(onset) values of **1** and **2** were found to be 93.3 and 99.9 °C, respectively. Both ILs containing the BH_4^- anion exhibited moderate thermal stability and a wide liquid range, with T_m (or T_g) values below −60 °C. The density of a fuel is an important property: the higher the density of the fuel, the smaller the volume required in the rocket fuel tank. The density of **1** and **2** is less than 1.0 g cm^{-3}. However, their density is 13 % larger than that of UDMH (0.793 g cm^{-3}; Table 1).

The addition of borane-based additives to hypergolic ILs is known to enhance their ignition properties. Neat triethylamine and borane have been reported to be hypergolic;[21,22] therefore, we expected that their combination as a triethylamine–borane (TEAB) complex would enhance hypergolicity. Solubility tests showed that the TEAB complex was miscible in any ratio with the IL BmimDCA, thus suggesting that TEAB would be unlikely to precipitate from its IL solution at 25 °C and could be utilized over a wider range of temperatures. Given that the melting point of TEAB is −4 °C, the TEAB/IL solutions may freeze with a high content of TEAB. DSC showed that when the mass ratio of TEAB/BmimDCA was ≤ 1:4, the T_m value of the TEAB/BmimDCA solution was lower than −60 °C. Thus, there is a wider liquid range for TEAB/BmimDCA solutions than for UDMH (Table 1).

The heats of formation (ΔH_f) and heats of combustion (ΔH_c) of ILs **1** and **2** and TEAB solutions were calculated (Table 1). The ΔH_f values of **1** and BmimDCA are higher than that of UDMH (Table 1). Also, the ΔH_f value of TEAB/BmimDCA solutions can be adjusted by changing the ratio of TEAB to BmimDCA. When the ratio of BmimDCA to TEAB was increased to more than 2.8:1, the ΔH_f value of the

Table 1: Physicochemical properties of the borohydride-based ILs and the TEAB/BmimDCA solutions.

Sample	T_m/T_g [°C]	T_d (onset) [°C]	ρ [g cm^{-3}]	η [mPa s]	ID [ms]	ΔH_f [kJ mol^{-1}]	ΔH_c [kJ mol^{-1}]
1	< −60	93.3	0.90	113.8	2	117.8	−5653
2	< −60	99.9	0.91	486.6	38	38.9	−6539
TEAB[23]	−4	223.0[a]	0.78	2.7	–[b]	−198.6	−5467
solution 1 (2:1)[c]	−9.0	116.3	0.87	7.0	3	−110.0	−5646
solution 2 (3:2)[c]	−10.6	109.8	0.89	8.3	4	−88.5	−5689
solution 3 (1:1)[c]	−13.3	112.1	0.92	10.9	4	−53.2	−5761
solution 4 (1:2)[c]	−19.8	85.5/121.0	0.96	15.1	3	15.3	−5899
solution 5 (1:4)[c]	< −60	88.7/124.1	1.01	19.4	4	81.3	−6032
solution 6 (1:6)[c]	< −60	90.8/127.5	1.03	21.4	12	113.4	−6097
solution 7 (1:9)[c]	< −60	91.7/129.0	1.05	23.6	20	139.2	−6149
BmimDCA[24]	−6/−90[d]	300.0	1.06	33.2[d]	46	206.2[24]	−6285
UDMH[25]	−57.2	64.0[a]	0.79	0.49	4.8[26]	48.3	−1979

[a] Boiling point. [b] Ignition occurred in the vapor phase (Figure 1 b). [c] Mass ratio of TEAB to BmimDCA. [d] −6 °C and −90 °C refer to the glass transition temperature and melting point of BmimDCA.

solution was higher than that of UDMH. TEAB has a density similar to that of UDMH. By increasing the IL content in the TEAB/BmimDCA solution, a density greater than that of UDMH was achieved. BmimDCA could be replaced with different ILs to adjust not only the ΔH_f value of the solution, but also other properties (density, viscosity, etc.). Our approach may thus serve as new methodology for preparing hypergolic fuels with adjustable properties.

Rapid ID times are perhaps the single most notable characteristic of tetrahydroborate-containing compounds. We carried out ignition tests to evaluate the hypergolicity of the two new systems. A series of high-speed-camera photographs (1000 fps) of the ignition tests are shown in Figure 1. During the drop test of IL **2**, intensive ignition took place, with a measured ID of 38 ms. The ID of IL **1** was 2 ms—faster than that of any known hypergolic IL.[7–15] Although the acceleration of ignition induced by the allyl substituent was expected, the unprecedented short ID time of IL **1** was particularly encouraging. This fast ID time was achieved despite the highly viscous nature of **1** (Table 1).

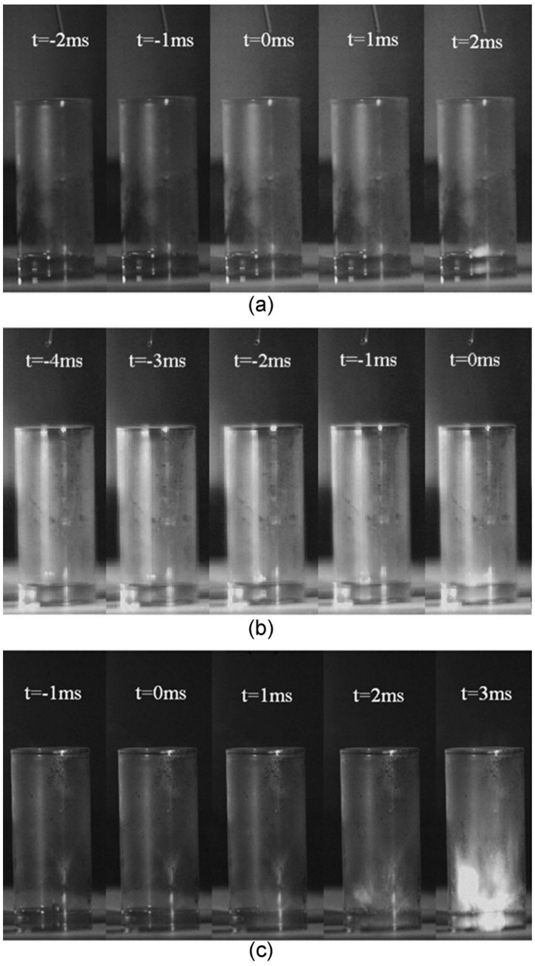


Figure 1. The ID tests shown as a series of high-speed-camera photographs of the fuel contacting WFNA: a) $AmimBH_4$; b) TEAB; c) a solution of 33% TEAB in BmimDCA.

The drop test of TEAB showed that TEAB ignited in the vapor phase with WFNA (Figure 1a; see also Figure S18 in the Supporting Information), thus suggesting superior hypergolicity. BmimDCA (ID time: 47 ms) was selected as the hypergolic solvent.[8] The IDs of TEAB/BmimDCA containing different ratios of TEAB were measured subsequently (Table 1). Initially, the experimental ID of the tested fluids was found to decrease with an increasing concentration of TEAB. With TEAB compositions greater than 20% (mass), the ID remained constant at 3 ms, which equals the shortest ID of any hypergolic fluid to date.[17] Clearly, as evident from the much smaller molar ratio of the borane additive to the IL component as compared to our earlier study (TEAB, 0.37:1; ammonia borane, 2.7:1; hydrazine borane, 2.4:1),[17] TEAB is the most efficient additive reported to date for decreasing IDs.

Besides the superior low IDs of the TEAB/BmimDCA solutions, lower toxicities of TEAB and BmimDCA relative to that of UDMH can be concluded from their Material Safety Data Sheets (see Table S2 in Supporting Information). Even though we were unable to measure the toxicity of the two new ILs, their negligible vapor pressures cause them to be more environmentally benign than UDMH. On the basis of these tables and discussion, we conclude that both TEAB and BmimDCA are less toxic than UDMH.

TEAB is a liquid at room temperature. It is not sensitive to moisture, and its vapor pressure (0.13 kPa at 28 °C)[27] is much lower than that of UDMH (22.3 kPa at 25 °C).[28] According to the Raoult law, TEAB/IL solutions have lower vapor pressures than pure TEAB and therefore present a lower inhalation risk in their applications when TEAB is used as an additive for hypergolic fuels.

Natural bond orbital (NBO) analysis was used to assess the electronic charge distribution. NBO analysis of TEAB (see Figure S16 and Table S1) indicated an electronic charge distribution similar to that found in ammonia borane and hydrazine borane.[17] It is assumed that TEAB shares a similar protonation mechanism during the ignition process, whereby a proton is accepted by the nitrogen atoms, and that the nitrate salt forms during the ignition process.[17]

The application of molecular-orbital theory has been successful in explaining and predicting chemical behavior for an enormous number of molecules.[29] The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) reflects the kinetic stability of the individual species and their reactivity toward chemical reactions in some sense.[30] The HOMO–LUMO energy gap ($\Delta E_{\text{L-H}} = 0.6040$ a.u.) of TEAB is higher than that of UDMH ($\Delta E_{\text{L-H}} = 0.5607$ a.u.; see Table S3 for the corresponding theoretical calculations). The larger value of the energy gap between the frontier molecular orbitals suggests that TEAB is more stable than UDMH (Figure 2).

In conclusion, borohydride-based ILs and an IL with a borane-based additive have been found to be hypergolic with WFNA. The ID times of the borohydride-based ILs were as short as 2 ms, whereas IL solutions of a borane-based additive had a lowest ID of 3 ms. Borohydride-based ILs possess the shortest IDs of any known hypergolic ILs, and the

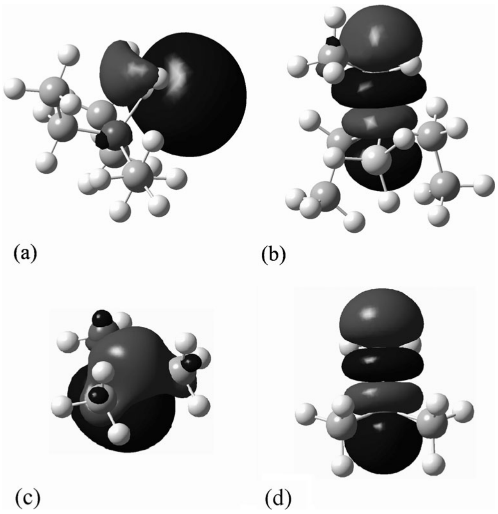


Figure 2. The frontier molecular orbitals of TEAB and UDMH: a) HOMO of TEAB; b) LUMO of TEAB; c) HOMO of UDMH; d) LUMO of UDMH.

triethylamine–borane complex is the most efficient hypergolic additive yet studied. Therefore, borohydrides and boranes have great potential not only in accelerating the ignition of hypergolic liquid fuels, but also perhaps for the replacement of hydrazine derivatives owing to their higher density, lower vapor pressure and toxicity, and adjustable heats of formation and viscosities. Further research into more stable and faster borohydride and borane systems is warranted, since they represent an exciting new class of hypergolic materials.

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