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Hypergolics

Dicyanoborate-Based Ionic Liquids as Hypergolic Fluids**

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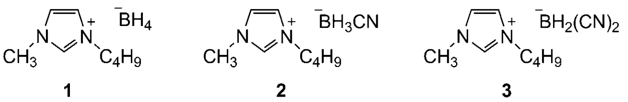
Hypergolicity, the spontaneous reaction of one chemical (fuel) when contacted with another (oxidizer), is not a new concept since suitable reactions have been reported where a very large variety of liquid–liquid, liquid–solid, and solid–solid combinations were and persist in being employed. In propellant systems, the fuels of choice continue to be hydrazine and its derivatives although they are a class of acutely toxic and carcinogenic substances, and have high vapor pressures so that costly safety precautions and handling procedures are required.[1–4] Common oxidizers include HNO_3, N_2O_4, and H_2O_2.[5–7] A few ionic liquids which characteristically exhibit low vapor pressure, and high thermal and chemical stability, have been found to be hypergolic with oxidizers such as N_2O_4 and white fuming nitric acid (WFNA), and thus show some promise as potential substitutes for hydrazine and its derivatives.[8–14]

In 2008, a few dicyanamide-containing ionic liquids were first reported to be hypergolic.[8] In the intervening time, ionic liquids comprised of a variety of cations and anions have been synthesized and tested for hypergolic properties. Currently the majority of ionic liquids that have been demonstrated to be hypergolic contain either the dicyanamide or nitrocyanamide anion; however, some ionic liquids are also hypergolic when comprised of nitrate,[11] azide,[14] and even chloride anions.[11] While it appears that the role of the cation is to tune the properties of the resulting ionic liquids, which is consistent with the point that the anions play the determinative role in the hypergolic ignition process,[8–14] hypergolicity is not strictly predictable—especially, for example, when with a common cation, the nitrocyanamide salt exhibits a shorter ignition delay (ID) time than the known dicyanamide analogue although the latter is most often the anion of choice.[14] Moreover, there are still no hypergolic ionic liquids which concomitantly meet all of the desired criteria, such as wide liquid ranges, high thermal and hydrolytic stabilities, low viscosities to enhance ease of mixing fuel and oxidizer, and short ID times which preclude a collection of fuel and oxidizer that could subsequently result in a concomitant explosion.[1,15] While some hypergolic ionic liquids may look promising because they display the occasional relatively short ID times, their melting points or viscosities are too high, or other properties may be less attractive and vice versa; for example, 2-azido-*N*,*N*,*N*-trimethylethylammonium nitrocyanamide which has the rather short ID time of 8 ms but a high melting temperature of 28 °C.[14] Among the reported hypergolic ionic liquids, 1-propargyl-3-methylimidazolium dicyanamide may be one of the better salts because of its balanced properties such as glass transition temperature $T_g = -61\,°C$, decomposition temperature $T_d = 144\,°C$, viscosity $\eta = 110$ mPa s, and an ID of 15 ms.[8] In order to enhance the application of ionic liquids as hypergolic propellants, to discover additional hypergolic ionic liquids, and to understand the mechanism which will enable the design of new hypergolic salts with better properties is a challenging task.

Now, for the first time, we can report that a new family of ionic liquids which contain the dicyanoborate anion in combination with a variety of cations is hypergolic and meets nearly all of the important criteria including wide liquid ranges, low viscosities, and short ignition delay times over a relatively limited time span.

Since, in preliminary experiments, it was found that sodium and potassium borohydride are hypergolic when contacted with WFNA, a borohydride-based ionic liquid, 1-methyl-3-butylimidazolium borohydride (**1**) was prepared and found to be hypergolic in WFNA (Scheme 1). However, the borohydride-based ionic liquids are very water-sensitive and thus require preparation in anhydrous organic solvents, and storage in an anhydrous environment. In an effort to find water-stable hypergolic ionic liquids, a cyanoborate-based ionic liquid, 1-methyl-3-butylimidazolium cyanoborate (**2**) was prepared, and it, also, was shown to be hypergolic with WFNA. Unfortunately, the cyanoborate-based ionic liquids are also water-sensitive, although they are less sensitive than the corresponding borohydrides. In the next borate-anion ionic liquid synthesis, using the dicyanoborate anion in 1-methyl-3-butylimidazolium dicyanoborate (**3**) gave a new ionic liquid which was an encouraging success.[16] Compound **3** is hypergolic with WFNA and not only is water-stable, but can be synthesized in water. A series of high-speed camera photos of a hypergolic drop test are shown in Figure 1. The light green flame is typical of the ignition of boron compounds. Considering that the borohydride-, cyanoborate-, and dicyanoborate-based compounds are all hypergolic with WFNA, it



Scheme 1. Boron-based hypergolic ionic liquids.

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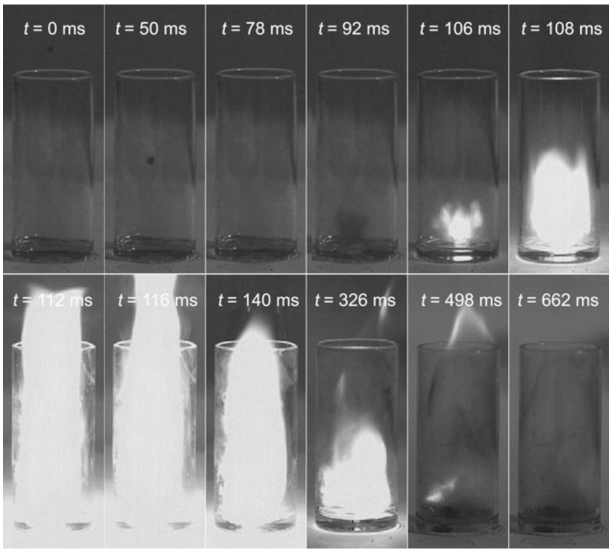
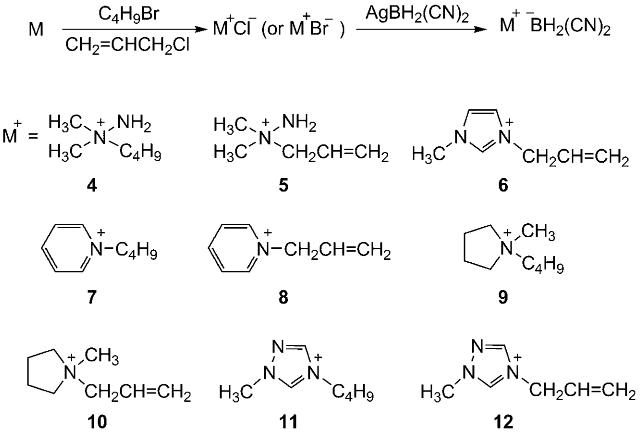


Figure 1. The ignition delay test process shown with a series of high-speed camera photos (a droplet of **3** contacting WFNA).

is the B–H bond that is most certainly responsible for the hypergolicity.

In an attempt to understand the process and to determine the extent of the value of the dicyanoborate anion for hypergolics, nine additional dicyanoborate-based ionic liquids (Scheme 2) were prepared using five different cations (*N*,*N*-dimethylhydrazinium, *N*-methylimidazolium, pyridinium, *N*-methylpyrrolidinium, and *N*-methyltriazolium) with two different substituents (butyl and allyl groups). The resulting ionic liquids were characterized by ^{1}H and ^{13}C NMR and IR spectroscopy, and elemental analysis. The characterization data support the proposed structures and compositions. Interestingly, the ten dicyanoborate-based ionic liquids are miscible with tetrahydrofuran and ethyl acetate in which ionic liquids are usually insoluble as well as being soluble in polar solvents such as ethanol, methanol, acetone, and acetonitrile. However, salts **5** and **12** are immiscible with CH_2Cl_2 which is normally a very good solvent for ionic liquids. The butyl-substituted dicyanoborate-based ionic liquids are immiscible with H_2O. When the substituent on the nitrogen is changed from a butyl to an allyl group, the ionic liquids with the exception of **10** become miscible with H_2O.



Scheme 2. New dicyanoborate-based ionic liquids.

Table 1: Properties of the dicyanoborate-based ILs and the corresponding dicyanamide- and nitrocyanamide-based ILs.[a]

IL	T_m/T_g [°C]	T_d [°C]	ρ [g cm^{-3}]	η [mPa s]	ID [ms]
3[b]	< −80	307	0.96	17.3	28
3 (DCA)[c]					47
3 (NCA)[d]	−90	256	1.13	57	81
4[b]	< −80	222	0.91	39.4	6
4 (DCA)[e]	20	263	1.01	113.9	46
4 (NCA)[e]	9	286	1.11	119.5	228
5[b]	< −80	189	0.93	35.0	4
5 (DCA)[e]		199	1.05	78.6	30
5 (NCA)[e]		208	1.16	84.9	130
6[b]	< −80	266	0.99	12.4	8
6 (DCA)[c]	−85	207		42	43
6 (NCA)[d]	−91	220	1.11	44	46
7[b]	< −80	252	0.96	19.8	18
8[b]	< −80	203	1.00	13.5	6
9[b]	< −80	303	0.92	22.3	26
9 (DCA)[c]					44
10[b]	< −80	259	0.94	16.6	8
11[b]	< −80	220	0.99	29.9	32
12[b]	< −80	217	1.03	21.0	6

[a] T_m/T_g: phase-transition temperature, T_d: decomposition temperature (onset), ρ: Density (25 °C), η: viscosity (25 °C), ID: ignition delay time (WFNA), DCA: corresponding dicyanamide-based ionic liquid, NCA: corresponding nitrocyanamide-based ionic liquid. [b] $^-BH_2(CN)_2$, this work. [c] Ref. [8]. [d] Ref. [13]. [e] Ref. [12].

The physicochemical properties of the ten new dicyanoborate ionic liquids such as phase-transition temperature (T_m or T_g), thermal decomposition temperature ($T_{d,onset}$), density (ρ), viscosity (η), and ignition delay (ID) time, were determined by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), gas pycnometry, viscometry, and droplet tests, respectively. In Table 1, it is seen that the dicyanoborate ionic liquids have a long liquid range. Their T_m (or T_g) are all −80 °C and $T_{d,onset}$ are > 200 °C except for **5** (189 °C). The thermal stabilities of the *N*-methylimidazolium and *N*-methylpyrrolidinium salts are similar and are greater than those of the *N*,*N*-dimethylhydrazinium, pyridinium, and *N*-methyltriazolium liquids. Compared with common ionic liquids, the densities of the dicyanoborate-based materials are lower and vary from 0.91 (**4**) to 1.03 g cm^{-3} (**12**), where *N*-methyltriazolium > pyridinium > *N*-methylimidazolium > *N*-methylpyrrolidinium > *N*,*N*-dimethylhydrazinium. The viscosities of these new ionic liquids which vary from 12.4 (**6**) to 39.4 mPa s (**4**) are much lower and over a much smaller range than those of the corresponding hypergolic ionic liquids comprised of other anions (Table 1). The *N*,*N*-dimethylhydrazinium and *N*-methyltriazolium ionic liquids have slightly higher viscosities than those of the *N*-methylimidazolium, pyridinium, and *N*-methylpyrrolidinium ionic liquids. The ID times of these ionic liquids are relatively short and vary over a narrow range from 4 (**5**) to 32 ms (**11**). Having such a small difference in ID values over a range of cations is very unusual and has not been observed previously for hypergolic ionic liquid systems.[8–14] The *N*,*N*-dimethylhydrazinium ionic liquids have shorter ID times at 4 (**5**) and 6 ms (**4**) than *N*-methylimidazolium, pyridinium, *N*-pyrrolidinium and *N*-methyltriazolium ionic liquids which have similar ID times. When the substituent is changed from butyl to allyl, the properties of the *N*,*N*-dimethylhydrazinium, *N*-methylimidazolium, pyridinium, *N*-methylpyrrolidinium, and *N*-methyltriazolium compounds all change in the following order: decomposition temperatures decrease, densities increase, viscosities decrease, and IDs decrease.

Comparing the dicyanoborate-based ionic liquids with those hypergolic ionic liquids which contain the most common anions, dicyanamide and nitrocyanamide, the dicyanoborate compounds have lower or similar phase transition temperatures, similar thermal decomposition temperatures, and slightly lower densities. Most importantly the viscosities and ID times of the new materials are much lower and shorter, respectively, than those of the nitrocyanamide and dicyanamide hypergolic ionic liquids, such as **3**, **4**, **5**, and **6** whose viscosities decrease from 57 to 17.3, 119.5 to 39.4, 84.9 to 35.0, and 44 to 12.4 mPa s, respectively, and IDs from 81 to 28, 228 to 6, 130 to 4, 46 to 8 ms, respectively.[8,12,13]

In conclusion, ionic liquids with three different boron-containing anions have been found to be hypergolic with WFNA as oxidizer. The dicyanoborate-based ionic liquids possess better properties such as lower viscosities and shorter ID times, than their dicyanamide and nitrocyanamide analogues. Nearly independent of the cations, these physical characteristics vary over a rather narrow range. Additionally, these ionic liquids are stable in aqueous solution and are, in fact, synthesized in water as the solvent of choice. With melting points and viscosities as low as −80 °C and 12.4 mPa s, and ignition delay times as short as 4 ms, the dicyanoborate-based compounds are the brightest hope to date to be the next class of hypergolic materials to replace hydrazine and its derivatives in hypergolic propellant systems.

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