Ionic Liquids as Hypergolic Fuels

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bipropellant · dicyanamide · energetic ionic liquids ·
hypergolic reactions · ignition delay · nitrocyanamide

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. Only recently (2008), ionic liquids (salts with melting points less than 100°C) with the dicyanamide anion were shown to exhibit hypergolic properties (instantaneous ignition when contacted with oxidizers (100% nitric acid, WFNA)). Such liquids tend to have low volatilities, and high thermal and chemical stabilities, and often exhibit long liquid ranges which could allow utilization of these substances as bipropellant fuels over a variety of conditions. A new family of dicyanoborates is presented, which can be synthesized in water, with substituted N-acyclic, N-cyclic, and azolium cations has met nearly all of the desired important criteria needed for well-performing fuels.

1. Introduction

Perhaps the most exciting ionic liquid development in the 21st century was the discovery by workers at Edwards Air Force Base, USA that certain ionic liquids do behave as fuels which undergo spontaneous hypergolic reactions when contacted with appropriate oxidizers![1,2] These unusual liquids play the leading role—no longer the spectator but now the star of the performance! Based on the number of publications, interest in ionic liquids (salts with melting points ≤ 100°C) which have evolved into hydrolytically stable moieties via the introduction of suitable anions has grown markedly since the year 2000. In general, these liquids are nonvolatile and nonflammable, thermally and chemically stable, and have rather high ionic conductivity. A very large fraction of their applications is in a solvent-related role, and a much smaller number is as a result of their chemical reactivity.[3–5]

Hypergolicity 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 continue to be utilized. Hypergol is a term invented during World War II to describe the phenomenon of spontaneous ignition, that is, the spontaneous reaction of one chemical (fuel) when contacted with another (oxidizer). In principal, real-life applications (e.g., as propellants to power spacecraft) would be markedly simplified since all ignition schemes and devices could be discarded, and chemistry could do the work.[6] It is desirable for these reactions to proceed as rapidly as possible (ignition delay) in order to preclude a collection of fuel and oxidizer which then may ignite with a concomitant explosion. In earlier times, 50 milliseconds was the goal for the maximum acceptable time for ignition delay; currently the target may be as low as a few milliseconds depending on the application.

Efforts to find satisfactory fuels as well as oxidizers were filled with frustration, and many, many false attempts were made on both sides of the Atlantic. During those exciting times many toxic systems were adopted as fuels including mixtures of hydrazine hydrate, methanol, and water, and others such as triethylamine, aniline, toluidine, xylidine, and N-methyl aniline.[6] A wide variety of oxidizers has been tested including liquid oxygen, inhibited red-fuming nitric acid (IRFNA, ca. 83% HNO_3 plus 14% N_2O_4 plus ca. 2% H_2O plus 0.6% HF), white fuming nitric acid (WFNA, ca. 100% HNO_3), N_2O_4, and hydrogen peroxide. During the ensuing 70–80 years, this subject has attracted much attention around the world from syntheses and toxicity considerations.[7–27]

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There are a number of Reviews which deal with hypergolic systems comprised primarily of hydrazine and hydrazine derivatives as fuels and the nitrogen oxide family as oxidizers where application is most often directed toward propellants.[7–10] In Table 1 an attempt is made to illustrate the range of fuels, oxidizers and applications that has been suggested over a considerable time (hydrazine and hydrazine derivatives have been omitted).[11–36]

The previous systems are in need of considerable improvement and are lacking in a variety of ways including the oxidizers and fuels themselves that have been examined. Although utilization of oxidizers, for example, nitric acid (in its various combinations), perchlorate salts, interhalogen alkali-metal fluoride complexes, and nitro explosives, and fuels, for example alkyl metal hydrides, hydrazine, amines, ionic liquids, in these hypergolic roles have been published and patented, there is a great need for alternate oxidizers and fuels that will concomitantly display low toxicity, high density, long-term storability, and excellent performance. Currently, even though environmental and health concerns have become more and more important in the world of both war and peacetime propellants, hydrazine and its methylated derivatives continue as the state-of-the-art fuels of choice. Most difficulties encountered in handling these compounds arise from their volatility since they are extremely carcinogenic. Much further work is needed for both oxidizers and fuels.

However, compounds with a wide liquid range and a low melting point (m.p. ca. $-54\,^{\circ}$C (hydrazine/water)) are highly desirable since ambient temperatures where they may be utilized as propellants may range from very cold to extremely hot. Additionally low viscosity to ensure ease of moving the fuel as well as high storability are concomitant requirements.

Table 1: Examples of fuels, oxidizers, and proposed uses in hypergolic reactions.

Fuel(s)	Oxidizer(s)	Use	Reference
tertiary amine azides cyclic amine azides	(a) red fuming nitric acid; N_2O_4, H_2O_2, $NH_3OH^+NO_3^-$, liq. O_2	bipropellant	[11, 13–15, 25]
mixture of *N,N,N',N'*-tetra-methylethylenediamine + DMAZ	as in (a)	bipropellant	[19]
N,N,N',N'-tetra-methylethylenediamine	90% nitric acid	bipropellant	[20]
hydroxylammonium nitrate; hydroxylammonium nitrate-triethanolammonium nitrate-water	H_2O_2	bipropellant	[29]
DMAZ or cyclic methylene azide	H_2O_2/metal catalyst	bipropellant	[12]
alkali metal hydrides	interhalogen alkali metal fluoride complexes, $CsClF_4$	(b) heat, light, or gas sources	[30]
alkali metal hydrides, BeH_2, methylboranes,	nitrosyl and nitronium compounds, NO_2ClO_4, metallic perchlorates	as in (b)	[31]
ionic liquids	N_2O_4, white fuming nitric acid	bipropellant	[4, 5, 32–36]

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Young-Hyuk Joo was born in Incheon, Korea, in 1974. He received his degree in chemistry from the Chemnitz University of Technology (Germany) in 2003 and also his PhD in organic chemistry in 2007. He was then a postdoctoral fellow with Professor Jean'ne M. Shreeve at the University of Idaho. In 2011, he joined the Hanwha Co. R&D center (Korea) as a Senior Researcher in the field of Explosives and Pyrotechnics. His interests include azide chemistry, nitro chemistry, and high energy density materials.
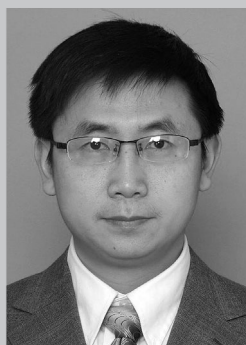
Haixiang Gao earned a degree in Chemistry at Lanzhou University in 1996, and his PhD with Professor Hanqing Wang in 2002. He was a postdoctoral fellow at the Institute of Chemistry, Chinese Academy of Sciences (2002–2004) with Professor Buxing Han, and at the University of Idaho with Professor Jean'ne M. Shreeve. In 2007 he joined the China Agricultural University, where he became a Full Professor in 2011. His interests include theoretical calculations, the design and synthesis of ionic liquids (salts), and their application in energetic materials and green chemistry.

Jean'ne M. Shreeve is a Montana native. She received a BA in chemistry at the University of Montana, an MS in analytical chemistry at the University of Minnesota, and a PhD in inorganic chemistry at the University of Washington, Seattle. She has been at the University of Idaho since 1961. In 2011, she was named a University Distinguished Professor. Her research interests include the design, syntheses, characterization, and reactions of energetic materials, and fluorine-containing compounds.

2. Ionic Liquids as Fuels

The design and synthesis of ionic liquids based on energetic materials provide a powerful methodology in the development of a new type of hypergolic fuel simply by the combination of different ions for a specific purpose. In addition, their properties are readily varied and tuned through the modification of the cationic and/or anionic components. Ionic liquids appear to offer a good fit for addressing the hard to realize requirements of the hydrazines (low vapor pressure, low toxicity, less environmentally harmful, long liquid range). This has been suggested, presented, and published by groups at Edwards Air Force Base[1,2] as well as presented and published by us.[32–36]

1-(Propargyl)-3-methylimidazolium dicyanamide and 1-methyl-4-amino-1,2,4-triazolium dicyanamide are examples of hypergolic ionic liquids in white fuming nitric acid (100% nitric acid; WFNA) with ignition delays (ID) of 15 and 31 milliseconds, respectively.[1,2] The standard method for determining ignition delay time is to record the length of time between contact of the liquid salt with the oxidizer and the first visible ignition using a high-speed camera (Figure 1). After ignition, self-sustained combustion of the hypergolic materials continues. Normally ionic liquids which are solid at 25°C can only be reproducibly measured using this methodology with difficulty. In addition, they would not be easily suitable in a liquid propellant role.

Initial considerations suggested imidazolium-containing ionic liquids because of their higher stability than the analogous triazolium or tetrazolium salts. Unsaturated side chains such as propargyl or allyl were introduced based on the premise that they would initiate or promote hypergolic ignition. In this first work, dicyanamide (DCA⁻) was invariably chosen as the anion because it is a fuel-rich anion and because dicyanamide-containing ionic liquids tend to be among the least viscous of any known liquid salts. These
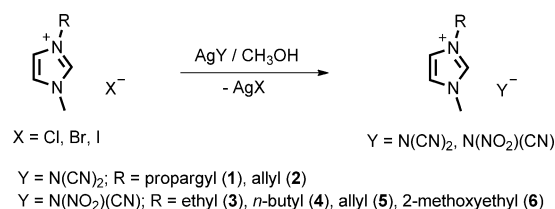
**Scheme 1.** Synthesis of azolium nitrocyanamide and dicyanamide hypergolic ionic liquids.

X = Cl, Br, I   Y = N(CN)₂, N(NO₂)(CN)

Y = N(CN)₂; R = propargyl (**1**), allyl (**2**)
Y = N(NO₂)(CN); R = ethyl (**3**), *n*-butyl (**4**), allyl (**5**), 2-methoxyethyl (**6**)

hypergolic ionic liquids (**1**, **2**) are given in Scheme 1. Thermal and physical data of **1**, **2**, **7–10** are included in Table 2.[1,2] Although **3–6** also exhibit hypergolic properties, the anion is nitrocyanamide (NCA⁻; Scheme 1, Table 2[34]). These liquids have viscosities that fall into the 23–57 cP range. Compounds **1–10** are hypergolic in WFNA with ignition delay (ID) times

Table 2: Properties of azolium nitrocyanamide and dicyanamide hypergolic salts.

Compd	$T_g(T_m)$[a] [°C]	T_d[b] [°C]	d[c] [g cm^{-3}]	η[d] [cP]	ID[e] [ms]	ΔH_f[f] [kJ g^{-1}]	I_{sp}[g] [s]
1[h]	−61(17)	144		110	43		
2[h]	−85	207		42	15		
3[i]	(−73)	253	1.18	23	78	0.80	192
4[i]	(−90)	256	1.13	57	81	0.57	186
5[i]	(−91)	220	1.11	44	46	1.31	197
6[i]	(−82)	266	1.21	54	65	0.19	187
7[h,j]	−66	143		92	31		
8[h,i,k]	−6(−90)	240	1.06	33 (20°C)	47	1.30	165
9[h,l]					44		
10[h,m]					37		

[a] Glass transition (melting point), DSC, 10°C min^{-1}. [b] Decomposition onset, DSC, 10°C min^{-1}. [c] Density, 25°C. [d] Viscosity, 25°C. [e] Ignition delay (WFNA). [f] Enthalpy of formation. [g] Specific impulse, calculated isobarically at 68 atm, (Cheetah 5). [h] Ref. [1,2]. [i] Ref. [34]. [j] 1-methyl-4-amino-1,2,4-triazolium. [k] 1-Butyl-3-methylimidazolium. [l] 1-Butyl-1-methylpyrrolidinium. [m] *n*-Butyl-3-methylpyridinium.

ranging between 15 to 81 ms. It was suggested that since the influence of the unsaturated substituents on the azole rings was minimal, the dicyanamide (DCA⁻) anion was the controlling factor in determining hypergolic properties. However, it can be seen that **3–6** are nitrocyanamide salts and exhibit ignition delay times that, although somewhat
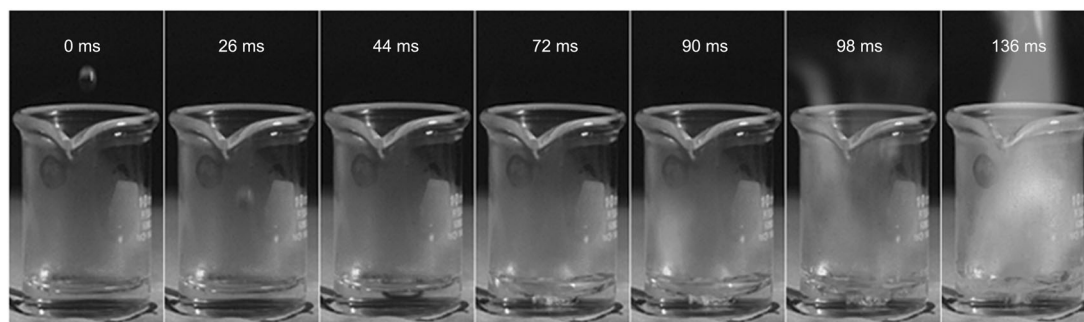

Figure 1. The ID test process shown with a series of high-speed-camera photos (a droplet of an ionic liquid falling into liquid WFNA).

longer, are not greatly different from the DCA-containing analogues. Density of the liquid fuel is an important property because density impulse—a measure of fuel performance—is the product of density and specific impulse (I_{sp}, measure of energy content). A desired I_{sp} is greater than 300 s; the values for **3–6** fall at approximately 200 s and the densities of all of the salts barely exceed one g cm^{-3} which leads to low volumetric specific impulse values.

3. Cations with Three Contiguous Nitrogen Atoms

There is significant interest in the development of new ionic liquids for use as aerospace propellants and fuels.[37–41] Based on our calculations,[43] we find that the heat of formation is one of the important characteristics for hypergolic salts which is directly related to the number of nitrogen–nitrogen bonds in the ionic species. Thus we began to search for new ions with a greater concentration of nitrogen–nitrogen bonds. In trying to understand hypergols, we synthesized new salts with the 2,2-dimethyltriazanium cation (Scheme 2).[32] The 2,2-dimethyltriazanium salts formed by
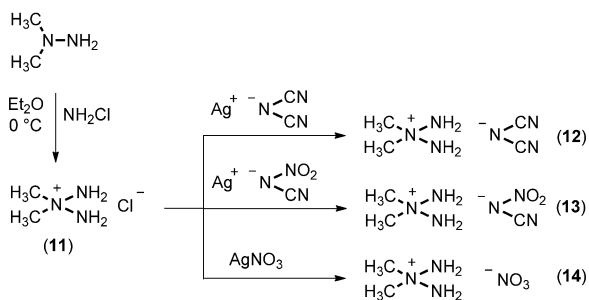
Scheme 2. Synthesis of 2,2-dimethyltriazanium salts.

chloramination reactions are the first known stable alkyl compounds which contain a chain of more than two contiguous nitrogen atoms linked by single bonds. A few salts (halide, nitrate, perchlorate, methanesulfonate) of 2,2-dimethyltriazanium (DMA) have been reported,[32] but otherwise this cation has been neglected. Compounds **11–14** are stable in air and in neutral aqueous solutions, can be recrystallized from boiling solvents, such as acetone, ethanol, and acetonitrile, and are hypergolic. Their properties are shown in Table 3.

In contrast with the earlier hypergolic ionic liquid report where it was claimed that the anion was all determining,[1,2] these hypergolic 2,2-dimethyltriazanium (DMA) salts have been synthesized and studied with a variety of anions.[32] In Table 3, it is shown that their properties are very encouraging; in fact, some of those salts which are potential hypergolic materials include both the chloride (**11**) and nitrate (**14**) salts. This is indeed quite surprising. From the limited group of four salts, (**11–14**) there seems to be little rationale on which to base predictions. Compound **14**, although barely an ionic liquid with a melting point at 99 °C, is thermally stable to 146 °C and at 1.47 g cm^{-3}, making it, and **11** the densest of the salts **1–14**. Compound **14** has an ignition delay time of 4 ms,

Table 3: Hypergolic ionic liquids with the 2,2-dimethyltriazanium cation.[32]

Compd	T_m[a] [°C]	T_d[b] [°C]	d[c] [g cm^{-3}]	ID[d] [ms]	ΔH_f[e] [kJ g^{-1}]	I_{sp}[f] [s]
11	–	–	1.47	26 N$_2$O$_4$	−0.45	–
12	11	134	1.15	22	2.56	201
13	−0.2	146	1.26	16	1.41	226
14	99	146	1.47	4	−0.69	228

[a] Melting point, DSC, 10 °C min^{-1}. [b] Decomposition onset, DSC, 10 °C min^{-1}. [c] Density, 25 °C. [d] Ignition delay (WFNA). [e] Enthalpy of formation. [f] Specific impulse, calculated isobarically at 68 atm (Cheetah 4.0).

and is extremely insensitive to impact. The drawback is that it is a solid but in rocket or other applications this could be compensated for by dissolution in, for example, a tertiary amine.

As demonstrated above, there is a morass of information about hypergolic systems, but this is not true for hypergolic ionic liquids. The question is how to utilize all of this detail to achieve transformative progress? Ionic liquids could be selectively developed from known molecular substances that are hypergolic but which may or may not exhibit the two other minimally important properties of low viscosity and low melting point as well as the important goal of low toxicity; new cations and/or anions could be based on information gained; all the while looking for signs of systematization which may drive future synthetic undertakings. Important generalizations (many of which are empirical) are given in Table 4.

## 4. Do Hypergolic Molecules Result in Hypergolic Ionic Liquids?

In a recent patent application,[19] several hypergolic liquids in bipropellant propulsion systems are disclosed as

***Table 4:*** Property–impact relationships for hypergolic ionic liquids.

Entry	Property	Impact
1	asymmetrically substituted cation	lower melting point
2	fewer than seven carbon atoms	encourages hypergolicity
3	unsaturated side chains, e.g., acetylenic	enhance tendency toward hypergolicity
4	secondary or tertiary amines	alternative to monomethyl hydrazine and unsymmetric dimethyl hydrazine
5	higher positive heat of formation	higher specific impulse
6	oxygen balance in fuel	unimportant—oxidizer provides
7	high specific impulse and density	improve density-impulse—measure of fuel performance
8	absence of N–N single bonds	reduces toxicity but decreases enthalpy
9	low viscosity	enhances flow characteristics and mixing with oxidizer
10	additives	increases density/decreases viscosity
11	anions	may govern viscosity

replacements for fuels which contain toxic monomethylhydrazine. These are used in fuel mixtures where one or more amine azides were mixed with one or more tertiary diamine, triamine or tetramine compounds. In general, these workers found that the hypergolic fuel mixture provided a reduced ignition delay when combining with an oxidizer. This is powerful! Using this technique, the viscosity of salts (ionic liquids) which is sometimes a major problem can be decreased while concomitantly leading to a diminution in the ignition delay time. For example, simple tetramethylenediamine is hypergolic at 14 ms and was shown to be useful as a diluent in lowering the ignition delay time of other more energetic species. Looking at the collection of compounds suggested in the referenced patent,[19] the common link between each of these hypergolic molecules is that the nitrogen atoms are most frequently tertiary and that azide-containing species appear to be useful. The question is "do hypergolic molecules result in hypergolic ionic liquids?" Interestingly, we have shown that while ethylene diamine or salts with the ethylene diammonium cation are not hypergolic, those salts which contain ethylene diammonium cations with alkyl substituents (and appropriate anions) are indeed hypergolic, for example, Equation (1).

(1)
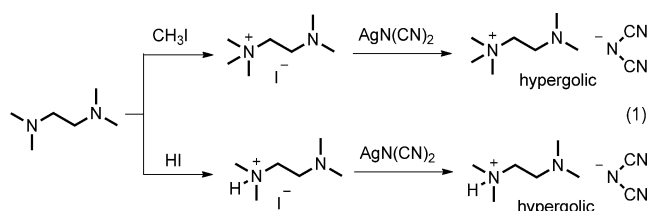
As proof of principle, while unsymmetric dimethylhydrazine is known to be hypergolic, we have now demonstrated that unsymmetric dimethylhydrazinium salts with different anions are also hypergolic.[33] The advantages of employing salts with regard to the molecular hydrazines include their low vapor pressures, high thermal and chemical stabilities, and tunable physicochemical characteristics. As can be seen in Scheme 3, *N,N*-dimethylhydrazinium ionic liquids were obtained by quaternizing *N,N*-dimethylhydrazine with alkyl halides followed by metathesis with silver nitrocyanamide or silver dicyanamide which allowed the direct comparison of these two families of salts. These liquids have densities and viscosities ranging from 1.01 to 1.26 g cm^{-1} and 79 to 270 cP, respectively (Table 5). Nitrocyanamide salts (**15–18**) exhibit higher densities and viscosities than the corresponding dicyanamides (**19–22**) due to the presence of the nitro group
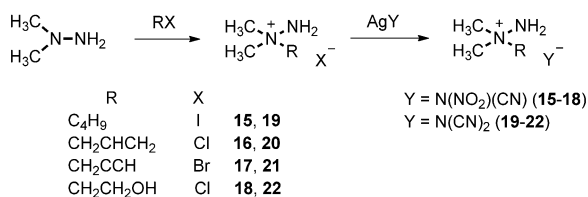
Scheme 3. Synthesis of *N,N*-dimethylhydrazinium salts.

Table 5: Properties of *N,N*-dimethylhydrazinium salts.[33]

Compd	T_d[a] [°C]	d[b] [g cm^{-3}]	η[c] [cP]	ID[d] [ms]	ΔH_f[e] [kJ g^{-1}]	I_{sp}[f] [s]
15	286	1.11	120	228	0.46	201
16	208	1.16	85	130	1.68	221
17	189	1.21	270	134	2.18	227
18	269	1.26	186	247	−0.15	206
19	263	1.01	114	46	1.27	180
20	199	1.05	79	24	2.71	204
21	174	1.13	229	30	3.26	210
22	236	1.15	162	40	0.64	186

[a] Decomposition onset, DSC, 10°C min^{-1}. [b] Density, 25°C. [c] Viscosity, 25°C. [d] Ignition delay (WFNA). [e] Enthalpy of formation. [f] Specific impulse, calculated isobarically at 68 atm (Cheetah 5.0).

with its greater proclivity to form hydrogen bonds. All of the *N,N*-dimethylhydrazinium salts are hypergolic with WFNA. Additionally, in this series of salts, nitrocyanamide salts invariably have longer ID values than the analogous dicyanamide liquids. These systems demonstrate that hypergolic substances can become hypergolic ionic liquids and thus further work can lead the way to a variety of new families of hypergolic ionic liquids.

5. Hypergolic Ionic Liquids with Azide-Functionalized Groups

The azido group is highly energetic adding approximately 280 kJ mol^{-1} to the energy content of a molecule. The linear azide anion (N_3^-) is the conjugate base of hydrazoic acid and is isoelectronic with CO_2 and N_2O. Our calculations show that the heat of formation of the azide anion in the gas phase is 197.2 kJ mol^{-1}, which is higher than that of the dicyanamide ($^-$N(CN)$_2$, 113.4 kJ mol^{-1}) and nitrocyanamide ($^-$N(CN)(NO$_2$), −27.1 kJ mol^{-1}) anions which have been used in the design of hypergolic ionic liquids.[1,2,32–35] Therefore, it is not surprising that azide-containing compounds sometimes are highly endothermic, and that their energy content increases with an increasing number of azido ligands.[35]

In our continuing efforts in this area, we synthesized new energetic ionic liquids with azide-functionalized groups in order to study their hypergolic properties. 2-Azido-*N,N*-dimethylethylamine (DMAZ)[44] is a reduced-hazard liquid fuel, which has been developed by the US Army.[13–15] Many of the physical properties of DMAZ are closely comparable to those of monomethylhydrazine (MMH) fuel, but whereas MMH is highly toxic, the data available to date suggests that DMAZ is relatively less toxic.[45, 46]

The preparation of DMAZ can be realized by a literature method.[44] After metathesis of the ammonium iodide, which is prepared by methylation of DMAZ with iodomethane, with a slight excess of the corresponding silver salts (silver nitrocyanamide, and silver dicyanamide), a series of energetic salts were obtained in excellent yields (Scheme 4). Their physical properties and ignition delay times are given in Table 6. Compounds **23** and **24**, the nitrocyanamide and dicyanamide salts of the 2-azido-*N,N,N*-trimethylammonium cation, exhibit excellent hypergolic ignition delay times at 8

R = CH₃; Y = N(NO₂)(CN) (**23**), N(CN)₂ (**24**)
R = CH₂CH₂N₃; Y = N(NO₂)(CN) (**25**), N(CN)₂ (**26**)
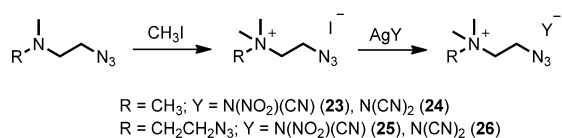
Scheme 4. Synthesis of hypergolic ionic liquids with mono- or bis-(azidoethyl)ammonium cations.

**Table 6:** Properties of azide-functionalized ionic liquids.[35]

Compd	$T_m^{[a]}$ [°C]	$T_d^{[b]}$ [°C]	$d^{[c]}$ [g cm^{-3}]	ID$^{[e]}$ [ms]	$\Delta H_f^{[f]}$ [kJ g^{-1}]	$I_{sp}^{[g]}$ [s]
23	28	245	1.24	8	1.9	218
24	9	235	1.15	20	2.4	202
25	–	222	1.32	226	3.2	231
26	–	222	1.21	16	3.8	221
27	75	subl.	0.99	hg$^{[h]}$ (N₂O₄)	3.3	249
28	80	subl.	1.01	hg$^{[h]}$ (N₂O₄)	3.2	245

[a] Melting point, DSC, 10 °C min^{-1}. [b] Decomposition onset, DSC, 10 °C min^{-1}; subl. = sublimes. [c] Density, 25 °C. [d] Viscosity, 25 °C. [e] Ignition delay (WFNA). [f] Enthalpy of formation. [g] Specific impulse, calculated isobarically at 68 atm (Cheetah 5.0). [h] Hypergolic.

and 20 ms in WFNA. The former (**23**) shows the same ID as shown by monomethylhydrazine. While also hypergolic in WFNA, bis(2-azidoethyl)dimethylammonium nitrocyanamide (**25**) has a much longer ID of 226 ms and the analogous dicyanamide (**26**) shows an ID of 16 ms.

When hydrazoic acid (HN₃) was employed with *N,N*-dimethylisopropylamine or triethylamine, the corresponding white solid ammonium azides (**27**, **28**) were obtained in good yields (Scheme 5, Table 6). Although they are both extremely hygroscopic, their hypergolicity was demonstrated in dinitrogen tetroxide (N₂O₄). These are the first examples of hypergolic salts (melting points at 75 and 80 °C, respectively) with an azide anion.


(**27**)

(**28**)
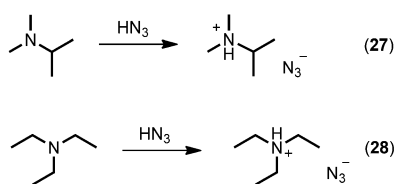
Scheme 5. Hypergolic ionic liquids with azide anion.

One of the useful properties of ionic liquids is that their compositions and thus properties can be readily modified by varying the combination of cation and anion until a suitable pair is found. To date, the anions most commonly employed for hypergolic studies include dicyanamide, azide, nitrate, chloride, nitrocyanamide, and dinitramide and some comparisons have been made but generalizations do not seem possible.[1,2,32–36] This is in part due to the fact that simply not enough work has been done and also because the cations play a role which is not understood.

6. Ionic Liquids with the Strongly Reducing Dicyanoborate Anion

A system that has been reported most recently is the case where the anion is a strongly reducing species; it would be expected that the interaction of an oxidizer with a fuel which is markedly reducing should result in excellent diminution of ignition delay time, for example, the dicyanoborate anion.[36] Preliminary work showed that sodium and potassium borohydride are hypergolic with WFNA. Therefore, in keeping with our interest in liquid hypergols, two imidazolium salts, 1-methyl-3-butylimidazolium borohydride and cyanoborate were synthesized. Although both are hypergolic, they required strictly anhydrous conditions for preparation and storage because they were hydrolytically unstable. This attribute markedly lessened their usefulness so 1-methyl-3-butylimidazolium dicyanoborate was synthesized (**31**); the solvent system of choice was aqueous, and this compound was hypergolic with WFNA. Ten dicyanoborate ionic liquids are shown in Scheme 6. All of these ionic liquids have an
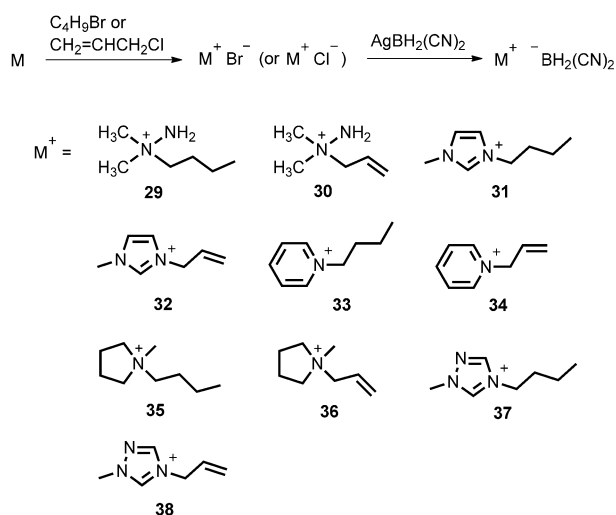
Scheme 6. Dicyanoborate ionic liquids.

extended liquid range between > −80 °C to < 200 °C, with rather low viscosities from 12.4 to 39.4 cP (water ≈ 1 cP). Not surprisingly densities fall very close to 1 g cm^{-3} which impacts the specific impulse values (Table 7). Their most remarkable attribute is the very short ignition delay time falling between 4 and 32 ms. Having such a small range in ID values over a rather broad selection of cyclic and acyclic cations is unexpected based on the results reported above. In Table 7 these dicyanoborate-based ionic liquids are compared with analogous cation-containing hypergols with the most common anions, nitrocyanamide and dicyanamide; the dicyanoborate compounds have similar thermal stabilities, with slightly lower densities and approximately similar phase-transition temperatures. However, ignition delay times (as short as 4 ms) and viscosities (as low as 12 cP) are markedly shorter and smaller than those for ⁻N(CN)₂ and ⁻N(CN)-(NO₂) hypergols. The behavior of these unique liquids

Table 7: Properties of dicyanoborate-based salts and of the corresponding nitrocyanamide and dicyanamide analogues.[36]

Compd.	T_m/T_g[a] [°C]	T_d[b] [°C]	d[c] [g cm^{-3}]	η[d] [cP]	ID[e] [ms]
29[f]	< −80	222	0.91	39.4	6
29 (NCA)[g,i]	9	286	1.11	119.5	228
29 (DCA)[h,i]	20	263	1.01	113.9	46
30[f]	< −80	189	0.93	35.0	4
30 (NCA)[g,i]		208	1.16	84.9	130
30 (DCA)[h,i]		199	1.05	78.6	30
31[f]	< −80	307	0.96	17.3	28
31 (NCA)[g,i]	−90	256	1.13	57	81
31 (DCA)[h,k]					47
32[f]	< −80	266	0.99	12.4	8
32 (NCA)[g,i]	−91	220	1.11	44	46
32 (DCA)[h,k]	−85	207		42	43
33[f]	< −80	252	0.96	19.8	18
34[f]	< −80	203	1.00	13.5	6
35[f]	< −80	303	0.92	22.3	26
35 (DCA)[h,k]					44
36[f]	< −80	259	0.94	16.6	8
37[f]	< −80	220	0.99	29.9	32
38[f]	< −80	217	1.03	21.0	6

[a] Phase-transition temperature, DSC, 10°C min^{-1}. [b] Decomposition temperature (onset), DSC, 10°C min^{-1}. [c] Density, 25°C. [d] Viscosity, 25°C. [e] Ignition delay time (WFNA). [f] $^-$BH$_2$(CN)$_2$, Ref. [36]; [g] [NCA] nitrocyanamide as anion with common cation. [h] [DCA] Dicyanamide as anion with common cation. [i] Ref. [33]. [j] Ref. [34]. [k] Ref. [1].

appears to be essentially independent of the cations. Since the borohydride, cyanoborate, and dicyanoborate salts are all hypergolic, it is likely that the hypergolicity of these salts is a function of the boron-hydrogen bond. Dicyanoborate-containing ionic liquids appear to offer the most promise for hydrazine substitutes at this time.

7. Understanding and/or Predicting Hypergolic Properties of Ionic-Liquid-Based Systems

The chemistry that has been accomplished to date is stimulating and interesting but it is largely empirical in nature. In order to make intelligent predictions about which ionic liquid based systems will be effective hypergols prior to laboratory testing, considerable additional theoretical and practical studies are necessary. Shortly after demonstrating the hypergolic ignition of dicyanamide ionic liquids with fuming nitric acid and postulating that the anion reaction with the oxidizer is responsible for initiating ignition,[1] the same group,[2] through Fourier transform infrared (FTIR) studies, observed the evolution of CO$_2$, N$_2$O and HNCO during preignition which indicates a complex reaction mechanism, perhaps through dinitrobiuret or nitramide intermediates. While evidence for the former was claimed for the dicyanamide reactions, it was not found for any of the other anions examined (N$_3^-$, $^-$N(CN)(NO$_2$), $^-$N(NO$_2$)$_2$). The details of the reaction between nitric acid and the dicyanamide anion are spelled out. They demonstrated that the initial reactivity of anions with WFNA varies dramatically with the degree of NO$_2$-substitution, for example, silver nitrocyanamide, 1-methyl-4-amino-1,2,4-triazolium nitrocyanamide, and 1-al-

lyl-4-amino-1,2,4-triazolium nitrocyanamide failed to ignite in acid drop tests. Potassium dinitramide reacted slowly to give N$_2$O without ignition.

A second FTIR study, this time by Litzinger and Iyer,[47] is essentially consistent with that of Chambreau et al.[2] with the exception that they were unable to demonstrate that dinitrobiuret will give a positive biuret test. The former was a key part of the earlier postulated mechanism. They suggest that another product in their NaN(CN)$_2$ reaction with 34 or 68% nitric acid such as dicyanic acid, formed by dimerization of cyanic acid, could give the positive biuret test. Recently an apparatus for probing preignition behavior of hypergolic materials has been developed which may be very helpful in the elucidation of the detailed condensed phase chemical kinetics responsible for ignition in the gas phase.[48]

It is most important to the improvement of the process to establish which chemical reactions lead to ignition. Knowing the mechanism of ignition is the initial step toward developing a chemical kinetic model that would allow prediction of the performance of the fuel. The chemical model allows the use of computational modeling to determine actual engine performance and to optimize propulsion system design where the fuel could be used. Additionally appreciating the main reactions which lead to ignition will give insight into routes which may lead to modification of the fuel and/or the oxidizer in order to improve performance.

With the goal of providing an understanding of the reactivity of ionic liquids as potential hypergolic fuels, a hybrid QM/MM-MD direct dynamics method of the study of Ar and O scattering from ionic liquids at hyperthermal energies was developed.[25] This enabled the first qualitative characterization of the chemical reactivity of a room temperature ionic liquid surface. It was found that 1-ethyl-3-methylimidazolium nitrate as the model ionic liquid contains an increased density at the surface with the largest nonpolar group (ethyl) protruding from the surface. Many of the collision results could be determined by these properties.

8. Summary and Outlook

Making use of any of the new hypergolic systems in practice will require a thorough understanding of the residual products obtained upon ignition, their impact on further ignitions, and on the rocket itself. However, having said that, it is true in this case, as in all of science, that serendipitous findings, which on this occasion give rise to highly successful bipropellants, will continue to play a role, irrespective of a thorough understanding of their reaction kinetics. Since one of the advantages of using liquid nonvolatile fuels and liquid oxidizers is the ability to turn the system on and off at will, much additional basic information must be acquired to preclude operational difficulties. Close collaboration between producers of the hypergolic ionic liquids and theorists is absolutely necessary to bring these systems to profitable conclusion. Either group working without input from the other will fail in giving ionic liquid hypergols their proper and likely very useful place in tomorrow's energy systems.[49]

9. List of Abbreviations and Symbols

atm	atmosphere
cP	centipoises
d	density
DCA^-	dicyanamide anion
DMA^+	2,2-dimethyltriazanium cation
DMAZ	2-azido-N,N-dimethylethylamine
DSC	differential scanning calorimetry
η	viscosity
FTIR	Fourier transform infrared
$g\,cm^{-3}$	grams per cubic centimeter
ΔH_f	heat of formation
ID	ignition delay
IRFNA	inhibited, red-fuming nitric acid
I_{sp}	specific impulse
$kJ\,g^{-1}$	kilojoules per gram
min	minute
MMH	monomethylhydrazine
ms	milliseconds
NCA^-	nitrocyanamide anion
QM/MM-MD	quantum mechanics/molecular mechanics-molecular dynamics
s	seconds
T_d	decomposition temperature
T_g	glass transition temperature
T_m	melting temperature
WFNA	100% nitric acid

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