Combustible ionic liquids by design: is laboratory safety another ionic liquid myth?

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The non-flammability of ionic liquids (ILs) is often highlighted as a safety advantage of ILs over volatile organic compounds (VOCs), but the fact that many ILs are not flammable themselves does not mean that they are safe to use near fire and/or heat sources; a large group of ILs (including commercially available ILs) are combustible due to the nature of their positive heats of formation, oxygen content, and decomposition products.

Ionic Liquids (ILs, organic salts that melt below 100 °C) have been well known to the broad scientific community for many years; however, a combination of unique physicochemical properties and a growing interest in green/sustainable chemistry has led to an amazing growth in the interest in ILs for specialized technological applications.[1] Interestingly, as ILs have grown in popularity, a mythology has developed portraying both positive and negative attributes that every 'IL' allegedly possesses. In reality, due to the generic nature of the definition of ILs as low-melting salts, the properties of ILs vary widely.

Many recent reports and web sites generally hail ILs as 'environmentally-benign' solvent replacements, with the properties of non-volatility and non-flammability highlighted in this regard. This is despite the growing knowledge that many examples of ILs can be decidedly non-green,[2,3] while others are approved for food grade use.[4,5] Such 'blind faith' may lead to inappropriate and even dangerous uses of ILs. In this communication, the combustibility of several ILs is reported, validating the use of caution when exploring ILs.

According to US Occupational Safety and Health Administration (OSHA) regulations, flammable liquids have flash points below 37.8 °C,[6] whereas combustible liquids are those having flash point above 37.8 °C. Based on the data presented below, as well as reports by Fox *et al.*,[7] a preferred description of many ILs might be non-volatile (up to the decomposition temperature) class IIIB combustible materials. However, this classification still implies that precautions must be taken working with them near their decomposition temperatures.

Recent publications by Drake *et al.*,[8] Ohno *et al.*,[9,10] Rogers *et al.*,[11–13] Shreeve *et al.*,[14,15] and others have introduced ILs designed to be energetic. These materials have thus far been prepared by incorporation of energetic functionalities (*e.g.*, NO_2, CN, N_3, *etc.*) with heterocyclic ring structures with high heats of formation (*e.g.*, imidazoles, triazoles, tetrazoles, *etc.*). During our own investigations, we have found many examples of ILs that are readily combustible.§

The 20 ILs we discuss here, can be divided into three main groups based on composition: protonated imidazolium nitrates and picrates (Fig. 1 first row); protonated *C*-nitro-substituted imidazolium nitrates and picrates (Fig. 1 second row); and 1-butyl-3-methylimidazolium azolates (Fig. 1 third and fourth rows—$[C_4mim][Az]$). Additionally, 2-hydroxyethylhydrazinium nitrate ($[2\text{-HEH}][NO_3]$) and the commercially produced trihexyltetradecylphosphonium chloride[16] ($[PC_6C_6C_6C_{14}][Cl]$) were investigated (Fig. 1 last row).

To determine combustibility, ~40 mg of each sample was loaded into a small aluminium pan with a diameter of 2.6 mm and heated with a small flame torch for no longer than 5–7 s. All of the 20 tested ILs will ignite under these conditions. The apparent rate of combustion appears to depend on the nitrogen and oxygen content. While some of the ILs burned for a short period of time and went out, others, after first ignition, burned quickly to complete or nearly complete combustion. The most rapid combustion was recorded for the $[C_4mim][4,5\text{-diNO}_2\text{-imidazolate}]$

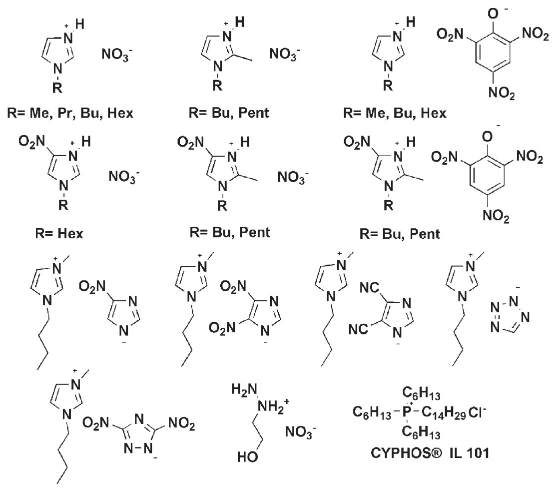

Fig. 1 Ionic liquids tested for combustibility.

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Fig. 2 Ignition test of 1 g of protonated [1-Bu-3-*H*-im][NO_3].

Table 1 Thermal properties of the analyzed ionic liquids[a]

	DSC		TGA	ARC		
Compound	T_g/°C	T_m/°C	$T_{5\%dec}$/°C	T_s/°C	SHR_{max}/°C min^{-1}	Pressure rate max/psi min^{-1}
[1-Me-3-*H*-IM][NO_3]	—	59.9	137	160	594.2 at 255 °C	503.0 at 264 °C
[1-Bu-3-*H*-IM][NO_3]	−76.4	5.5	150	150	200.0 at 225 °C	642.4 at 215 °C

[a] Melting points (T_m) and glass transitions (T_g) were determined by DSC from the second heating cycle after initially melting the salts, then cooling to −110 °C. Decomposition temperatures ($T_{5\%dec}$) were determined by TGA from onset to 5 wt% mass loss, heating at 5 °C min^{-1} under air, which provides a more realistic representation of thermal stability at elevated temperatures. Onset temperature of the exothermic decomposition process (T_s), self-heat rate maximum (SHR_{max}), and pressure rate max were determined using an accelerating rate calorimeter under an oxygen atmosphere (initial pressure *ca.* 100 psi).

and [C_4mim][3,5-diNO_2-triazolate] salts. In contrast, a very similar compound, [C_4mim][4,5-diCN-imidazolate] burned very slowly.

For better understanding of the described phenomena, two specific ILs were chosen and their combustibility analyzed in more depth. Protonated 1-methyl-3-*H*-imidazolium nitrate ([1-Me-3-*H*-im][NO_3]) and 1-butyl-3-*H*-imidazolium nitrate ([1-Bu-3-*H*-im][NO_3]) were obtained by the equimolar addition of concentrated HNO_3 to an aqueous solution of 1-alkylimidazole. After stirring for 1 h at 60 °C, the solvent was evaporated and each product was dried under vacuum.

Approximately 1 g of either [1-Me-3-*H*-im][NO_3] or [1-Bu-3-*H*-im][NO_3] was placed on a watch glass, and heated with a propane torch flame for 10–15 s (Fig. 2). Each of the samples ignited and burned almost completely. The semi-solid/oily residue left after burning was less than ~7% of the starting mass of the sample. The liquid [1-Bu-3-*H*-im][NO_3] visually burned even more rapidly with a loss greater than 96% of the original mass.

The melting, glass, and crystallization transitions for the two ILs were determined using differential scanning calorimetry (DSC) and the thermal stabilities were measured using thermogravimetric analysis (TGA). The decomposition temperatures (~137 °C and 150 °C; Table 1) are in good agreement with the general trend in ILs: (i) protonated ILs decompose at relatively low temperatures in comparison with their alkylated derivatives and, (ii) in homologous derivatives of a particular cation, the decomposition temperatures are usually only dependent on the selected anion and do not change significantly across the series.

Previously collected accelerating rate calorimeter (ARC) data were analyzed for a better understanding of the decomposition processes, energetic character, and the origin of the ability of the ILs to combust. A modified Arthur D. Little ARC 2000™ (typically used to identify and simulate self-heating, runaway reaction conditions) was used in conducting thermal studies under adiabatic conditions. The ARC data (Fig. 3, Table1) were used to evaluate the energetic potential, as well as to estimate the onset temperatures of the exothermic decomposition reactions. The data clearly reveal that the energetic characteristics of both salts are similar. The exothermic reaction is first recorded for both samples around their onset decomposition temperatures (160 °C and 150 °C, respectively). The self-heating exothermic reaction continues from this point, resulting in a gradual increase of the temperature and pressure in the calorimetric bomb. Both the temperature and the pressure curves indicate that the samples have explosive potential when heated above a certain temperature: ~220 °C for [1-Me-3-*H*-im][NO_3] and ~213 °C for [1-Bu-3-*H*-im][NO_3].¶ Furthermore, the self-heat rate and pressure rate increase exponentially until at 255 °C and 225 °C, respectively, both systems reach their self-heating rate maximum (SHR_{max}). This value indicates the temperature at which the increase of the temperature, caused by the exothermic decomposition process, is the highest.

When [1-Me-3-*H*-im][NO_3] is heated to ~220 °C, an explosive reaction begins, with a recorded temperature jump from 220 °C to 303 °C within 16 s. The SHR reaches its peak value of 594.2 °C min^{-1} at 255 °C, and its average value during this explosive reaction was recorded to be ~320 °C min^{-1}.

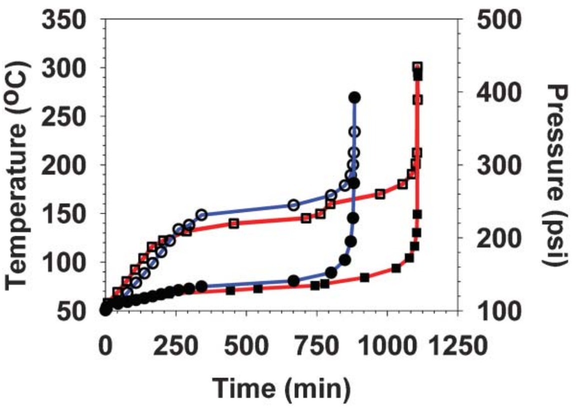

Fig. 3 ARC run of 0.41 g [1-Bu-3-*H*-im][NO_3] in oxygen (○—temperature, ●—pressure) and 0.39 g [1-Me-3-*H*-im][NO_3] in oxygen (□—temperature, ■—pressure).

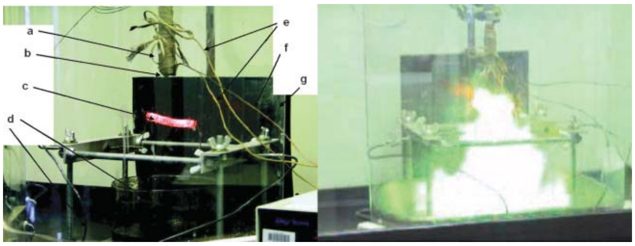

Fig. 4 Open-Air Ignition Apparatus (left): (a) heat tape, (b) spray nozzle, (c) large ignition coil, (d) ignition coil connections to the voltage regulator, (e) heating coils connections from the heat regulator, (f) temperature sensor wire, (g) blast shield. Open-Air Ignition Test of [2-HEH][NO_3] (right).

Corresponding to the sharp increase in temperature, a sudden jump in pressure from 220 psi to 428 psi is also observed. The noted rise in pressure may be explained not only from the thermal expansion of the gases present in the bomb, but, more importantly, from the formation of large quantities of gaseous products during the thermal, exothermic decomposition reaction.

The ARC data show that the energetic value of [1-Bu-3-*H*-im][NO_3] is slightly smaller than that of [1-Me-3-*H*-im][NO_3]. Surprisingly, absence of molecular oxygen (under vacuum) in the process did not prevent an explosive reaction from occurring. Thus, both [1-Me-3-*H*-im][NO_3] and [1-Bu-3-*H*-im][NO_3] are highly energetic ILs, even in the absence of oxygen.

The ARC results, especially the increase in the pressure during the decomposition process, suggest formation of gaseous products during the exothermic decomposition. Taking the TGA and ARC data together, we conclude that exothermic decomposition reactions occur, which start at onset decomposition temperatures. The result is a release of thermal energy and large volumes of highly flammable (combustible) gases, which can easily ignite upon contact with a flame source.

To test if some of the slower burning ILs could also be readily ignited under suitable conditions, spray ignition tests were conducted on the IL 2-hydroxyethylhydrazinium nitrate ([2-HEH][NO_3]) in an open-air combustion chamber (Fig. 4 (left)). The IL was delivered in a fine spray using a small-orifice nozzle, pressurized nitrogen (400 psi), and electrical heater (to lower the viscosity of IL needed to generate the fine spray). The IL spray was ignited using an electrically heated nickel–chromium wire either in open air or in a combustion chamber (Fig. 4 (right)).

The ignition testing described earlier using a torch flame (Fig. 2), revealed that [2-HEH][NO_3] burns very slowly and non-energetically under those conditions. Combustibility, however, increases drastically when it is delivered as a spray for energetic ignition. The positive results from combustion testing in an inert atmosphere (which demonstrated that the [2-HEH][NO_3] can be ignited using only a red-hot ignition coil) suggest that this IL could also be utilized in vacuum conditions as well.

Interestingly, additional testing showed that a commercially available IL, not thought to be energetic, could be ignited as a fine spray in air. The phosphonium IL [$PC_6C_6C_6C_{14}$][Cl] (Cyphos® IL 101) has a fuel-rich cation, but a decidedly non-oxidizing anion. A puddle of this IL could not be ignited with a torch as described above. However, when sprayed into air using the apparatus shown in Fig. 4 (left), a very vigorous flame was produced, much like that in Fig. 4 (right). This result is somewhat surprising, since the thermal stability of [$PC_6C_6C_6C_{14}$][Cl] in air is reported to be *ca.* 300 °C. The manufacturer, however, does report a flash point of 118 °C and a purity level of 93–95%. We suspect that the impurities are responsible for the observed spray ignition.

Additionally, it was pointed out by one of the reviewers, that special precautions should be taken when trying to completely dry some ILs because the condition of dryness may influence their shock and friction sensitivities.

Taking into the account the combined testing conducted on 20 ILs, it is quite clear that even though many ILs may have negligible vapor pressure, ILs as a class should not be necessarily considered safe when working with or near a heat or ignition source. The decomposition products formed during the thermal decomposition of some ILs are sensitive to combustion. All necessary precautions must be maintained and the usage of particular ILs near a source of heat, flame, or ignition must be reconsidered.

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Notes and references

§ **Caution**: although, we have not seen deflagration or detonation of any unconfined samples in the ignition experiments, some salts with high-oxygen and high-nitrogen content are known to be explosives, so appropriate precautions are advisable with new compounds.

¶ **Caution**: it should be noticed that recorded temperature values in an ARC experiment can vary depending on a number of factors, among which the sample size plays a very important role. The T_s temperatures can be underestimated, and in reality (larger sample quantities) translate to significantly lower T_s temperature values.

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