STABILITY AND THERMAL DECOMPOSITION OF QUATERNARY AND PROTONATED IMIDAZOLIUM NITRATE AND PICRATE SALTS

J. D. Holbrey, W. M. Reichert, M. Smiglak, S. K. Spear, H. Yang*, K. Manju†, K. Kirichenko†, A. R. Katritzky†, J. S. Thrasher, L. Y. Sun, and R. D. Rogers

Center for Green Manufacturing and Department of Chemistry
The University of Alabama
Tuscaloosa, AL 35487

†Center for Heterocyclic Compounds
Department of Chemistry
University of Florida
Gainesville, FL 32611

ABSTRACT

The stability, liquid ranges, and thermal decomposition of a series of quaternized and protonated imidazolium nitrate and picrate salts have been investigated. The quaternized, $N,N'$-dialkylated imidazolium salts are more stable than the protonated examples, and salts with picrate anions are surprisingly more stable than the corresponding nitrate salts and in each case, decompose exothermically yielding volatile decomposition products.

INTRODUCTION

Ionic liquids (ILs) are not new materials - they have been known for over 100 years (1). The renewal of interest particularly from the mid-1990s onwards (2) in using ILs in applications in areas as diverse as liquid battery electrolytes, gas separations membranes, and catalytically active solvents for synthetic chemistry (3,4) has led to increased understanding in the features required to produce ILs. This in turn, has led to phenomenal growth in the discovery of different types of salts that can support low melting ionic liquid phases. Either cation and anion selection or modification can permit very precise tuning of solvent properties. Changes in density, viscosity, melting point, and solvation properties are possible in this way, thus enabling the rational design of application specific ILs.

The properties of ILs that result from suppression of ion-ion interactions are, in general, low melting points, reduced lattice energies in the solid phases, a tendency for glass formation upon cooling, polymorphism, and multiple phase transitions (5). In addition, and probably of greatest consequence as a driver for recent interest in ionic liquids - reduction of ion-ion associations results in only limited ion-ion pairing (clusters are extensively observed by MS, rather than cation-anion pairs) (6), such that ionic liquids have, in general, no measurable vapor pressure, and do not evaporate or boil. The upper liquid range is limited by thermal decomposition of the liquids.
The interesting, and unique, property sets of ILs – in particular, an intrinsic lack of vapor pressure and potential for wide, stable liquid ranges, and easily accessible and versatile chemical modification - may provide a range of valuable advances in the development of new energetic materials. High energy density materials are of great interest for energy storage and as propellants. There are number of benefits from having liquid, rather than solid materials. However, in most cases liquids tend to have vapor pressures that can result in losses, composition changes, or increased hazards. Thus, the development of non-volatile liquid high energy density material, an energetic liquid, is a desirable goal (7).

Energetic ionic liquids (ILs) are potential new materials with thermodynamically high-energy yields on combustion that are 'ionic liquid' in physical form. Many energetic materials (for example ammonium nitrate/perchlorate, urea perchlorate, hydrazine hydrate/nitrates, etc.) are salts or can be made into salts (8), and many salts can be designed, or modified to be ionic liquids. Klapötke (9) has reported a number of explosive salts, hydrazinium azides for example, which can be prepared as viscous room temperature liquids, or low melting solids, depending on the substitution on the hydrazinium cation. The set of materials reported is, however, too small to extract general trends for the formation of liquid vs. solid materials.

Drake and co-workers (10) have demonstrated how energetic ILs can be prepared by combining cations containing energetic functionality (in this case from 1H-1,2,4-triazole, 4-amino-1,2,4-triazole, and 1H-1,2,3-triazole as the cation precursors) with relatively small inorganic energetic anions ([NO3]−, [ClO4]−, and [N(NO2)2]2−). Importantly, it was suggested that the ready formation of ionic liquids with these cations appeared to be due to topographical shape and charge distribution similarity with more conventional imidazolium cations. A limited number of conventional ILs with ‘energetic’ anions are known (e.g., nitrate [NO3]−, perchlorate [ClO4]−, and dicyanamide [(N(CN)2)]−), but have not been systematically investigated from this perspective (11).

While, on this basis, the principles for developing and investigating energetic ionic liquids are well established (12), there exists a need to develop design criteria for formation of ionic liquids (13) containing energetic functional groups, to help understand, and hopefully predict, the relationships between addition of specific functional groups and the behavior of the resultant salts as potential ILs. We set out to evaluate whether conventional IL design approaches could be used to extend the range of IL energetic materials, and describe here our current progress in the evaluation of the applicability of conventional ionic liquid design to the formation of energetic salts. Initial studies, on the formation, stability, and thermal decomposition properties of simple protonated and quaternized imidazolium nitrate and picrate salts, which are currently under investigation as archetypal models for energetic ILs, are reported herein.

**EXPERIMENTAL**

**Materials**

All reagents were purchased from Aldrich and were used as received. 1,3-Dimethylimidazolium nitrate I-NO3 and picrate (I-pic) were prepared by neutralization of 1,3-dimethylimidazolium-2-carboxylate (14) with 1 equivalent of the
appropriate ethanolic acid solution. 1,2,3-Trimethylimidazolium nitrate (II-NO₃) and picrate (II-pic) were prepared from 1,2,3-trimethylimidazolium methylcarbonate, prepared using an analogous method to 1,3-dimethylimidazolium-2-carboxylate. 1-Methylimidazole or 1,2-dimethylimidazole (0.20 M) and dimethylcarbonate (0.26 M) were sealed in a screw-top pressure tube (Ace Glass) and heated at 80-83 °C for 7 days. The precipitated 1,3-dimethylimidazolium-2-carboxylate or 1,2,3-trimethylimidazolium methylcarbonate were separated from unreacted starting materials by filtration, washed with cold acetone and dried in vacuo, to give colorless crystalline powders (yield ~80 %). 1-Butyl-3-methylimidazolium nitrate (III-NO₃) was prepared from 1-butyl-3-methylimidazolium chloride salt by metathesis with silver nitrate, and 1-butyl-3-methylimidazolium picrate (III-pic) from the chloride salt by ion exchange with aqueous picric acid followed by solvent extraction into dichloromethane. The protonated salts, 1-methyl-3H-imidazolium nitrate (IV-NO₃) and picrate (IV-pic), 1,2-dimethyl-3H-imidazolium nitrate (V-NO₃) and picrate (V-pic), 1-butyl-3H-imidazolium nitrate (VI-NO₃) and picrate (VI-pic) were obtained on neutralization of the appropriate imidazoles with 1 equivalent of either ethanolic nitric or picric acid, and the salts isolated by slow evaporation in a dry atmosphere. In all cases, the salts were obtained in good yields and were characterized by ¹H and ¹³C NMR spectroscopy in dmsø-d₆ and IR spectroscopy.

Analysis

Melting points of the isolated salts were determined by differential scanning calorimetry (DSC) using a TA Instruments model 2920 Modulated DSC (New Castle, DE) cooled with a liquid nitrogen cryostat. The calorimeter was calibrated for temperature and cell constants using indium (melting point 156.61 °C, ΔH 28.71 J g⁻¹). Data were collected at constant atmospheric pressure, using samples between 10-40 mg in aluminum sample pans sealed using pin-hole caps. Experiments were performed heating at 5 °C min⁻¹. The DSC was adjusted so that zero heat flow was between 0 and -0.5 mW, and the baseline drift was less than 0.1 mW over the temperature range 0-180 °C. An empty sample pan was used as reference; matched sample and reference pans (within ± 0.20 mg) were used.

Thermal decomposition temperatures were measured in the dynamic heating regime using a TGA 2950 TA Instrument under both argon and air atmospheres. Samples between 2-10 mg were heated from 40–500 °C under constant heating at 10 °C min⁻¹.

Accelerating rate calorimetry measurements were obtained under adiabatic conditions in a sealed titanium bomb under oxygen at 100 psig pressure using an Arthur D. Little ARC 2000™ accelerating rate calorimeter. Samples (0.2–0.5 g) were heated 10 °C min⁻¹, using a stepping heat-wait-search protocol with each step of 10 °C to determine the onset of self-heating (excess heating rate > 0.02 °C min⁻¹).

RESULTS AND DISCUSSION

The effects of introducing different functional groups around the periphery of the cations, and varying the types of anions of organic salts has been investigated using simple substituted imidazolium and pyrrolidinium systems. The thermal stability of simple imidazolium (alkylated and protonated) salts with nitrate and picrate anions
(Table 1) were investigated as model compounds. The synthetic approaches used to obtain the different salts are shown in Figure 1. The thermophysical properties of the salts isolated were determined using DSC, TGA, and accelerating rate calorimetry (ARC) to measure melting points, enthalpy of fusion, upper liquid limit and decomposition profiles. Solid-state packing and hydrogen-bonding interactions were determined based on single crystal X-ray structures obtained for some of the salts.

Figure 1. Synthetic schemes used to obtain the salts described in these studies; A) protonation; B and C) methylation with dimethyl carbonate (14) followed by reaction with acid, and; D) alkylation with chlorobutane followed by metathesis.

The introduction of active anions as protonated salts makes a wide range of simple binary ionic liquids available. The disadvantages of protonated ionic liquids – namely that of decreased thermal stability relative to quaternized analogs – is offset at the screening stage by the advantages in preparation. The systems described here, containing only short-chain \( \text{N} \)-substituents, were chosen for investigation with the anticipation that solid, though low melting, salts could be obtained from which single crystal X-ray diffraction could be used to probe interactions in the solid state.

Alkylation was achieved either using dimethyl carbonate or chlorobutane followed by metathesis (quaternized systems) or by neutralization of the heterocyclic bases with appropriate acids (protonated salts). The quaternized salts with 1,3-dimethylimidazolium or 1,2,3-trimethylimidazolium cations and protonated imidazolium salts were prepared directly by neutralization of (i) 1,3-dimethylimidazolium-2-carboxylate, (ii) 1,2,3-trimethylimidazolium methyl carbonate, or (iii) respective 1-alkylimidazoles with 1 equivalent of either ethanolic nitric or picric acid, and the products isolated by slow evaporation. 1-Butyl-3-methylimidazolium nitrate was obtained from the chloride salt by metathesis with silver nitrate, and the picrate salt was obtained from the chloride salt by ion exchange with aqueous picric acid followed by solvent extraction into dichloromethane. In all cases, the salts were obtained in good to excellent yields.
Table 1. Melting points of the simple substituted imidazolium nitrate and picrate salts investigated.

| Cation Quaternized Salts | Anion | mp °C | T<sub>dec</sub> °C<sup>a</sup> |
|---------------------------|-------|-------|-----------------|
| I 1,3-dimethylimidazolium  | nitrate | 161   | 275             |
|                           | picrate | 149   | 195             |
| II 1,2,3-trimethylimidazolium | nitrate | 119   | 271             |
|                           | picrate | 119   | 271             |
| III 1-butyl-3-methylimidazolium | nitrate | 18    | 272 (190-200)   |
|                           | picrate | 46    | 203 (195-205)   |

| Protonated Salts | Anion | mp °C | T<sub>dec</sub> °C<sup>a</sup> |
|------------------|-------|-------|-----------------|
| IV 1-methyl-3-H-imidazolium | nitrate | 67     | 156 (150-160)   |
|                           | picrate | 161    | 233             |
| V 1,2-dimethyl-3-H-imidazolium | nitrate | 84     | 151 (130-140)   |
|                           | picrate | 182    | 236 (205-215)   |
| VI 1-butyl-3-H-imidazolium | nitrate | 26     | 174 (145-155)   |
|                           | picrate | 40     | 246             |

<sup>a</sup>ARC decomposition temperature range in parentheses, in oxygen

The quaternized nitrate salts (I-III-N<sub>3</sub>) show the expected steady decrease in melting point with increasing length of the N-alkyl substituent. Whereas these salts with symmetric di- and tri-methylated cations are high melting solids (mps > 150 °C), the corresponding salts with protonated cations (IV-VI) have significantly lower melting points, with all three protonated imidazolium nitrate salts melting below 100 °C. Typical DSC traces showing sharp, first order melting transitions on heating of the protonated salts IV-N<sub>3</sub> and V-N<sub>3</sub> are shown in Figure 2. Screening thermal stability, under dynamic heating at 10 °C min<sup>-1</sup> showed typical single step thermal decomposition profiles for all the nitrate salts, as shown in the TGA traces in Figure 3.

![Figure 2](image.png)
Crystal structures of the two protonated methylimidazolium nitrate salts (IV-$\text{NO}_3$ and V-$\text{NO}_3$) were determined, and are shown in Figure 4. The structure of IV-$\text{NO}_3$ had previously been reported by Wilkes and Zaworotko (15), however coordinates were not available in the CSD. The two salts show remarkably similar hydrogen-bonding and ion-ion packing, with five anions surrounding each cation in both systems, providing a series of weak, bifurcated hydrogen-bonds between all the ring-protons of the cation and surrounding imidazolium anions.

Figure 3. TGA mass loss profiles for I, III, IV, and VI-$\text{NO}_3$ salts showing the relative differences in thermal stability of protonated and quaternized imidazolium nitrate ILs.

Figure 4. Diagrams showing the close contacts between cations and anions in the X-ray crystal structures of protonated imidazolium salts, 1-methyl-3-H-imidazolium nitrate (IV-$\text{NO}_3$, left) and 1,2-dimethyl-3H-imidazolium nitrate (V-$\text{NO}_3$, right).
The trends in melting points also appeared in the picrate salts synthesized; DSC traces for the higher melting point salts are shown in Figure 5. The 1-butyl-3-methylimidazolium picrate formed a relatively viscous oil that eventually solidified, and it showed a sharp melting transition at 46 °C. Although the formation of crystalline picrate salts has been used as a common method of isolating salts for characterization, the imidazolium salts isolated here show just how readily low melting point IL phases can be formed from organic salts, even with such large, complex anions.

![Figure 5. DSC traces showing the sharp melting transitions for selected higher melting point protonated and quaternized picrate salts, I-pic (□), IV-pic (○), and V-pic (▲).](image)

The melting points of the picrate salts decrease with decrease in the availability of hydrogen-bond donor sites on the cation. This is the 'normal' behavior for hydrogen-bonding salts, but is uncharacteristic of IL salts, where C(2)-methylation tends to produce a corresponding increase in melting point.

Examination of the crystal structures of the key picrate salts isolated gives some indication of the inter-ion interactions governing the structure of the solid state and the melting points. A strong directional hydrogen-bond is observed in each case from the imidazolium cation to the phenolate group of the picrate anion (illustrated in the crystal structure of IV-pic, Figure 6). This is an example of classical solid state hydrogen-bonding between cation and anionic species, and it is clearly a significant feature in governing the melting points of these salts. The melting points of the salts decrease as the ability of the cation to maintain this strong hydrogen-bond, either through substitution of the hydrogen-bond donor sites or increased steric hindrance.

The upper limit of stability for the picrate salts was determined by TGA. The protonated imidazolium picrate salts showed decomposition temperatures that were slightly variable between samples, but in each case showed a single mass loss event. In contrast, the quaternized examples I-III-pic showed complex multi-step mass loss profiles (Figure 7) that look similar, in terms of the number of steps and shape of the curve, but with differing temperatures of the initial mass loss.
Figure 6. Interactions of cation and anion in the asymmetric unit from the X-ray crystal structure of 1-methyl-3-H-imidazolium picrate (IV-pic) crystallized from ethanol, showing the strong bifurcated hydrogen-bonding from the protonated cation to the picrate anion. In the solid state, two of the nitro-groups on the picrate anion are in the plane of the ring, with the third nitro-group twisted almost perpendicularly to the ring.

Thermal Analysis and Investigation

The overall trends in melting points and thermal stability observed in these salts fits reasonably well with the expected results. The quatemized salts show higher thermal stability than corresponding protonated analogs. In the case of the picrate salts, some variability in the upper decomposition temperature was observed. Nitrate salts with quatemized cations tended to be more thermally stable than the corresponding picrate salts, but with protonated cations, the picrate salts tended to be approximately 70-80 °C more stable than the nitrate salts. Notably, the thermal decomposition temperatures of these protonated picrate salts are higher than the boiling points of the corresponding imidazole.

Figure 7. TGA traces showing the decomposition profiles for the quatemized imidazolium picrate salts (I-III picrate) showing the multi-step mass loss on heating. Note that even at 400 °C, up to 50% residual char (nonvolatile material) was observed.
Accelerating rate calorimetry was used to investigate the thermal decomposition of some of these salts in more detail. The decomposition temperature range for samples studies, in an oxygen atmosphere in a titanium bomb, are shown in Table 1. The temperature and pressure vs. time profile for the protonated ionic liquid, 1-methyl-3-H-imidazolium nitrate, is shown in Figure 8 in an oxygen atmosphere pressurized to 100 psig. The IL shows thermal stability on heating, indicated by the small residual increase in internal pressure until the thermal decomposition temperature (150-170 °C) is reached, at which point self-heating of the sample starts resulting in an exothermic decomposition and evolution of gaseous products. For example, after approximately 1100 minutes of run time, a very rapid increase in the internal pressure with an associated rise in internal bomb temperature is observed, corresponding to decomposition at 170 °C (Figure 8).

Figure 8. ARC gas evolution data for 1-methyl-3-H-imidazolium nitrate heating under adiabatic conditions in oxygen (initial pressure, 100 psig) showing the internal temperature profile with time (solid line) and internal pressure (circles). The heating profile follows 10 °C heating steps until the onset of self-heating, and shows the stability of the ionic liquid (no significant increase in pressure) until the thermal decomposition temperature (~150-170 °C) is reached. At this point, exothermic decomposition with generation of gaseous products is observed.

In all the examples investigated, the nitrate salts show a moderate to high exothermic decomposition (based on the rate of self-heating through the decomposition event). The decomposition temperatures determined by ARC in oxygen roughly correspond with those found by TGA (using either an inert atmosphere, or in air). The lower decomposition temperatures found by ARC may reflect the lower heating rates used in these experiments than in the TGA method and/or may be a result of the increased sensitivity afforded by increased sample sizes in ARC. The relative stabilities show that the protonated salts are less stable by ~50 °C versus the quatemized example, 1-butyl-3-methylimidazolium nitrate. The two picrate salts studied showed excellent thermal stability in the ARC, and high self-heating rates on decomposition, consistent with the nature of the picrate anion.
Flammability of protonated imidazolium nitrate ionic liquids

While ILs are often considered to be non-flammable liquids, and studies on trialkylimidazolium examples were unable to determine flash points below 200 °C (16), non-flammability cannot be considered as a generic feature of all ionic liquids. Thermal decomposition can lead to the evolution of flammable components, and for ILs with relatively low decomposition temperatures such as the protonated imidazolium nitrate systems described herein, a significant potential exists for the ILs to sustain combustion if ignited. Initial screening of the combustibility of the protonated salts IV-VI with both nitrate and picrate anions by heating small samples on a watch glass with a naked flame demonstrated that these salts could be ignited, and once lit, continue to burn in air. This is demonstrated in the photograph (Figure 9) showing self supported combustion of IV-NO₃. It is notable, that these N-protonated ionic liquids have significantly lower decomposition temperatures than those containing N-alkylated cations. Thus, not all ionic liquids are non-flammable, and thus they cannot be generically described as non-flammable.

Figure 9. Photograph showing a 1 g sample of IV-NO₃ burning in air. Combustion resulted in a 93% loss in mass.

CONCLUSIONS

Low-melting imidazolium salts can be prepared with both N,N'-dialkylated and protonated alkylimidazolium cations and nitrate or picrate anions. The salts can have low melting points and thermal ranges up to the limit of decomposition, which is an exothermic event, with considerable self-heating for both picrate and nitrate salts. Protonated imidazolium nitrate ionic liquids have been shown to be flammable, and once ignited will burn in air under ambient conditions, which has particular implications for the safe handling and use of such simple protonated ILs under elevated thermal conditions.
ACKNOWLEDGMENT

This work was supported by the Air Force Office of Scientific Research (Grant F49620-03-1-0357).

REFERENCES

1. O. Wallach, *Chem. Ber.*, 16, 535 (1884); S. Sudgen, and H. Wilkens, *Chem. Soc. J.*, 51, 1291 (1929).
2. J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, *Inorg. Chem.*, 21, 1263 (1982); C. L. Hussey, *Adv. Molten Salt Chem.*, 5, 185 (1983); C. L. Hussey, *Pure Appl. Chem.*, 60, 1763 (1988); K. R. Seddon, *Molten Salt Forum*, 5, 53 (1998); Y. Chauvin, and H. Olivier-Bourbigou, *Chemtech*, Sept 25, 30 (1995).
3. See for example, *Ionic Liquids: Industrial Applications for Green Chemistry*, R. D. Rogers and K. R. Seddon, Eds., ACS Symposium Series 818, American Chemical Society, Washington DC (2002).
4. T. Welton, *Chem. Rev.*, 99, 2071 (1999); J. D. Holbrey and K. R. Seddon, *Clean Prod. Proc.*, 1, 223 (1999); P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, 39, 3772 (2000); R. Sheldon, *Chem. Commun.*, 2399 (2001); C. M. Gordon, *Appl. Catal. A*, 222, 101 (2001).
5. J. Golding, S. Forsyth, D. R. MacFarlane, M. Forsyth, and G. B. Deacon, *Green Chem.*, 4, 223 (2002).
6. A. K. Abdul-Sada, A. E. Elaiwi, A. M. Greenway, and K. R. Seddon, *Eur. Mass. Spectrom.*, 3, 245 (1997).
7. R. Meyer, J. Köhler, and A. Homburg, *Explosives*, 5th edition, Wiley-VCH, Weinheim (2002).
8. P. F. Pagoria, G. S. Lee, A. R. Mitchell, and R. D. Schmidt, *Thermochim. Acta*, 384, 187 (2002).
9. A. Hammerl, G. Holl, M. Kaiser, T. M. Klapötke, R. Kranzle, and M. Vogt, *Z. Anorg. Allg. Chem.*, 628, 322 (2002).
10. G. Drake, T. Hawkins, A. Brand, L. Hall, M. Mckay, A. Vij, and I. Ismail, *Propellants, Explosives, Pyrotechnics*, 28, 174 (2003).
11. J. S. Wilkes and M. J. Zaworotko, *Chem. Commun.*, 965 (1992).
12. J. C. Bryan, M. C. Burnett, and A. A. Gakh, *Acta Cryst. C.*, 54, 1229 (1998); A. A. Gakh, J. C. Bryan, M. N. Burnett, and P. V. Bonnesen, *J. Mol. Struct.*, 520, 221 (2000); M. A. Petrie, J. A. Sheehy, J. A. Boatz, G. Rasul, G. K. S. Prakash, G. A. Olah, and K. O. Christie, *J. Am. Chem. Soc.*, 119, 8802, (1997); W. Fraenk, H. Noth, T. M. Klapötke, and M. Suter, *Z. Naturforsch.*, 57b, 621 (2002).
13. J. D. Holbrey and R. D. Rogers, in *Ionic Liquids in Synthesis*, P. Wasserscheid and T. Welton, Eds., VCH-Wiley, Weinheim, 41-54 (2003); J. D. Holbrey, A. E. Visser, and R. D. Rogers, in *Ionic Liquids in Synthesis*, P. Wasserscheid and T. Welton, Eds., VCH-Wiley, Weinheim, 68-81 (2003).
14. J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, and R. D. Rogers, *Chem. Commun.*, 28 (2003).
15. J. S. Wilkes and M. J. Zaworotko, *Supramol. Chem.*, 1, 191, (1993).
16. D. M. Fox, W. H. Awad, J. W. Gilman, P. H. Maupin, H. C. De Long, and P. C. Trulove, *Green Chem.*, 5, 724 (2003).