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Short communication

Limited thermal stability of imidazolium and pyrrolidinium ionic liquids

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ABSTRACT

Ionic liquids, with their vast applications, have been touted as being thermally stable to very high temperatures. However, decomposition not detected by standard TGA and NMR techniques are observed with spectroscopic techniques sensitive enough to see small amounts of impurities. Decomposition temperatures of common ionic liquids appear to occur at hundreds of degrees below those temperatures previously reported.

1. Introduction

The unique properties of room temperature ionic liquids have generated a tremendous amount of interest in both their chemistry and potential applications [1–3]. As with all new materials the initial claims as to their “remarkable” properties were sometimes overstated. These liquids originally believed to be nonvolatile have recently been shown to have a vapor pressure and can even be distilled [4]. Many are now known to be toxic [5], and their early claims of chemical [6] and thermal stabilities [7] and low flammability need to be carefully scrutinized or qualified as applicable to specific classes of ionic liquids.

We recently described a route to high quality ionic liquids [8] and have been employing these materials in spectroscopic applications [9,10]. During these studies it became apparent that the thermal stabilities of the imidazolium and pyrrolidinium ionic liquids are much lower than was previously suspected. We selected butylmethylpyrrolidinium bis(trifluoromethanesulfonyl)amide [C4mpy][Tf_2N], and butylmethylimidazolium bis(trifluoromethanesulfonyl)amide, [C4mim][Tf_2N], as representative ionic liquids consisting of commonly studied cations paired with the generally robust Tf_2N^- anion. Typical decomposition temperatures for these ionic liquids are reported to be near 400 °C; however, we observe significant decomposition at much lower temperatures (250 °C) that is readily observed in the optical quality (Fig. 1).

2. Experimental

Ionic liquids were prepared using the methods described in Ref. [8]. UV–vis measurements were carried out using an HP Model 8453. Fluorescent measurements were carried out using a PTI GL-3300 fluorimeter with an R955 photomultiplier. Nuclear magnetic resonance (NMR) spectra were measured at 400 MHz (1H), on a Bruker Avance 400 Ultrashield spectrometer. All NMR spectra were recorded in deuterochloroform unless otherwise stated, with reference to tetramethylsilane.

TGA was carried out using a Mettler Toledo TGA SDTA 851(e) and N_2 as the flow gas. The temperature range for TGA was 30–400 °C at 10 °C min^{-1}, followed by isothermal at 400 °C for 15 min. Mass spectrometry (MS) was carried out using a Pfeiffer quadrupole spectrometer. The heated stainless steel capillary inlet was positioned in a stream of argon flowing across the sample, which was heated at 30–400 °C with a ramp rate of 10 °C min^{-1}, then held isothermal at 400 °C for 15 min.

3. Results and discussion

3.1. Thermal gravimetric analysis

The traditional method for determining the thermal stability of an ionic liquid has been thermal gravimetric analysis (TGA) and

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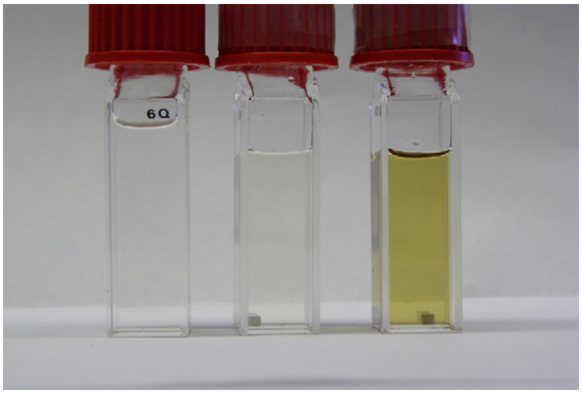

Fig. 1. [C4mim][Tf_2N] with pure (left – before heating), and after heating at 250 °C for 12 h under dynamic vacuum (center) and under an atmosphere of N_2 (right).

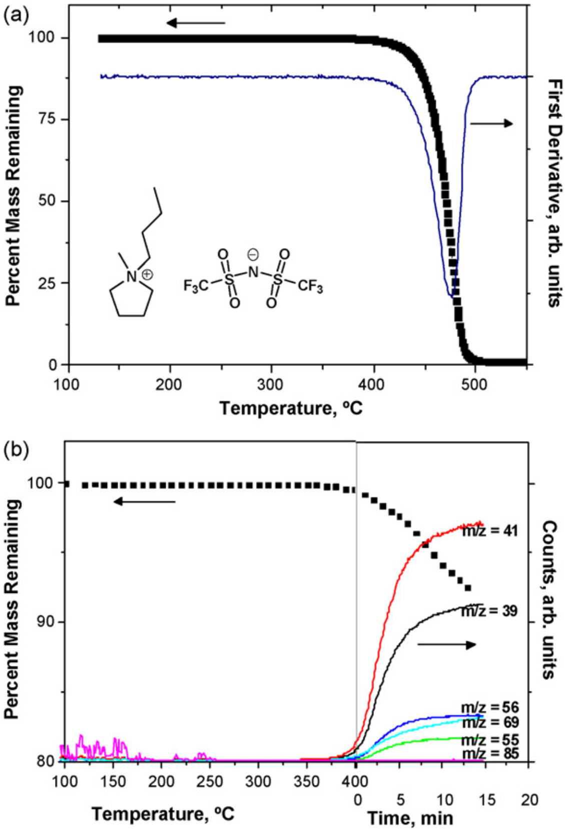

Fig. 2. TGA (a) of [C4mpy][Tf_2N] and TGA-MS (b) with heating to 400 °C at 10 °C min^{-1}, followed by isothermal at 400 °C for 15 min.

detection of decomposition products [11], as shown in Fig. 2a for [C4mpy][Tf_2N]. The effluent gas was analyzed via mass spectrometry, and no appreciable volatile species are observed below 400 °C (Fig. 2b) at which point fragments are observed for Hoffmann elimination products from the pyrrolidinium ring of $C_3H_5^{\bullet+}$ (41 amu) and $C_3H_6N^{\bullet+}$ (56 amu), $C_5H_{11}N^{\bullet+}$ (85 amu), and decomposition of the anion though loss of $CF_3^{\bullet+}$ (69 amu).

Using TGA as the sole analytical technique it would appear that there is no decomposition in [C4mpy][Tf_2N] until at least 400 °C based on the “onset” temperature of decomposition. It is important to remember that TGA only measures weight loss, and since significant chemistry can occur before this the onset temperatures are often inaccurate in describing thermal stability. Indeed MacFarlane and co-workers [7], have redefined the decomposition temperature for [C4mpy][Tf_2N] using $T_{0.01/10}$, the temperature at which 1% degradation – as determined by mass loss – occurs in 10 h. Using this definition they determined the thermal stability of [C4mpy][Tf_2N] to be as low as 271 °C. Similar isothermal measurements have been previously used to determine thermal stabilities, however TGA is still standard [6,7].

3.2. UV–vis and fluorescence spectroscopy

We report here that some chemical changes occur at temperatures as low as 150 °C. We have demonstrated that fluorescence spectroscopy is a sensitive method for probing the decomposition in imidazolium and pyrrolidinium ionic liquids. Changes in both fluorescence and visible absorption occur well before the formation of volatile by-products observed in TGA measurements. Decomposition to yield colored and fluorescent impurities can have significant implications for many practical applications of ionic liquids. With access to high purity ionic liquids it has been possible to probe the changes that temperature induces in these materials. The background color and fluorescence due to impurities in good quality ionic liquids is extremely low, and therefore impurities formed by decomposition can be detected at much lower levels.

Heating the ionic liquids at temperatures above 150 °C, even under a dry inert nitrogen atmosphere, causes significant increase in the color (Fig. 3) and concomitant changes in the UV–vis spectra, as seen in Fig. 3. No detectable mass loss is observed in either heated sample.

We initially considered that these changes were primarily due to the presence of small amounts of dissolved oxygen in the liquids. However, heating carefully degassed samples, under nitrogen or dynamic vacuum still resulted in similar changes in the UV–vis spectrum. The samples heated under dynamic vacuum do show

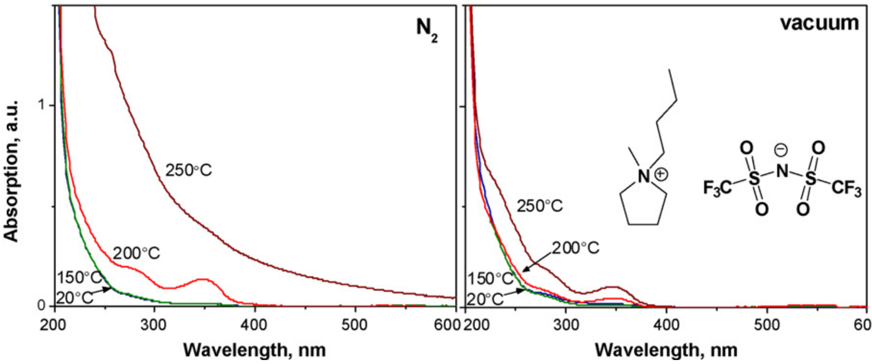

Fig. 3. UV/vis spectra for [C4mpy][Tf_2N] with heating for 12 h at 20, 50, 100, 150, 200, and 250 °C under an atmosphere of N_2 (left) and under dynamic vacuum (right). Pathlength = 1 cm.

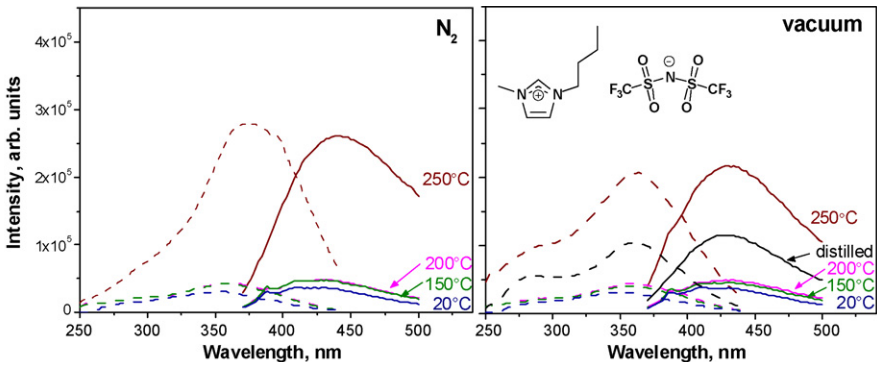

Fig. 4. Fluorescence spectra for [C4mim][Tf_2N] after heating for 12 h at 20, 100, 150, 200, and 250 °C under (left) an atmosphere of N_2, and (right) under dynamic vacuum, and the distilled product. Excitation wavelength is 359 nm, emission wavelength is 440 nm.

significantly smaller changes in their absorptions, but the effect due to decomposition is still observed. The changes in the UV–vis were much more marked for the [C4mpy][Tf_2N] than the [C4mim][Tf_2N].

The changes observed in the fluorescence spectra upon heating were much more pronounced than the absorption spectra, as seen in Fig. 4. We observe growth in the fluorescence emission at temperatures over 150 °C, Fig. 4, and significant increase in emission at 250 °C, again well below the temperatures necessary to generate volatile by-products observed by TGA experiments.

NMR is a commonly utilized technique for determination of purity of ionic liquids, but the sensitivity is not sufficient to determine impurities produced by decomposition at levels less than about 1%. Distillation of the ionic liquid [C4mim][Tf_2N] yields a deeply colored liquid, as evidenced by UV–vis with significant fluorescent impurities (Fig. 4, and in supporting information), but NMR reveals no impurities.

The first observable indication of thermal degradation of the ionic liquids appears as fluorescent decomposition products are formed. The nature of these impurities will be difficult to determine as they do not appear to be sufficiently volatile for analysis by GC–MS. In fact, they distill over with the ionic liquid itself. In addition we have not been able to identify the impurities using electrospray mass spectrometry (ESI-MS). During these experiments, only ion pairs belonging to the parent ions and their expected fragments are observed (similar to the TGA-MS experiments). Even at very low ionization potentials, only parent ions and the higher associated ion pairs ($[C_xA_{x-1}]^+$, and $[C_xA_{x+1}]^-$) are observed. It is possible that the impurities may be present in some form of oligomeric or polymeric species.

4. Conclusions

While the pyrrolidinium and imidazolium ionic liquids do have unique properties, their thermal stabilities are much lower than previously thought. Chemistry which yields impurities begins at temperatures above 150 °C and is readily observed by an increase in fluorescence, and colored impurities are formed well below the TGA onset decomposition of 400 °C. Oxygen is the most apparent culprit, but it is advisable to consider that any chemistry performed in imidazolium and pyrrolidinium ionic liquids at temperatures above 150 °C may be influenced by the degradation of the liquids themselves. Additionally, care must be taken in preparing and drying ionic liquids such that high temperatures are avoided, as the heat may encourage formation of fluorescent impurities, which must be removed through extensive work up [8]. The desired purity of the ionic liquids is, however, dependent on their application.

Acknowledgments

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Appendix A. Supplementary data

NMR of pure, heated, and distilled ionic liquids are available in the supplementary data associated with this article which can be found, in the online version, at doi:10.1016/j.tca.2009.02.023.

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