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Vaporisation of a Dicationic Ionic Liquid

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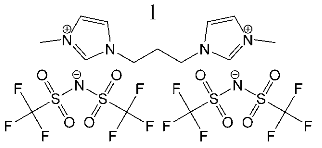
Ionic liquids (ILs) are liquids below 100°C consisting solely of ions. They exhibit a combination of properties, for example, electrical conductivity, involatility and tuneable solvent behaviour, which has led to a large number of potential applications.[1] Of particular interest here is the large enthalpy of vaporisation ($\Delta_{vap}H$), and hence low volatility, which is particularly useful for validation of force fields in molecular dynamics simulations,[2] and the nature of the IL vapour itself. Recently, monocationic ILs of the type C^+A^-[3] have been successfully evaporated,[2,4,5] and distilled,[6,7] and the vapour was shown to consist of neutral ion pairs (NIPs).[4,8–10] Here we report the first $\Delta_{vap}H$ measurement of a geminal dicationic IL, $C^{2+}\,2A^-$, 1,3-bis(3-methylimidazolium-1-yl) propane bis[(trifluoromethyl)sulfonyl]imide, $[C_3(C_1Im)_2][Tf_2N]_2$[11] (**1** in Scheme 1), together with the nature of its vapour, and the electron-induced appearance potentials for key ionic fragments from the vapour. We found that $\Delta_{vap}H_{298} = 190\ \text{kJ mol}^{-1}$, which is much higher than the values measured so far for ILs of the kind C^+A^-. The $C^{2+}\,2A^-$ vapour consists of neutral ion triplets (NITs), and an anomalously large energy is required to produce the gas phase dication, C^{2+}.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Scheme 1. $[C_3(C_1Im)_2][Tf_2N]_2$, compound 1.

Geminal dicationic ILs have a doubly charged cation (C^{2+}) composed of two singly charged cations linked by an alkyl chain, with a singly charged anion associated with each singly charged cation.[12] Dicationic ILs offer enhanced synthetic opportunities[13] and exhibit greater thermal stability[12,14,15] than monocationic ILs, allowing them to be used as solvents[15–18] and lubricants[19] at elevated temperatures. Furthermore, they also find application in analytical chemistry, particularly as the stationary phase in gas chromatography columns,[20–22] electrospray ionisation mass spectrometry and to detect small quantities of anions via gas-phase ion association.[23,24] The ability of dications to form gaseous ions containing distonic cations (charged and radical sites formally placed apart in the molecular framework) may also be used to investigate radical reactions in the gas phase.[24]

The subject of this study, **1**, was selected as it is reported to have a relatively low melting point, 269 K,[12,25] and it contains $[Tf_2N]^-$ as anion. Monocationic ILs containing $[Tf_2N]^-$ have low $\Delta_{vap}H$ values[4] and are thermally more stable than those containing more nucleophilic anions. The short C_3 linker chain also minimises the extra mass associated with linking the two imidazolium ions. The vapour was formed by evaporation from a thin film of the IL on a heated silver "dip-stick" in ultra-high vacuum (UHV) and it was analysed by line-of-sight mass spectrometry (LOSMS)[26–28] to eliminate extraneous gaseous background signals. We have already successfully applied this technique to the determination of $\Delta_{vap}H$ values for monocationic ILs.[4]

Compound **1**, $[C_3(C_1Im)_2][Tf_2N]_2$, was synthesised[12] and characterised at Nottingham (see the Supporting Information). The IL (a solid at room temperature) was melted in UHV ($T \approx 333$ K, significantly higher than the literature value of 269 K[12,25]) and a thin liquid layer was formed on a silver dip-stick by immersing it in the melted IL. The dip-stick was heated to evaporate the IL using either a constant elevated temperature for mass spectral analysis, or a linear heating programme for TPD.[4] LOS mass spectra of the vapour were acquired using a pulse-counting mass spectrometer shrouded by a cryopump (80 K) with two apertures that define a line of sight (i.e. form a molecular beam of the vapour) between a small circular patch on the liquid surface and the ionisation volume of the mass spectrometer. A flag was used to intercept the IL molecular beam, allowing decomposition products produced within the mass spectrometer itself to be identified and removed from the measured mass spectrum, leaving a pure IL vapour spectrum. The temperature was measured using a type K thermocouple attached to the dip-stick.

Figure 1a shows the LOSMS for compound **1** vapour at 554 K, taken with a movable flag positioned out of the line-of-sight beam, such that both the pure IL mass spectrum and contamination peaks due to decomposition of the IL within the mass spectrometer are recorded. Figure 1b, taken with the flag positioned in the line-of-sight molecular beam, shows just the contamination peaks, while the subtracted spectrum, Figure 2c (Spectrum c = Spectrum a − Spectrum b), shows the peaks for the pure IL. The molecular ion, $\{[C_3(C_1Im)_2][Tf_2N]_2\}^{+\bullet}$, or $[C^{2+}\,2A^-]^{+\bullet}$ (**2** in Scheme 2) is too heavy to be accessible to our mass spectrometer, but we would have expected it to be absent from the spectrum anyway (see below). The three most intense peaks are **3**, $[C^{2+}\,A^-]$ ($m/z = 486$), where one anion has been lost from the molecular formula; **4**, $[(C_3H_5)C_1Im]^+$ ($m/z =$

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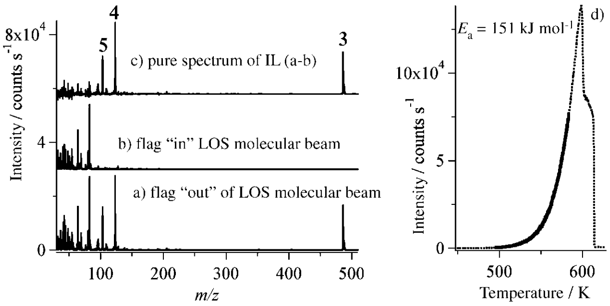


Figure 1. LOS mass spectra of **1** for vapor at 554 K: a) flag "out", b) flag "in" molecular beam, c) pure IL, = a−b. d) TPD for a thin film of **1** monitored using **3**, *m/z* 486, solid line shows analysis range.

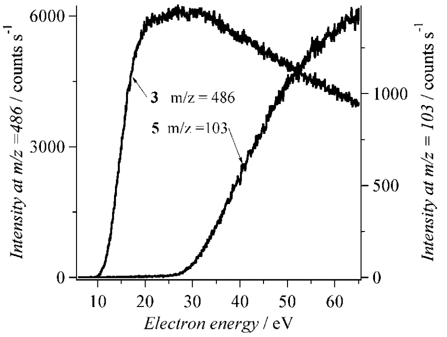
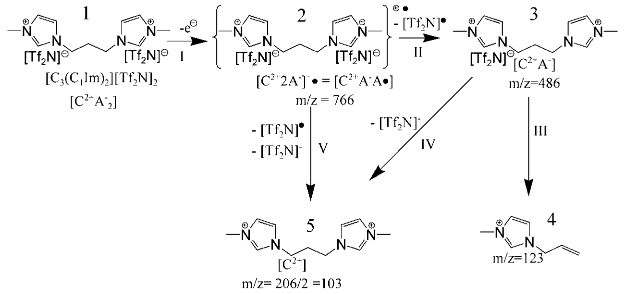


Figure 2. Ion efficiency curves for **3** (486), and **5** (103).



Scheme 2. Ionisation of **1** in the vapor phase (I), followed by fragmentation (II–V) of the transitory ion **2**.

123), a fragmentation product already observed for monocationic imidazolium ILs; and **5**, the doubly charged parent cation, $[C^{2+}]$ (*m/z* = 103). No peak was observed for $[Tf_2N]^+$ (*m/z* = 280) and on reducing the electron bombardment energy to <8 eV, no ions were detected in the mass spectrometer, showing that the IL vapour is composed solely of neutral species.

The presence of **3** strongly indicates that the vapour is composed of neutral ion triplets (NITs) of the form $[C_3(C_1Im)_2][Tf_2N]_2$. In Scheme 2, the gas-phase NIT is ionised in step I to form a transitory excited molecular ion, $[C^{2+}2\,A^-]^{+\bullet}$, **2**. The ionised electron effectively comes from one of the A^- species, forming $[C^{2+}\,A^-A^\bullet]$ which rapidly dissociates due to loss of electrostatic bonding to produce the $[C^{2+}\,A^-]$ ion, **3** (detected), and neutral $A^\bullet$ (not detected). Very recently Gross[29] has managed to observe the "molecular ion", $[C^+A^-]^{+\bullet}$, from monocationic ILs (CA), by employing the very soft gas phase ionisation method of field ionisation. By contrast our results for monocationic ILs[4] using the more energetic electron impact ionisation method caused dissociation of the "molecular ion", and hence no observation of the $[C^+A^-]^{+\bullet}$ ion occurs. From this, we predict that the $[C^{2+}2A^-]^{+\bullet}$ species **2**, is too short-lived to be detected using electron impact ionisation (as herein), but should probably be observable when using softer ionisation methods. Formation of **4** probably occurs by cleavage of a C–N bond (step III) while formation of the ion **5** involves either stepwise elimination of the second A^- (step IV), or simultaneous elimination of $A^\bullet$ and A^- (step V).

Figure 2 shows ion efficiency curves for the production of **3** and **5** from **1**, while Table 1 shows the appearance potentials (E_p) for these and **4** (see the Supporting Information). If we assume that the dissociation energy for step II is small, then E_p for **3**, 11.7 eV, is also that for the molecular ion **1** (step I), and is of a similar magnitude to the ionisation energies of neutral molecules.[30]. E_p for **4**, 15.7 eV, is 4.0 eV greater than for **3**, strongly suggesting that this ion is formed by fragmentation of **3** (step III). E_p for **5**, 30 eV (step V), is far greater than for the other fragment ions, the difference between E_p for **3** and **5** being 18.3 eV. This is the dissociation energy required to break the second electrostatic bond in **3** between the dication and the remaining $[Tf_2N]^-$ anion (step IV). A simple electrostatic calculation, using point charges, with A^- equidistant (*r*) from each charge on C^{2+}, gives $r = 1.6$ Å for the measured dissociation energy of 18.3 eV. This distance (shorter than a Li–F bond length) is unfeasibly small for an imidazolium–[Tf2N] distance. However, using more realistic distances and charge distributions on the ions leads to calculated dissociation energies much lower than the measured value. We therefore conclude that **5** must be formed in a highly excited state, possibly due to vibration of the two positive charges which are tethered by the C_3 alkyl chain.

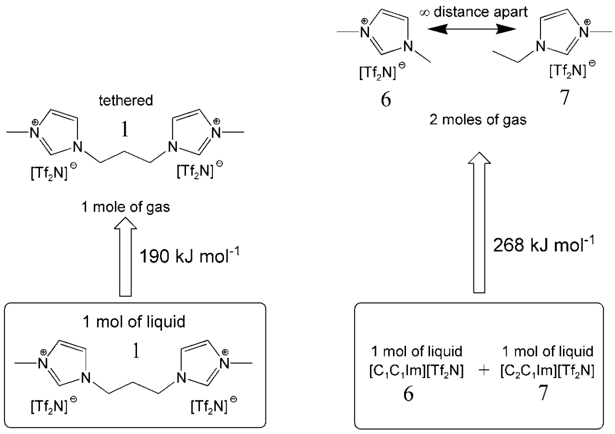
Table 1. Appearance potentials for ions.

m/z	Ion (Compound in Scheme 2)	E_p/eV
486	$[C^{2+}A^-]$ (**3**)	11.7 ± 0.4
123	$[C_3H_5(C_1Im)]^+$ (**4**)	15.7 ± 0.4
103	$[C^{2+}]$ (**5**)	30.0 ± 0.4

Temperature programmed desorption (TPD) of **1**, monitored using **3**, Figure 1, exhibits an exponential increase in intensity as expected for zero-order desorption.[4] A $\log_e$(*intensity*) versus $1/T$ analysis (Figure 1 d and see the Supporting Information), yields the activation energy, E_a, for desorption.[4] Ten desorption experiments gave $E_a = \Delta_{vap}U_{Tav} = 153 \pm 3\ \text{kJ mol}^{-1}$ for an average desorption temperature of $T_{av} = 545$ K, where $\Delta_{vap}U_{Tav}$ is the internal energy of vaporisation, (as evaporation occurs into a vacuum). Addition of RT_{av} to $\Delta_{vap}U_{545}$ gives $\Delta_{vap}H_{545} = 158\ \text{kJ mol}^{-1}$, the enthalpy of vaporisation at T_{av}. To convert this to $\Delta_{vap}H_{298}$, we need the difference in heat capacity between gas and liquid at constant pressure, $\Delta^g_l C_P$ ($=C_{P,gas}-C_{P,liquid}$). Using a fixed value of $-94\ \text{J K}^{-1}\text{mol}^{-1}$ ($=\Delta^g_l C_P$ for [C4C1Im]-

$[Tf_2N]$[31] used in previous work for monocationic ILs[4]), we obtain $\Delta_{vap}H_{298} = 181\ kJ\,mol^{-1}$ for **1**. However, **1** (m.wt. 766.58) is 1.83x more massive than $[C_4C_1Im][Tf_2N]$ (419.36), so one would expect $\Delta^{g}_{l}C_P$ to be corresponding larger, $-172\ J\,K^{-1}\,mol^{-1}$, giving $\Delta_{vap}H_{298} = 200\ kJ\,mol^{-1}$. Because of this uncertainty in $\Delta^{g}_{l}C_P$, we set $\Delta_{vap}H_{298} = 190 \pm 15\ kJ\,mol^{-1}$ for **1**.

$\Delta_{vap}H_{298}$ for **1** ($190\ kJ\,mol^{-1}$) is far higher than any so far measured for monocationic ILs (refs. [4,32] and references therein). This can be explained as follows. If we cleave one mole of **1** asymetrically at a C–C bond in the alkyl linkage and add a hydrogen to each resulting half, we obtain a mixture of 1 mole of $[C_1C_1Im][Tf_2N]$[33] (**6**), $V_m = 242.8\ cm^3$,[34] and one mole of $[C_2C_1Im][Tf_2N]$ (**7**), $V_m = 257.2\ cm^3$[34] (Scheme 3). This is a mixture with a volume approximately equal to the sum of the individual V_m values ($= 500\ cm^3$), where V_m is the molar volume. For **1**, $V_m = 476.1\ cm^3$,[34] a value only 5% smaller than that of the mixture of **6** and **7**. Evaporation of the mixture of **6** and **7** to form two moles of NIPs requires $\Delta_{vap}H_{298} = 134^{[35]} + 134^{[36]} = 268\ kJ\,mol^{-1}$. One might expect evaporation of **1** to form one mole of NITs to be similar, but the value, $190\ kJ\,mol^{-1}$ is only 72% of the value for the mixture. This is because the bis dication effectively tethers two NIPs together at a finite distance in the gas phase, preventing them from moving to an infinite distance apart (and hence absorbing more energy) to form two moles of NIPs (as for the mixture of **6** and **7**). We would therefore predict that as the linkage in the dication gets longer, the $\Delta_{vap}H_{298}$ value should tend towards the sum of the $\Delta_{vap}H_{298}$ values for the appropriate mixture of ILs. Hence $\Delta_{vap}H_{298}$ for $[C_{12}(C_1Im)_2][Tf_2N]_2$ might be expected to be $\leq 278\ kJ\,mol^{-1}$ ($= 2x\Delta_{vap}H_{298}$ for $[C_6C_1Im][Tf_2N]$[35]). Similar reasoning can be applied to dicationic ILs containing other cations, and to tri-, tetra- and higher cationic species where the heat of vaporisation will have an upper limit, for long linkage chains, equal to the sum of the $\Delta_{vap}H_{298}$ values for the equivalent mixture of binary ILs.



Scheme 3. Enthalpy of vaporisation for 1 mole of the dicationic $[C^{2+}2A^-]$ IL (left) and the equivalent combination of two moles of monocationic, $[C^+A^-]$, ILs (right).

We have shown that the dicationic IL **1** can be vaporised with an enthalpy of vaporisation of $\Delta_{vap}H_{298} = 190 \pm 15\ kJ\,mol^{-1}$ to give neutral ion triplets in the gas phase. These neutral ion triplets can be ionised to form singly and doubly charged ions, the latter requiring a particularly large energy to overcome the ionic bond between $[C_3(C_1Im)_2]^{2+}$ and $[Tf_2N]^-$.

Acknowledgements

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Keywords: ion pairs · ionic liquids · ionization potentials · mass spectrometry · phase transitions

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[36] $\Delta_{vap}H^{298}$ for [C_1C_1Im][Tf_2N] estimated using [C_nC_1Im][Tf2N] data in Figure 7 of ref. [4].

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