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# The Nature of Protic Ionic Liquids in the Gas Phase Revisited: Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Study of 1,1,3,3-Tetramethylguanidinium Chloride

Joana Vitorino,<sup>†,‡</sup> João P. Leal,<sup>†,‡</sup> Manuel E. Minas da Piedade,<sup>\*,†</sup> José N. Canongia Lopes,<sup>§,||</sup> José M. S. S. Esperança,<sup>§</sup> and Luís Paulo N. Rebelo<sup>§</sup>

*Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1649-016 Lisboa, Portugal, Unidade de Ciências Químicas e Radiofarmacêuticas, Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal, Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. República, Apartado 127, 2780-901 Oeiras, Portugal (www.itqb.unl.pt), and Centro de Química Estrutural, Complexo Interdisciplinar, Instituto Superior Técnico da Universidade Técnica de Lisboa, 1049-001 Lisboa, Portugal*

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The sublimation/vaporization of the protic ionic liquid 1,1,3,3-tetramethylguanidinium chloride, [Htmg]Cl, was studied by Fourier transform ion cyclotron resonance mass spectrometry in the temperature range 298–488 K and under a reduced pressure of  $3.2 \times 10^{-6}$  to  $1.5 \times 10^{-5}$  Pa. The results show that no charged species are present in the vapor over the condensed phase. Furthermore, ion–molecule reaction studies found no evidence of neutral ion pairs in the gas phase. This indicates that the sublimation/vaporization of [Htmg]Cl conforms to the general mechanism postulated for the distillation of protic ionic liquids, which involves a proton transfer leading to the formation of the neutral acid and base precursors, in this case hydrogen chloride and 1,1,3,3-tetramethylguanidine.

## Introduction

Ionic liquids are a class of substances in which interest has flourished in the past decade, due to the challenges and opportunities offered in terms of fundamental research and technological applications.<sup>1–4</sup> They are normally regarded as organic salts which, conventionally, melt below 373 K and may be considered as either protic or aprotic in character. Protic ionic liquids (PILs) are formed by proton transfer from a Brønsted acid, AH, to a Brønsted base, B, to yield, strictly speaking, a  $[\text{BH}^+][\text{A}^-]$  species:<sup>5</sup>



There is, however, a gray area associated with the practical application of this definition. For  $[\text{BH}^+][\text{A}^-]$  to be commonly considered as a pure liquid, the amounts of the neutral AH and B precursors involved in the equilibrium stated by eq 1 should be negligible. It has therefore been proposed, as a guideline, that a pure protic ionic liquid should contain less than 1% of the neutral species.<sup>6</sup> Significant proton transfer must also occur if the liquid is to be considered ionic, otherwise the product of the reaction of AH with B will be better described as an adduct sustained by a  $\text{AH} \cdots \text{B}$  hydrogen bond. It was recently discussed that, actually, the underlying structure can be even more complex—for instance, the possible existence of multiple equilibria leading to the formation of electrically charged aggregates.<sup>7</sup> Nonetheless, serious efforts have been undertaken to quantify the extent of proton transfer and the ionicity of PILs by using, for example, differences in the aqueous  $\text{p}K_{\text{a}}$  values of AH and  $\text{BH}^+$ ,<sup>8–10</sup> ionic conductivities in the form of Walden

plots,<sup>8,9</sup> and data from  $^1\text{H}$  NMR,<sup>10–12</sup> vibrational spectroscopy,<sup>12</sup> or cyclic voltammetry experiments.<sup>13</sup> The matter, however, has yet to be settled.<sup>5,12</sup>

Aprotic ionic liquids (AILs) contain substituents other than a proton (typically an alkyl group) at the site occupied by the labile proton in an analogous protic ionic liquid. In this case an equilibrium such as that expressed in eq 1 cannot be established, thus removing the ambiguities of definition mentioned above for PILs. They also require synthetic strategies which are different from the simple acid–base reactions used to obtain most protic ionic liquids.<sup>14</sup>

Aprotic ionic liquids were initially considered as essentially involatile, but this belief has been shown to be incorrect, and it is now well established that many ILs of this type can be distilled under reduced pressure without decomposition.<sup>15</sup> The vapor pressures and/or enthalpies of vaporization of some of them have also been experimentally determined by various methods including Knudsen effusion,<sup>16–18</sup> transpiration,<sup>19</sup> mass spectrometry,<sup>20</sup> calorimetry,<sup>21</sup> and thermogravimetry.<sup>22</sup> A critical review of these studies has recently been published.<sup>23</sup>

We previously investigated the nature of the species present in the gaseous phase during the reduced pressure distillation of aprotic ionic liquids using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS).<sup>24</sup> The results indicated that the ionic liquids 1-methyl-3-alkylimidazolium bis{(trifluoromethyl)sulfonyl}amide,  $[\text{C}_n\text{mim}][\text{NTf}_2]$  ( $n = 2, 4, 6, 8, \text{ or } 10$ ), 1-methyl-3-butylimidazolium hexafluorophosphate,  $[\text{C}_4\text{mim}][\text{PF}_6]$ , and trihexyltetradecylphosphonium trifluoromethyl sulfonate,  $[\text{P}(\text{C}_{14}\text{H}_{29})(\text{C}_6\text{H}_{13})_3][\text{OTf}]$ , distill under reduced pressure ( $10^{-6}$ – $10^{-4}$  Pa) as neutral anion–cation pairs. This conclusion corroborated the mass spectrometric results of Armstrong et al.<sup>20</sup> for the evaporation of thin films of aprotic ionic liquids into ultrahigh vacuum, and has subsequently been confirmed by more recent work.<sup>25,26</sup> Furthermore FT-ICR-MS studies of the binary mixtures  $[\text{C}_4\text{mim}][\text{NTf}_2] + [\text{C}_4\text{mim}][\text{PF}_6]$

\* To whom correspondence should be addressed. E-mail: memmp@fc.ul.pt.

<sup>†</sup> Universidade de Lisboa.

<sup>‡</sup> Instituto Tecnológico e Nuclear.

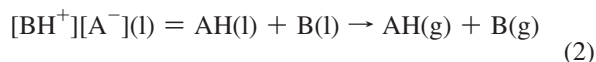
<sup>§</sup> Universidade Nova de Lisboa.

<sup>||</sup> Instituto Superior Técnico da Universidade Técnica de Lisboa.

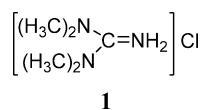
and  $[(\text{C}_4\text{mim})][\text{NTf}_2] + [\text{P}(\text{C}_{14}\text{H}_{29})(\text{C}_6\text{H}_{13})_3][\text{OTf}]$  indicated the occurrence of fractional distillation.<sup>24</sup>

We also examined the distillation of molten salts composed of a Group 1 metal cation and a commonly used ionic liquid anion,  $\text{M}(\text{NTf}_2)$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ), at 600–680 K and  $6 \times 10^{-6}$  to  $2 \times 10^{-4}$  Pa. It was concluded that similarly to the studied aprotic ionic liquids, the vapor phase essentially consists of neutral ion pairs, although, in the case of the lithium and sodium derivatives, a minor contribution from  $[\text{M}_2(\text{NTf}_2)_2]$  neutral aggregates was observed.<sup>27</sup> These substances therefore exhibit a behavior somewhat intermediate between that of aprotic ionic liquids and Group 1 metal halides,  $\text{MX}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ;  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ). Vapors originating from the latter under low pressure show significant fractions of aggregates larger than ion pairs (particularly dimers), with the tendency for aggregation decreasing as the sizes of the  $\text{M}^+$  or  $\text{X}^-$  ions increase (e.g.,  $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$  and  $\text{NaF} > \text{NaCl} > \text{NaI}$ ).<sup>28–30</sup>

Because of the equilibrium stated in eq 1, protic ionic liquids tend to vaporize by an intrinsically different mechanism from those of aprotic ILs,  $\text{M}(\text{NTf}_2)$ , or  $\text{MX}$  salts, decomposing into the two neutral acid and base precursors:<sup>15</sup>



This tendency seems, however, to significantly depend on the nature of these precursors and on the “strength” of the donor–acceptor interaction.<sup>8,9,12</sup> FT-ICR-MS experiments carried out in our laboratory indicated that once inside the vacuum chamber of the spectrometer 1-methylimidazolium ethanoate,  $[\text{Hmim}][\text{O}_2\text{CCH}_3]$ , immediately decomposed and vaporized at  $\sim 298$  K to yield the parent neutral base and acid (in this case 1-methylimidazole and ethanoic acid).<sup>24</sup> In contrast, Berg et al.<sup>31</sup> indicated that 1,1,3,3-tetramethylguanidinium chloride,  $[\text{Htmg}]\text{Cl}$  (**1**), which melts at  $\sim 483$  K, could be sublimed at 473

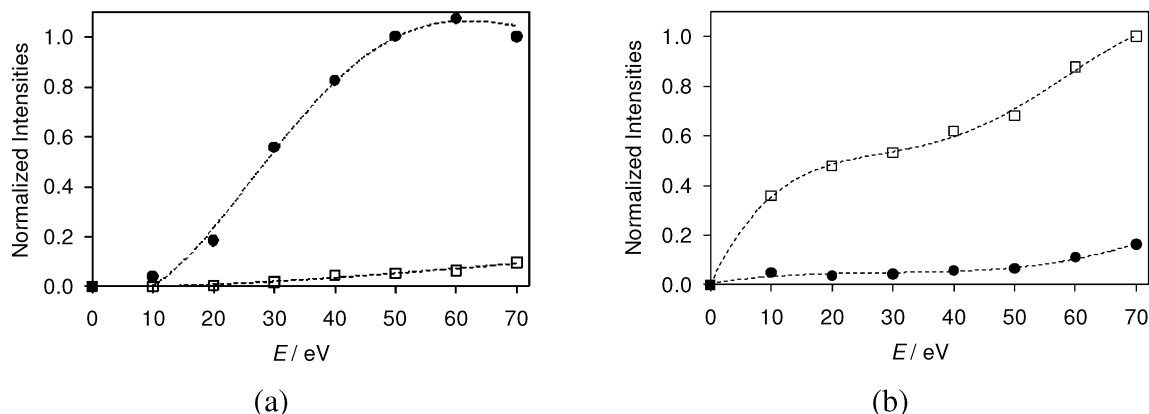


K and recondensed in the solid state without decomposition. Using a combination of Raman spectroscopy and Density Functional Theory (DFT) calculations, these authors also concluded that the vapor over a liquid sample of  $[\text{Htmg}]\text{Cl}$  kept in sealed glass ampules at 498 K, under reduced pressure, probably consisted of monomeric ion pair molecules sustained by a  $\text{N}-\text{H}^+\cdots\text{Cl}^-$  hydrogen bond. No experimental evidence for the dissociation of  $[\text{Htmg}]\text{Cl}(\text{s})$  or  $[\text{Htmg}]\text{Cl}(\text{l})$  producing gaseous 1,1,3,3-tetramethylguanidine (tmg) and  $\text{HCl}$  was found under those conditions. This conclusion was further supported by the results of B3LYP/6-311+G(d,p) calculations, which indicated that the formation of  $\text{tmg}(\text{g})$  and  $\text{HCl}(\text{g})$  from  $[\text{Htmg}]\text{Cl}(\text{g})$  was energetically unfavorable. These findings raised three fundamental questions which we tried to address in this work by using FT-ICR-MS, namely: (i) is the vaporization channel corresponding to eq 2 completely shut down in the case of  $[\text{Htmg}]\text{Cl}(\text{s})$  or  $[\text{Htmg}]\text{Cl}(\text{l})$ ? (ii) does the compound vaporize according to eq 2, although the gaseous neutral species may readily recombine when in a closed container? and (iii) are there ionic species in the vapor over  $[\text{Htmg}]\text{Cl}(\text{s})$  or  $[\text{Htmg}]\text{Cl}(\text{l})$ ?

## Materials and Methods

**General.** Elemental analyses (C and H) were performed on an automatic analyzer CE-Instruments EA-110 CHNS-O. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained at ambient temperature, on a Bruker Ultrashield-plus magnet 400 MHz spectrometer. Deuterated dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) was used as solvent. The differential scanning calorimetry (DSC) experiments were made on a TA Instruments DSC Q200 apparatus. The samples were sealed under nitrogen in a hermetic aluminum pan, and weighed to  $\pm 0.01$  mg on a Precisa balance. Nitrogen at a flow rate of  $50 \text{ cm}^3 \cdot \text{min}^{-1}$  was used as the purging gas. The scan rate was  $\beta = 10 \text{ deg} \cdot \text{min}^{-1}$ . Thermogravimetric analyses (TG) were carried out on a TA Instruments TGA Q50 apparatus, in the temperature interval 313–873 K. The samples were placed inside hermetic aluminum pans with a pinhole. Nitrogen (BOC) at a flow rate of  $60 \text{ cm}^3 \cdot \text{min}^{-1}$  was used as the purging gas. Dynamic and isothermal experiments were made. The former were carried out at  $10 \text{ deg} \cdot \text{min}^{-1}$ . The latter involved data collections over 24 h periods, with the temperature set to 373 or 433 K.

**Materials.** Two samples of 1,1,3,3-tetramethylguanidinium chloride were used in the experiments. Both were stored in an oxygen- and water-free ( $<5$  ppm) nitrogen atmosphere, inside a glovebox, prior to the FT-ICR-MS experiments. Sample 1 was prepared as follows:  $8.5 \text{ cm}^3$  (102.6 mmol) of a concentrated  $\text{HCl}$  aqueous solution (Pronolab; mass fraction 0.37;  $d = 1.19 \text{ g} \cdot \text{cm}^{-3}$ ) was added dropwise to a solution of  $12.5 \text{ cm}^3$  (99.6 mmol) of 1,1,3,3-tetramethylguanidine (Aldrich; mass fraction 0.99;  $d = 0.918 \text{ g} \cdot \text{cm}^{-3}$ ) in  $100 \text{ cm}^3$  of 2-propanol (Riedel-de Haen; mass fraction  $\geq 0.99$ ) under magnetic stirring. Because the reaction is highly exothermic the round-bottomed glass flask containing the reaction mixture was immersed in a water bath kept at ambient temperature throughout the neutralization process. Following neutralization, stirring was continued for 4 h and the solvent was finally removed at 323 K under vacuum (1 Pa) during 3 h, to yield a white solid. Recrystallization of the crude product from  $120 \text{ cm}^3$  of 2-propanol led to well-formed white needles. These were separated from the mother liquor by filtration, washed with three  $20 \text{ cm}^3$  portions of ethyl ether (Panreac; mass fraction  $\geq 0.99$ ), and dried under reduced pressure at 323 K under vacuum (1 Pa) to produce 13.74 g (90.5 mmol; yield 92%) of the final product. Elemental analysis for  $\text{C}_5\text{H}_{14}\text{N}_3\text{Cl}$ : expected C 39.60%, H 9.31%, N 27.71%; found (average of two determinations) C 39.16%, H 9.23%, N 27.80%.  $^1\text{H}$  NMR (Bruker, 400 MHz,  $\text{DMSO}-d_6/\text{TMS}$ ):  $\delta/\text{ppm}$  2.91 (s,  $\text{CH}_3$ , 12H), 8.03 (s,  $\text{NH}$ , 2H).  $^{13}\text{C}$  NMR (Bruker, 100 MHz,  $\text{DMSO}-d_6/\text{TMS}$ ):  $\delta/\text{ppm}$  39.42 ( $\text{NCH}_3$ ), 160.9 ( $\text{N}=\text{C}$ ). The onset ( $T_{\text{on}}$ ) and maximum ( $T_{\text{max}}$ ) temperatures of the fusion peak obtained by DSC with a sample of 3.750 mg mass were  $T_{\text{on}} = 480.0$  K and  $T_{\text{max}} = 482.4$  K, respectively, and the corresponding molar enthalpy of fusion  $\Delta_{\text{fus}}H_{\text{m}}^0 = 26.8 \text{ kJ} \cdot \text{mol}^{-1}$ . The obtained  $T_{\text{on}}$  and  $T_{\text{max}}$  are in line with the previously reported fusion temperature intervals for  $[\text{Htmg}]\text{Cl}$ ,  $T_{\text{fus}} = 481\text{--}482 \text{ K}^{31}$  and  $T_{\text{fus}} = 484\text{--}485 \text{ K}^{32}$ . A second heating run carried out after cooling the liquid sample 1 to ambient temperature led to significantly lower temperatures and enthalpies of fusion than those observed in the first run, namely  $T_{\text{on}} = 472.2$  K,  $T_{\text{max}} = 479.5$  K, and  $\Delta_{\text{fus}}H_{\text{m}}^0 = 22.1 \text{ kJ} \cdot \text{mol}^{-1}$ . This suggests that  $[\text{Htmg}]\text{Cl}$  partially decomposes on fusion. A TG analysis carried out at  $10 \text{ deg} \cdot \text{min}^{-1}$ , in the range 298–773 K, with a sample of 9.350 mg mass, showed that total mass loss occurred through an overlapping two-step event with onset temperature of 525 K. In experiments performed isothermally over 24 h periods, continuous mass losses that reached 0.5% at 373 K (initial



**Figure 1.** Ion intensities (normalized relative to the most intense peak at 70 eV) versus the electron ionization energy,  $E$ , for [Htmg]Cl sample 1 (a) subliming at 373 K and  $3.2 \times 10^{-6}$  Pa and (b) vaporizing at 513 K and  $1.5 \times 10^{-5}$  Pa. The filled circles correspond to  $[tmg]^+$  ( $m/z$  115) and the open squares to  $[Htmg]^+$  ( $m/z$  116).

sample mass: 12.794 mg) and 53.6% at 433 K (initial sample mass: 12.794 mg) were observed.

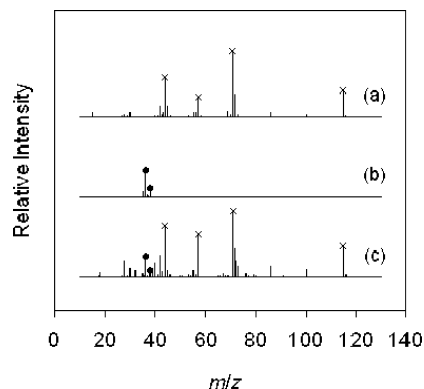
Sample 2 was prepared by sublimation of sample 1 at 10 kPa and 443 K. Elemental analysis for  $C_5H_{14}N_3Cl$ : found (average of two determinations) C 39.40%, H 9.74%, N 27.77%. The DSC experiments carried out with a sample of 1.020 mg mass led to  $T_{on} = 481.0$  K,  $T_{max} = 482.1$  K, and  $\Delta_{fus}H_m^\circ = 28.1$  kJ·mol $^{-1}$ . These values are in agreement with those mentioned above for the unsublimed sample. As noted for sample 1 a significant decrease in  $T_{on}$ ,  $T_{max}$ , and  $\Delta_{fus}H_m^\circ$  was observed when sample 2 was melted, cooled to ambient temperature, and reheated to above the fusion temperature ( $T_{on} = 474.0$  K,  $T_{max} = 480.1$  K, and  $\Delta_{fus}H_m^\circ = 22.2$  kJ·mol $^{-1}$ ). This suggests that both the sublimed and unsublimed [Htmg]Cl samples partially decompose upon fusion.

**Fourier Transform Ion Cyclotron Resonance Mass Spectrometry.** The FT-ICR-MS experiments were performed in a Finnigan FT/MS 2001-DT instrument equipped with a 3 T superconducting magnet and a Finnigan Venus Odyssey data system. The experimental procedure was previously described.<sup>24</sup> In brief, samples ( $\sim 3$  mg) of [Htmg]Cl were placed into small glass capillary tubes, which were mounted on the temperature-controlled tip of the probe arm of the FT-ICR mass spectrometer. The arm was inserted into the high-vacuum chamber of the spectrometer, kept at 303 K and at a pressure of  $\sim 1.3 \times 10^{-6}$  Pa, leaving the capillary opening positioned close to the FT-ICR cell. The FT-ICR electron ionization (EI) mass spectra of the corresponding vapor phases were recorded as a function of temperature (298–488 K) or electron-beam energy (0–70 eV) and at pressures in the range  $3.2 \times 10^{-6}$  to  $1.5 \times 10^{-5}$  Pa.

The ion–molecule reactions were carried out with an electron-beam energy  $E = 70$  eV. The ions formed upon electron ionization were trapped in the FT-ICR cell under cyclotron movement for different periods of time before detection. The recording of a series of mass spectra at different delay times provided information about the reactivity of those ions with the neutral species present in the vapor originating from the sublimation/vaporization of [Htmg]Cl. When necessary continuous ejection of specific ions was performed with single-frequency excitation.<sup>33</sup> Neutral pressures were measured with a Bayard–Alpert type ionization gauge.

## Results and Discussion

Both [Htmg]Cl samples (1, unsublimed and 2, sublimed) were used in the FT-ICR-MS studies. The conclusions were found to be sample-independent.

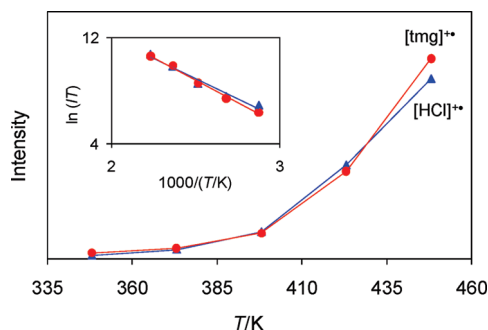


**Figure 2.** Comparison of the EI positive ion mass spectra of (a) pure tetramethylguanidine, tmg, and (b) pure hydrogen chloride, HCl, with the positive ion FT-ICR mass spectrum of (c) [Htmg]Cl (sample 1). The two former spectra are reported in the NIST webbook (ref 34); the latter spectrum was obtained in this work at 300 K and  $5.7 \times 10^{-6}$  Pa. To guide the eye, selected peaks of tmg ( $m/z$  44, 57, 71, and 115) and HCl ( $m/z$  36 and 38) are marked with symbols  $\times$  and  $\bullet$ , respectively. Spectra a and b were scaled so that the parent peaks at  $m/z$  115 and 36, respectively, have the same intensities as the corresponding peaks in spectrum c.

The presence of dissociated gaseous charged species in the vapor resulting from the sublimation/distillation of [Htmg]Cl was ruled out by studying the variation of the positive and negative ion FT-ICR mass spectra of a sample kept at a constant temperature inside a capillary adapted to the probe arm of the spectrometer, while the energy of the ionization beam,  $E$ , was decreased from 70 to 0 eV. As illustrated in Figure 1 for the positive species, no ions were detected when the electron beam energy reached zero, both when the sample vaporized at a temperature below (Figure 1a) or above (Figure 1b) the melting point of [Htmg]Cl. This demonstrates the absence of any species with an overall charge in the vapor phase of 1,1,3,3-tetramethylguanidinium chloride under those sublimation or vaporization conditions.

The FT-ICR-MS experiments also showed that under reduced pressure ( $3.2 \times 10^{-6}$  to  $1.5 \times 10^{-5}$  Pa) and temperatures in the range 298–488 K, solid or liquid [Htmg]Cl dissociates to yield tmg(g) and HCl(g), without any detectable amount of gaseous cation–anion pairs. This can be inferred from Figure 2 where the results obtained in this work at 300 K and  $5.7 \times 10^{-6}$  Pa are compared with the electron ionization mass spectra (EI-MS) of HCl and tmg reported in the NIST webbook.<sup>34</sup> The comparison indicates that the FT-ICR mass spectrum of



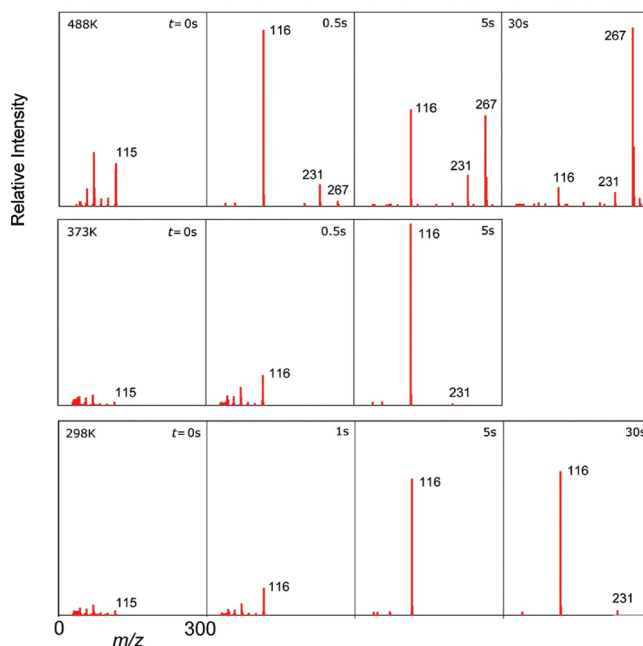


**Figure 3.** Variation of the intensities (arbitrary units) of the peaks at  $m/z$  115 ([tmg]<sup>+</sup>, closed circles) and  $m/z$  36 ([HCl]<sup>+</sup>, closed triangles) with temperature for sample 2. The inset shows the corresponding Clausius–Clapeyron-type plot.

[Htmg]Cl is a combination of the spectra of tmg ( $m/z$  115) and HCl ( $m/z$  36).

Therefore, under those experimental conditions, the compound vaporizes according to the conventional mechanism postulated for protic ionic liquids (eq 2),<sup>8,15,35,36</sup> which was also the sole detected pathway in the case of liquid 1-methylimidazolium ethanoate.<sup>24</sup> This may perhaps account for the slow and continuous mass loss (which reached  $\sim 1.5\%$  over a 24 h period) detected by thermogravimetry for a [Htmg]Cl sample kept at ambient pressure and 373 K (see the Supporting Information). Furthermore, the amounts of tmg and HCl present in the gas phase increase with temperature as expected for a sublimation process. This is illustrated in Figure 3 where the intensities corresponding to the peaks at  $m/z$  115 ([tmg]<sup>+</sup>) and 36 ([HCl]<sup>+</sup>) are plotted as a function of temperature.

Further evidence for the vaporization of [Htmg]Cl to yield tmg(g) and HCl(g) was inferred from the study of ion–molecule reactions. In these experiments the ions produced by electron ionization were trapped in the FTICR-MS cell under cyclotron movement for various periods of time before detection. During these trapping periods reactions with the neutral species inside the cell region of the spectrometer may occur and their kinetic profiles obtained by recording a series of mass spectra at different delay times. We previously showed that this type of experiments can lead to the identification of the neutral species present in the vapor of the compound under study.<sup>24,27</sup> At 298 K, without delay, the spectra showed only the presence of tmg (detected as [tmg]<sup>+</sup> at  $m/z$  115) and HCl (detected as [HCl]<sup>+</sup> at  $m/z$  36). As the delay was increased peaks corresponding to [Htmg]<sup>+</sup> ( $m/z$  116), [H(tmng)<sub>2</sub>]<sup>+</sup> ( $m/z$  231), and [(Htmg)<sub>2</sub>Cl]<sup>+</sup> ( $m/z$  267) started to appear (Figure 4). Continuous ejection of  $m/z$  115 throughout the delay period led to a complete loss of the  $m/z$  116 signal, thus showing that [tmg]<sup>+</sup> is the precursor of [Htmg]<sup>+</sup>. This behavior was also observed when pure tmg was introduced into the spectrometer indicating that the [Htmg]<sup>+</sup> species results from the reaction of [tmg]<sup>+</sup> with a proton donor in the background, e.g., traces of water. The peak at  $m/z$  231 corresponds to [H(tmng)<sub>2</sub>]<sup>+</sup> formed by the reaction of [Htmg]<sup>+</sup> with neutral tmg present in the gas phase. This further supports the conclusion mentioned above that [Htmg]Cl(s) vaporizes to yield tmg(g) and HCl(g). The peak at  $m/z$  267 could in principle originate from the reaction of [Htmg]Cl(g) with [Htmg]<sup>+</sup>. However, the continuous ejection of  $m/z$  231 throughout the delay period led to the complete loss of the [(Htmg)<sub>2</sub>Cl]<sup>+</sup> ( $m/z$  267) signal. This indicates that the [(Htmg)<sub>2</sub>Cl]<sup>+</sup> species results from the reaction of [H(tmng)<sub>2</sub>]<sup>+</sup> with HCl(g), thus ruling out the presence of the neutral, anion–cation pair ([Htmg]Cl) in the gas phase over the solid at this temperature. Hence, under



**Figure 4.** FTICR-MS spectra of [Htmg]Cl vapor (sample 2) at different temperatures and delay times. At each temperature the spectra were scaled so that the most intense peak for any delay corresponds to 100%.

these sublimation conditions, the vapor phase consists of neutral tmg and HCl molecules, as expected for a protic ionic liquid. The experiments were repeated at higher temperatures and the results are also illustrated in Figure 4. The observed ion–molecule reaction trends are similar, although at higher temperatures the peak intensities are higher and the formation of the higher mass species proceeds at faster rates. It must be stressed that the spectra at 488 K were recorded above the fusion temperature of [Htmg]Cl ( $\sim 480$ – $482$  K according to DSC analysis, see the Materials section).

## Conclusions

The Fourier transform ion cyclotron resonance mass spectrometry experiments carried out in this work indicated that the pathway for sublimation or vaporization of 1,1,3,3-tetramethylguanidium chloride under reduced pressure ( $3.2 \times 10^{-6}$  to  $1.5 \times 10^{-5}$  Pa) is similar to that we previously observed for 1-methylimidazolium ethanoate,<sup>24</sup> with no evidence of either ionic species or neutral ion pairs in the vapors over [Htmg]Cl(s or l) or [Hmim][O<sub>2</sub>CCH<sub>3</sub>](l). Both systems therefore conform to the general mechanism postulated for the distillation of protic ionic liquids,<sup>8,9,15</sup> which involves a proton transfer with the formation of the gaseous acid and base precursors (HCl and 1,1,3,3-tetramethylguanidine or ethanoic acid and 1-methylimidazole in these cases), that may later recombine in the gaseous phase or upon condensation to yield the starting material. This suggests that the observation, by Raman spectroscopy, of gaseous [Htmg]Cl as the sole species over the corresponding liquid phase in a sealed glass ampule at  $\sim 15$  K above the fusion temperature does not necessarily result from a direct vaporization of the intact ion pair, as proposed by Berg et al.,<sup>31</sup> but to a recombination of gaseous HCl and guanidine under those conditions. Facile recombination is in fact predicted by computational chemistry calculations carried out by those authors at the B3LYP/6-311+G(d,p) level of theory, which indicate the electronic energy of [Htmg]Cl to be lower by  $70.8 \text{ kJ}\cdot\text{mol}^{-1}$

than the sum of the electronic energies of the separate tmg and HCl molecules.<sup>31</sup>

The conclusion that in the low pressure region of the FT-ICR-MS experiments the vapor was formed by tmg and HCl and in the higher pressure conditions of the Raman experiments by Berg et al.<sup>31</sup> by [Htmg]Cl is in line with what should be expected for gaseous phases where a dissociation–association equilibrium is operative. Indeed, in these cases, thermodynamics predicts that for a given temperature the extent of dissociation increases as the pressure is lowered.<sup>37</sup>

Those equilibria, and the fact that they are affected by temperature and pressure, may have a significant impact on the composition of the vapors over condensed phases of protic ionic liquids. Therefore, if not appropriately accounted for, they may play havoc with measurements of vapor pressures or enthalpies of vaporization/sublimation of protic ionic liquids by techniques, such as transpiration or Knudsen effusion, which rely on an accurate knowledge of the vapor composition.<sup>38–40</sup> The same is also true for calorimetric determinations of enthalpies of vaporization/sublimation under saturation pressures. In the analogous and well-documented case of ethanoic acid, for example, ignoring the monomer–dimer equilibrium in the gas phase leads to a decrease of the calorimetrically obtained standard molar enthalpy of vaporization at 298.15 K, from 51.6 kJ·mol<sup>−1</sup> to 23.4 kJ·mol<sup>−1</sup>.<sup>41</sup>

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**Supporting Information Available:** Figures S1–S6 with the results of the <sup>1</sup>H NMR and <sup>13</sup>C NMR analysis of [Htmg]Cl and tmg and Figures S7–S11 corresponding to the DSC and TG characterization of [Htmg]Cl. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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