

Imidazolium-Based Ionic Liquids. 1-Methyl Imidazolium Nitrate: Thermochemical Measurements and Ab Initio Calculations

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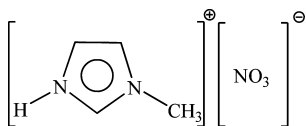
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In this work data of the molar enthalpies of formation of the ionic liquid 1-methylimidazolium nitrate [H-MIM][NO₃] was measured by means of combustion calorimetry. The molar enthalpy of fusion of [H-MIM][NO₃] was measured using DSC. Experiments to vaporize the ionic liquid into vacuum or nitrogen stream in order to obtain vaporization enthalpy have been performed. Ab initio calculations of the enthalpy of formation in the gaseous phase have been performed for the ionic species using the G3MP2 theory. The combination of traditional combustion calorimetry with modern high-level ab initio calculations allow the determination of the molar enthalpy of vaporization of the ionic liquid under study. The ab initio calculations indicate that [H-MIM][NO₃] is most probably separated into the neutral species methyl-imidazole and HNO₃ in the gaseous phase at conditions of the vaporization experiments.

Introduction

Imidazolium-based ionic liquids are among the most investigated species. However, as a rule, ionic liquids with dialkyl substituted imidazolium cations (e.g., [C_nMIM]) have been studied intensively¹ in contrast to the monoalkyl substituted cations [H-MIM] which could exhibit unusual physical properties due to the additional proton donor on the nitrogen atom of the imidazolium ring.^{2–4} The [H-MIM] cation containing ionic liquids can be easily obtained by neutralization. For instance, the combination of 1-methylimidazole with HNO₃ (67%) in a 1:1 molar ratio produces, after water removal, a white solid identified as 1-methylimidazolium nitrate [H-MIM][NO₃].



This compound could be used as a cosolvent and even as promoter in the oxidative aromatic chlorination and has a considerable potential as a reaction medium.^{2,3} Here we report the experimental determination of the enthalpy of formation, $\Delta_f H_m^\circ(\text{cr})$, obtained from the calorimetrically measured enthalpy of combustion, as well as the experimental determination of the enthalpy of fusion of [H-MIM][NO₃] using differential scanning calorimetry (DSC). Ab initio calculations of thermodynamic properties of the cation, the anion, and the neutral ion pair of [H-MIM][NO₃] in the gas phase using the DFT and G3 method are also reported.

TABLE 1: Formula, Density ρ ($T = 293$ K), Specific Heat Capacity c_p ($T = 298$ K), and Expansion Coefficients $(\delta V/\delta T)_p$ of the Materials Used in the Present Study

compounds	formula	ρ (g·cm ⁻³)	c_p^a (J·K ⁻¹ ·g ⁻¹)	$10^{-6} \cdot (\delta V/\delta T)_p^b$ (dm ³ ·K ⁻¹)
[H-MIM][NO ₃]	C ₄ H ₇ N ₃ O ₃	1.25 ^c	2.10 ^b	0.1
polyethene ^d	CH _{1.93}	0.92 ⁶	2.53 ⁶	0.1
cotton ^e	CH _{1.774} O _{0.887}	1.50 ⁶	1.67 ⁶	0.1

^a From DSC measurements. ^b Estimated. ^c Measured with a pycnometer. ^d From 10 combustion experiments, $\Delta_c u^\circ = -(46354.5 \pm 4.0)$ J·g⁻¹. ^e From 10 combustion experiments, $\Delta_c u^\circ = -(16945.2 \pm 4.2)$ J·g⁻¹.

Experimental Section

Materials. The sample of 1-methylimidazolium nitrate [H-MIM][NO₃] = C₄H₇N₃O₃, used for the experiments was of commercial origin (IOLITEC, product CS-0282-SG). Prior to using it, the IL samples were subjected to vacuum evaporation at 333 K and 10⁻² mbar for more than 24 h to reduce possible traces of solvents and moisture. The water concentration in [H-MIM][NO₃] of 1515.7 ppm was determined by Karl Fischer titration shortly before combustion experiments. An appropriate correction for water content in the sample was applied when the combustion results were evaluated. We used Mettler DL35 Karl Fischer Titrator with Hydranal Composite 2, Hydranal Methanol Dry, and Hydranal Eichstandard 5.0 (Riedel-de Haen). A sample of the IL was kept and handled under nitrogen stream in a special glass device furnished with a septum for the sample extraction using a hot syringe.

Thermochemical Measurements. Combustion Calorimetry. An isoperibol bomb calorimeter was used for the measurement of energy of combustion of [H-MIM][NO₃]. Six successful experiments were carried out (see Tables 1 and 2). The detailed procedure has been described previously.^{5,6} The combustion

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TABLE 2: Results for Typical Combustion Experiments at $T = 298$ K ($p^\circ = 0.1$ MPa) of the [H-MIM][NO₃]^a

m (substance) (g) ^b	0.770854	0.732935	0.951513	0.799818	0.539679	0.808113
m' (cotton) (g) ^b	0.00131	0.001317	0.001304	0.001106	0.001085	0.001189
m'' (polythen) (g) ^b	0	0.236599	0.274517	0.306543	0.32757	0.314487
ΔT_c (K) ^c	0.85801	1.55726	1.91746	1.84983	1.62761	1.88279
(ϵ_{calor})($-\Delta T_c$) (J)	-12712.4	-23072.4	-28409.1	-27407.2	-24114.7	-27895.5
(ϵ_{cont})($-\Delta T_c$) (J)	-13.04	-25.37	-32.51	-31.11	-26.59	-31.66
ΔU_{decomp} HNO ₃ (J)	69.88	88.4	105.12	100.64	80.63	95.56
ΔU_{corr} (J) ^d	9.78	12.77	16.62	14.9	11.5	13.07
$-m'\Delta_c u'$ (J)	22.2	22.32	22.1	18.74	18.39	20.15
$-m''\Delta_c u''$ (J)	0	10967.43	12725.1	14209.65	15184.34	14577.89
$\Delta_c u^\circ$ (cr) (J·g ⁻¹) ^e	-16376	-16381.8	-16366.2	-16371.6	-16392	-16359.6
average $\Delta_c u^\circ$			$-16374.5 \pm 4.7 \text{ J} \cdot \text{g}^{-1}$			

^a For the definition of the symbols see ref 8: $T_h = 298.15$ K; $V(\text{bomb}) = 0.320 \text{ dm}^3$; $p^i(\text{gas}) = 3.04 \text{ MPa}$; $m^i(\text{H}_2\text{O}) = 1.00 \text{ g}$. ^b Masses obtained from apparent masses. ^c $\Delta T_c = T^f - T^i + \Delta T_{\text{corr}}$; (ϵ_{cont})($-\Delta T_c$) = (ϵ_{cont}^i)($T^i - 298.15 \text{ K}$) + (ϵ_{cont}^f)($298.15 \text{ K} - T^f + \Delta T_{\text{corr}}$). ^d ΔU_{corr} , the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in ref 8. ^e $\epsilon = 14816.0 \pm 1.0 \text{ J} \cdot \text{K}^{-1}$.

TABLE 3: Thermochemical Data at $T = 298$ K ($p^\circ = 0.1$ MPa) for [H-MIM][NO₃]

$\Delta_c u^\circ$ (J·g ⁻¹)	$\Delta_c H_m^\circ$ (cr) (kJ·mol ⁻¹)	$\Delta_f H_m^\circ$ (cr) (kJ·mol ⁻¹)	$\Delta_{\text{cr}} H_m^\circ$ (kJ·mol ⁻¹)	T_{fus} (K)	$\Delta_{\text{cr}} H_m^\circ$ (kJ·mol ⁻¹)	$\Delta_f H_m^\circ$ (l) (kJ·mol ⁻¹)
-16374.5 ± 4.7	-2373.1 ± 1.5	-201.3 ± 1.6	19.2 ± 0.2	342.6^b	16.6	-184.7 ± 1.6

^a At the T_{fus} . ^b The onset temperature measured by DSC. ^c Adjusted to the reference temperature 298 K.

products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter ϵ_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39i, NIST). Correction for nitric acid formation was based on the titration with 0.1 mol·dm⁻³ NaOH (aq). The atomic weights used were those recommended by the IUPAC Commission.⁷ For converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states, the conventional procedure⁸ was applied. Values of the standard specific energies of combustion $\Delta_c u^\circ$, together with the necessary auxiliary quantities, are given in Tables 1 and 2. To derive the molar standard enthalpy of formation, $\Delta_c H_m^\circ(\text{l})$, from the standard molar enthalpy of combustion, $\Delta_f H_m^\circ$, molar enthalpies of formation of H₂O (l) and CO₂ (g) were used, as assigned by CODATA.⁹ Experimental results for [H-MIM][NO₃] are given in Table 3. The total uncertainty was calculated according to the guidelines presented by Olofsson.¹⁰ The uncertainty assigned to $\Delta_f H_m^\circ$ is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H₂O and CO₂.

Thermochemical Studies. Transpiration Method. In our previous paper, vapor pressures and enthalpies of vaporization, $\Delta_f H_m^\circ$, of several ILs such as [BMIM][N(CN)₂] and [EMIM][NTf₂] have successfully been determined using the method of transference in a saturated stream of an inert gas.⁵ In short, the sample of the IL (approximately 0.5 g) is mixed with glass beads and placed in a thermostatted U-tube of length 10 cm and diameter 0.5 cm. A preheated helium stream is passed through the U-tube at constant temperature (± 0.1 K). The flow rate of the helium stream is optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The material transported is condensed in a cold trap. The amount of condensed product in the trap is determined by weighing (± 0.0001 g). In this work we tried to perform the transpiration experiments on [H-MIM][NO₃] in the temperature range 373 to 453 K at a flow rate of 7–11 dm³·h⁻¹. Such a flow rate is close to the upper limit of our apparatus 12 dm³·h⁻¹, where the saturation of the transporting gas with the IL in the saturation tube is still ensured. However, no condensate was detected in the cold trap. Observation of the sample in the saturation tube revealed an intense brown coloration of the IL

after the heating. Clearly, neither the vapor pressure nor the enthalpy of vaporization of this IL can be determined using the transpiration method. Consequently, another possible technique—the temperature programmed desorption (TPD) in the ultra high vacuum (UHV) using line of sight mass spectrometry (LOSMS)¹¹ has been applied for this purpose.

Thermochemical Studies. MS-TPD Study of [H-MIM][NO₃]. Problems were already experienced when attempting to melt [H-MIM][NO₃]. Two experiments were carried out which involved melting and then degassing the sample on a Schlenk line under a low vacuum ($\approx 10^{-2}$ mbar). The sample melted at the expected temperature (≈ 333 K), but changed color (from colorless to yellow) during the degassing process (held at ≈ 333 K while being rotated in a glass bulb at 10^{-2} mbar). On cooling, so as to transfer the sample from the preparation lab to the UHV lab, the sample solidified. The glass bulb was found to contain a yellow solid in the bottom of the bulb and a white solid further up around the edges of the bulb. The sample at the bottom of the bulb was melted with a hot air gun and a small quantity of it was transferred to a vial for use in the UHV chamber. The sample resolidified in the vial. After insertion in the UHV load lock/transfer system, the sample was melted again under low vacuum. Considerable effervescence was observed as the sample melted. Opening the valve to the main UHV chamber, thus exposing the sample to much higher pumping speeds and potentially high vacuum, caused excessive effervescence resulting in the sample being forced out of the vial and making quite a mess in the load lock.

A third experiment was carried out to more carefully observe how the sample reacted to being heated. A small quantity of the solid sample was placed in a vial, which was loaded into the UHV load lock/transfer arm of the vacuum chamber. This was evacuated to $\approx 10^{-8}$ mbar with the sample at room temperature and the sample then isolated from the analysis chamber. The sample was then heated very slowly. It began to melt at ≈ 328.5 K (though the temperature measurement is not very accurate) and was held at this temperature until it was all melted (which took about 1 h). A few minutes after the sample finished melting, bubbles were observed evolving from it and then it began to turn yellow. The rate of effervescence continued to increase with time. The valve to the analysis chamber was then opened and the pressure in the main chamber was observed to increase from 10^{-8} mbar to 10^{-5} mbar (the increase in

pressure at this point would normally be only about half an order of magnitude for a normal IL). This indicates that significant quantities of gas were produced by the sample.

Clearly it was not possible to carry out TPD experiments on this sample because of the excessive effervescence under low and high vacuum conditions. It apparently could be suggested that the decomposition reaction occurred where the Me-imidazole and HNO₃ are volatile products (see later eq 7). The volatility of the products of this reaction, under vacuum conditions, will tend to cause complete decomposition of the ionic liquid by constant removal of the products so forcing the reaction to the right. Also, the pale yellow color of the residue material may be due to oxidation of the imidazole by the nitric acid. We were unsuccessful in our attempts to collect any of the material from the gas phase by condensing it on a liquid nitrogen cooled finger. Thus, there was no possibility of measuring the enthalpy of vaporization of this IL using TPD method.

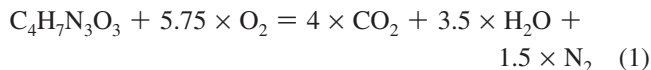
Phase Transitions in the Solid State. DSC-Measurements.

The thermal behavior of [H-MIM][NO₃] including melting temperature and enthalpy of fusion were determined with a computer controlled Mettler 823e DSC. For all measurements, an empty pan was used as reference. The fusion temperature and enthalpy were determined as the peak onset temperature and by using a straight baseline for integration, respectively. The temperature and heat flow rate scale of the DSC was calibrated by measuring high-purity indium ($T_0 = 429.8$ K and $\Delta H_{\text{ref}} = 28.4$ J·g⁻¹). The thermal behavior of the specimen was investigated at heating rate of 10 K·min⁻¹. The uncertainty for temperature is ± 0.5 K and for enthalpy of fusion ± 1 J·g⁻¹. The DSC measurements on the sample of [H-MIM][NO₃] were repeated twice and values agreed within the experimental uncertainties ± 0.2 kJ·mol⁻¹ for the enthalpy of fusion and ± 0.5 K for the melting temperature. The onset, peak, and endset temperatures of the melting peak were as follows: 342.6, 343.4, and 344.7 K. The enthalpy of fusion calculated from the melting peak area was 19.24 ± 0.2 kJ·mol⁻¹. Check of thermal stability of [H-MIM][NO₃] using DSC has revealed decomposition starting at 425 K. The onset, peak, and endset temperatures of the exothermic decomposition peak were as follows: 425.2, 455.0, and 476.8 K.

Ab Initio Calculations. Standard ab initio molecular orbital calculations were performed using the Gaussian 03 revision 04 program package.¹² Conformation analysis of the IL was performed using B3LYP/6-31+G(d,p)¹³ with the help of the procedure developed in our previous work.⁶ Energy and optimized structure of the most stable conformer of the ionic pair was further obtained using the DFT B3LYP/6-311++G(3df,3pd) or the G3MP2^{14,15} composite method. Calculated values of the enthalpy and Gibbs energy of ions and ion pairs are based on the electronic energy calculations obtained by the DFT or G3MP2 methods using standard procedures of statistical thermodynamics.¹⁶

Results and Discussion

Combustion Calorimetry. Results of combustion experiments on [H-MIM][NO₃] are summarized in Table 3. The values of the standard specific energy of combustion, $\Delta_c u^\circ$, the standard molar enthalpy of combustion, $\Delta_c H_m^\circ$, and the standard molar enthalpy of formation in the crystalline state $\Delta_f H_m^\circ$ (cr) were based on the reactions



$\Delta_f H_m^\circ$ (cr) of [H-MIM][NO₃] has been obtained from the enthalpic balance according to eq 1 and Hess's law using the molar enthalpies of formation of H₂O (l) and CO₂ (g) as assigned by CODATA.⁹

Determination of the Liquid Phase Enthalpy of Formation of [H-MIM][NO₃]. The enthalpy of formation, $\Delta_f H_m^\circ$ (cr), derived from the combustion experiments is referred to the crystalline state at the reference temperature $T = 298$ K. Using the equation

$$\Delta_f H_m^\circ(\text{l}) = \Delta_f H_m^\circ(\text{cr}) + \Delta_{\text{cr}}^1 H_m \quad (2)$$

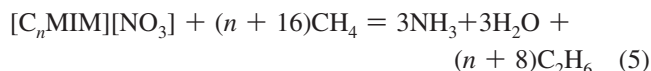
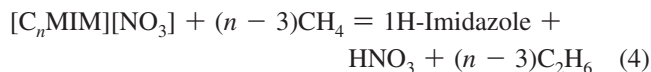
we are able to calculate, $\Delta_f H_m^\circ(\text{l})$, the standard molar enthalpy of formation in the liquid phase, when the enthalpy of fusion, $\Delta_{\text{cr}}^1 H_m$, is known. As a rule, all three thermodynamic quantities in eq 2 should be referred to the same temperature, that is, $T = 298$ K. However, the experimental result for the enthalpy of fusion of [H-MIM][NO₃] measured by DSC (see Table 3) was obtained at the melting temperature T_{fus} . Because of the difference from the reference temperature, the experimental enthalpy of fusion was formally adjusted to $T = 298$ K. The adjustment was calculated using the equation:¹⁷

$$\{\Delta_{\text{cr}}^1 H_m(T_{\text{fus}}/\text{K}) - \Delta_{\text{cr}}^1 H_m(298 \text{ K})\}/(\text{J} \cdot \text{mol}^{-1}) = \{(0.75 + 0.15C_p^{\text{cr}})(T_{\text{fus}}/\text{K}) - 298 \text{ K}\} - \{(10.58 + 0.26C_p^{\text{l}})(T_{\text{fus}}/\text{K}) - 298 \text{ K}\} \quad (3)$$

where the isobaric molar heat capacities, $C_p^{\text{cr}} = 305.8$ J·mol⁻¹·K⁻¹, $C_p^{\text{l}} = 353.5$ J·mol⁻¹·K⁻¹ of the solid and the liquid [H-MIM][NO₃] were assessed to be essential the same as those for [C₄MIM][NO₃] measured in the recent work.¹⁸ With this adjustment (the uncertainty of the correlation was not taken into account), the molar enthalpy of fusion, $\Delta_{\text{cr}}^1 H_m$ (298 K), was calculated (Table 3). Substituting these values into eq 2, the standard molar enthalpy of formation in the undercooled metastable liquid phase, $\Delta_f H_m^\circ(\text{l})$, has been derived (Table 3).

Ab initio Results and Thermodynamics in the Gas Phase.

In standard Gaussian-*n* theories, theoretical enthalpies of formation are calculated through atomization reactions.¹⁹ Raghavachari et al.²⁰ have proposed to use a set of isodesmic reactions, the "bond separation reactions" to derive theoretical enthalpies of formation. We have calculated the enthalpy of formation of [H-MIM][NO₃] and also for comparison enthalpies of formation of alkyl substituted ILs of general formula [C_{*n*}MIM][NO₃] with the help of both standard atomization reactions as well as "bond separation" reactions. For the latter method we have chosen the following two reactions:



Using enthalpies of these reactions calculated by G3MP2 and enthalpies of formation $\Delta_f H_m^\circ(\text{g})$, for the reactions participants

TABLE 4: G3MP2 Total Energies at 0 K, Enthalpies (in hartree) at 298 K, and Experimental Enthalpies of Formation for the Molecules Studied in This Work

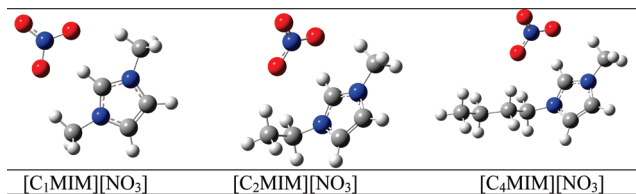
compounds	E_{298}	H_{298}	$\Delta_f H_m^\circ \text{ exp}$
[H-MIM][NO ₃]	−545.706566	−545.695487	
[C ₁ MIM][NO ₃]	−584.914047	−584.900864	
[C ₂ MIM][NO ₃]	−624.153690	−624.139248	
[C ₄ MIM][NO ₃]	−702.623897	−702.606625	
methane	−40.422100	−40.418284	−74.9 ^a
ethane	−79.651199	−79.646714	−83.8 ^a
1H-imidazole	−225.867843	−225.863074	132.9 ^b
methyl-imidazole	−265.097296	−265.090855	125.2 ^c
HNO ₃	−280.583605	−280.579203	−134.3 ^d
NH ₃	−56.470142	−56.466333	−45.9 ^d
H ₂ O	−76.342404	−76.338629	−241.8 ^d

^a Data from ref 21. ^b Data from ref 28. ^c Unpublished data (private communication by S.P. Verevkin). ^d Data from ref 9.

TABLE 5: Results of G3MP2 Calculation of the Standard Enthalpy of Formation $\Delta_f H_m^\circ(\text{g})$ for the ILs Studied in This Work in the Gas Phase at 298 K in kJ·mol^{−1}

compounds	G3MP2			average
	atomization	bond separation		
		reaction 4	reaction 5	
[H-MIM][NO ₃] ^a	−62.2	−75.9 ^b	−70.9	−69.7 ± 4.0
[C ₁ MIM][NO ₃]	−11.0	−23.7	−19.2	−18.0 ± 3.7
[C ₂ MIM][NO ₃]	−46.6	−58.8	−54.3	−53.2 ± 3.7
[C ₄ MIM][NO ₃]	−93.9	−104.2	−99.7	−99.3 ± 3.0

^a The most stable conformer shown in Figure 1 was taken into account. ^b Calculated according to the reaction [H-MIM][NO₃] = MIM + HNO₃.

**Figure 1.** Stable conformations of [C_nMIM][NO₃] from G3MP2.

in eqs 4–5, recommended by Pedley et al.²¹ (see Table 4), enthalpies of formation in the gaseous state, $\Delta_f H_m^\circ(\text{g})$, of [C_nMIM][NO₃] and [H-MIM][NO₃] have been calculated (see Table 5). As shown in Table 5 these $\Delta_f H_m^\circ(\text{g})$ -values calculated by G3MP2 using the atomization procedure, as well as eqs 4–6 are in moderate agreement, and we averaged them for further discussion.

In recent papers^{6,18,22} we have shown that the aprotic ILs such as [C₄MIM][N(CN)₂], [Pyr_{1,4}][N(CN)₂], and [C_nMIM][NO₃] exist in the gaseous phase as contact ion pairs and not as a gas of separated ions. Corresponding calculations of the [H-MIM][NO₃] ion pair structure have revealed that the anion [NO₃][−] does not take the expected place (as in the [C_n-MIM][NO₃] homologous series) close to the proton of the C₂-carbon of the imidazolium cation (see Figure 1). In the [H-MIM][NO₃] the anion [NO₃][−] has been found to be located near the proton in the N₁-position of the imidazolium cation (see Figure 2). We have calculated the energy difference of these two conformers of [H-MIM][NO₃] (see Figure 2). According to the (B3LYP/6-311++g(3df,3pd)) results the structure II is by 67.2 kJ·mol^{−1} less stable. It is also apparent from Figure 2, that a proton in conformation I is effectively transferred to the anion and that is typical for salts like ammonium chloride²³ or protic ionic liquids like ethylammonium nitrate.²⁴ Especially for



Structure I [H-MIM][NO ₃]	Structure II [H-MIM][NO ₃]
Relative energies at the (B3LYP/6-311++g(3df,3pd)) level	
0.0 kJ·mol ^{−1}	67.2 kJ·mol ^{−1}

Figure 2. Stable conformations of [H-MIM][NO₃] from DFT calculations.

ammonium chloride, NH₄Cl, it is well established that this salt in the gaseous phase is entirely dissociated to ammonia NH₃ and HCl due to the proton shift.²³ Using *ab initio* calculations it is possible to assess whether such a proton transfer is also favorable for [H-MIM][NO₃]. For the following possible dissociation reactions:



(with MIM = methyl imidazole) G3MP2 calculations have been performed with the aim to obtain absolute values of the molar standard Gibbs energy of reaction, $\Delta_r G^0$, the standard molar reaction entropy, $\Delta_r S^0$, and the molar reaction enthalpy, $\Delta_r H^0$. Details of this procedure are described elsewhere.^{6,18} The chemical equilibrium constants K_p for reactions 6 and 7 in the ideal gas state have been calculated at 298 K (see Table 6). We have obtained the $K_p = 4.3 \times 10^{-242}$ bar for reaction 6 and $K_p = 9.9 \times 10^{-5}$ bar for reaction 7. Such a low value for the reaction 6 indicates that the dissociation of [H-MIM][NO₃] into the separated ions is impossible. However, proton transfer in the gaseous phase according to reaction 7 could be possible to a certain extent. The same trend has been confirmed using the B3LYP/6-311++g(3df, 3pd) method and results are listed in Table 7.

Enthalpy of Vaporization $\Delta_f H_m^\circ$ of [H-MIM][NO₃]. Vapor pressures and enthalpy of vaporization, $\Delta_f H_m^\circ$, of several ILs such as [BMIM][N(CN)₂] and [EMIM][NTf₂] have successfully been determined using the method of transference in a saturated stream of helium.⁶ In contrast, the ionic liquids [C₂MIM][NO₃] and [C₄MIM][NO₃] were not stable enough during the transpiration experiments to obtain reliable results, hence, no experimental enthalpies of vaporization could be determined using this technique.¹⁸ In the present work on [H-MIM][NO₃], both methods, transpiration and MS-TPD have failed to determine enthalpy of vaporization as well. However, in the recent paper¹⁸ we have developed an alternative procedure to obtain vaporization enthalpies of ILs using a combination of the traditional combustion calorimetry with the high-level *ab initio* calculations. For that purpose, the following thermodynamic relationship has been used to obtain the molar enthalpy of vaporization at 298 K:

$$\Delta_f H_m^\circ(298 \text{ K}) = \Delta_f H_m^\circ(\text{g}) - \Delta_f H_m^\circ(\text{l}) \quad (8)$$

where the molar enthalpy of formation in the liquid state, $\Delta_f H_m^\circ(\text{l})$, is obtained by high precision combustion calorimetry, and $\Delta_f H_m^\circ(\text{g})$, the gaseous enthalpy of formation, is calculated by one of the suitable *ab initio* method (e.g.,

TABLE 6: G3MP2 Calculations of the Thermodynamic Properties of the Ions $[\text{NO}_3]^-$, $[\text{H-MIM}]^+$, the Ionic Pair $[\text{H-MIM}][\text{NO}_3]$, HNO_3 , and Methyl-Imidazole Used for Predicting Standard Reaction Properties $\Delta_r G^\circ$, $\Delta_r H^\circ$, and $\Delta_r S^\circ$ and the Equilibrium Constant K_p of Dissociation of Ionic Liquid at 298 K in Gas State

components	Gibbs energy (hartree)	enthalpy (hartree)	property, unit	value
$[\text{H-MIM}][\text{NO}_3] = [\text{H-MIM}]^+ + [\text{NO}_3]^-$				
$[\text{NO}_3]^-$	-280.093256	-280.063756	$\Delta_r G^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	1377.7
$[\text{H-MIM}]^+$	-265.12641	-265.090846	$\Delta_r H^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	1420.1
$[\text{H-MIM}][\text{NO}_3]$	-545.744404	-545.695487	$\Delta_r S^\circ$, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	142.2
			K_p , bar	4.3×10^{-242}
$[\text{H-MIM}][\text{NO}_3] = \text{Me-imidazole} + \text{HNO}_3$				
HNO_3	-280.609233	-280.579203	$\Delta_r G^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	22.8
Me-Imidazole	-265.126467	-265.090855	$\Delta_r H^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	66.8
$[\text{H-MIM}][\text{NO}_3]$	-545.744404	-545.695487	$\Delta_r S^\circ$, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	147.3
			K_p , bar	9.9×10^{-5}

TABLE 7: DFT B3LYP/6-311++G(3df,3pd) Calculations of the Thermodynamic Properties of the Ions $[\text{NO}_3]^-$, $[\text{H-MIM}]^+$, the Ionic Pair $[\text{H-MIM}][\text{NO}_3]$, HNO_3 , and Methyl-Imidazole Used for Predicting Standard Reaction Properties $\Delta_r G^\circ$, $\Delta_r H^\circ$, and $\Delta_r S^\circ$ and the Equilibrium Constant K_p of Dissociation of Ionic Liquid at 298 K in Gas State

components	Gibbs energy (hartree)	enthalpy (hartree)	property, unit	value
$[\text{H-MIM}][\text{NO}_3] = [\text{H-MIM}]^+ + [\text{NO}_3]^-$				
$[\text{NO}_3]^-$	-280.486123	-280.456532	$\Delta_r G^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	1367.7
$[\text{H-MIM}]^+$	-265.553318	-265.518035	$\Delta_r H^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	1408.0
$[\text{H-MIM}][\text{NO}_3]$	-546.560377	-546.510835	$\Delta_r S^\circ$, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	135.0
			K_p , bar	2.4×10^{-240}
$[\text{H-MIM}][\text{NO}_3] = \text{Me-imidazole} + \text{HNO}_3$				
HNO_3	-280.999525	-280.96933	$\Delta_r G^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	20.0
Me-imidazole	-265.553226	-265.518048	$\Delta_r H^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$	61.6
$[\text{H-MIM}][\text{NO}_3]$	-546.560377	-546.510835	$\Delta_r S^\circ$, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	139.4
			K_p , bar	3.1×10^{-4}

$$\alpha = p_{\text{MIM}}/(p_{[\text{H-MIM}][\text{NO}_3]} + p_{\text{MIM}}) \quad (9)$$

G3MP2). We already demonstrated good agreement between $\Delta_r H_m$ value derived from eq 8 with the experimental results.^{6,18,22} Therefore, we have also applied this method in the present work to derive the vaporization enthalpy of $[\text{H-MIM}][\text{NO}_3]$. Thus, we used the averaged values of $\Delta_r H_m^\circ(\text{g})$ calculated by G3MP2 (Table 5, column 5) first under the assumption that an ion pair (structure I) exists in the gas phase while the enthalpy of formation in the liquid state was taken from Table 3 (last column). Using eq 8 the following results have been obtained: $\Delta_r H_m([\text{H-MIM}][\text{NO}_3]) = 115.0 \pm 4.3 \text{ kJ}\cdot\text{mol}^{-1}$. In comparison with the enthalpies of vaporization of other homologues¹⁸ $\Delta_r H_m([\text{C}_2\text{MIM}][\text{NO}_3]) = 163.7 \pm 5.3 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r H_m([\text{C}_4\text{MIM}][\text{NO}_3]) = 162.4 \pm 5.7 \text{ kJ}\cdot\text{mol}^{-1}$ our result for $[\text{H-MIM}][\text{NO}_3]$ seems to be lower than expected. Indeed, it is already well established^{18,25} that for vaporization enthalpies of the $[\text{C}_n\text{MIM}][\text{NTf}_2]$ and $[\text{C}_n\text{MIM}][\text{NO}_3]$ families there is no difference between ethyl and butyl derivatives, so it is reasonable to expect enthalpy of vaporization of the $[\text{H-MIM}][\text{NO}_3]$ at the level of 150–160 $\text{kJ}\cdot\text{mol}^{-1}$. However, on the one hand it is well-known that enthalpies of vaporization of the first representatives in homologues series are anomalous for the molecular liquids,^{26,27} and it follows that a similar anomaly could be also expected for ionic liquids. On the other hand, according to the Figures 1 and 2, it is apparent, that due to the quite different favorable position of the anion in $[\text{H-MIM}][\text{NO}_3]$ any direct comparison of enthalpies of vaporizations within this particular family is hardly valid. However, we have to account for the fact shown by the results in Tables 6 and 7, that $[\text{H-MIM}][\text{NO}_3]$ dissociates in neutral molecules MIM and HNO_3 , and this enables us to estimate the degree of association of $[\text{H-MIM}][\text{NO}_3]$ according to eq 7 in the gas phase even though the vapor pressure of the IL could not be determined. From our experimental experience⁶ we can be sure that $p_{\text{sat}} < 1 \text{ Pa}$ at 298 K. The degree of dissociation α defined as

can be calculated with $p_{\text{sat}} = p_{[\text{H-MIM}][\text{NO}_3]} + 2 p_{\text{MIM}}$ (see ref 6) according to:

$$\alpha = [(K_p/p_{\text{sat}})/(1 + K_p/p_{\text{sat}})]^{0.5} \quad (10)$$

Assuming $p_{\text{sat}} = 10^{-5} \text{ bar}$, 10^{-6} bar , and 10^{-7} bar , we obtain from eq 10 with $K_p = 3.1 \times 10^{-4} \text{ bar}$:

$$\begin{aligned} \alpha &= 0.984 & \text{for } p_{\text{sat}} &= 10^{-5} \text{ bar} \\ \alpha &= 0.998 & \text{for } p_{\text{sat}} &= 10^{-6} \text{ bar} \\ \alpha &= 0.9998 & \text{for } p_{\text{sat}} &= 10^{-7} \text{ bar} \end{aligned}$$

Since we can expect that p_{sat} is distinctly lower than 10^{-5} bar (or 1 Pa) we conclude that $[\text{H-MIM}][\text{NO}_3]$ is almost completely dissociated into the neutral molecules MIM and HNO_3 in the gas phase at 298 K. The result will also be valid at higher temperatures because with increasing p_{sat} the value of K_p will also increase due to the positive value of $\Delta_r H = (66.8 \pm 4.9) \text{ kJ}\cdot\text{mol}^{-1}$ (see Table 6 for the G3MP2 method). The uncertainty of ($\pm 4.9 \text{ kJ}\cdot\text{mol}^{-1}$) was assessed for the G3MP2 calculations.⁶ As a consequence the vaporization enthalpy obtained under assumption of ion pairing in the gas phase has to be corrected by the enthalpy of dissociation leading to $\Delta_r H_m = (115.0 + 66.8) = 181.8 \pm 6.9 \text{ kJ}\cdot\text{mol}^{-1}$. This result is somewhat overestimated due to the assumption of the complete dissociation of $[\text{H-MIM}][\text{NO}_3]$, but it is now in line with the corresponding results for $[\text{C}_2\text{MIM}][\text{NO}_3]$ and $[\text{C}_4\text{MIM}][\text{NO}_3]$. The experimental and theoretical work which has been done in this study complements and extends the general research on

the prediction of macroscopic properties of protic ionic liquids by ab initio calculations.^{29,30}

Conclusions

The combination of combustion calorimetry and differential scanning calorimetry with the ab initio calculations allows one to obtain the molar enthalpy of vaporization, $\Delta_f^\circ H_m$, of the IL [H-MIM][NO₃]. This procedure provides indispensable data material for testing ab initio procedures and molecular dynamic simulations techniques in order to understand thermodynamic properties of ionic liquids on a molecular basis. It could be shown that [H-MIM][NO₃] is almost completely dissociated into the neutral molecules methyl-imidazole and HNO₃ in the gas phase, and the energetics of vaporization process include the dissociation enthalpy contribution.

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