

The Gaseous Enthalpy of Formation of the Ionic Liquid 1-Butyl-3-methylimidazolium Dicyanamide from Combustion Calorimetry, Vapor Pressure Measurements, and Ab Initio Calculations

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Abstract: Ionic liquids are attracting growing interest as alternatives to conventional molecular solvents. Experimental values of vapor pressure, enthalpy of vaporization, and enthalpy of formation of ionic liquids are the key thermodynamic quantities, which are required for the validation and development of the molecular modeling and ab initio methods toward this new class of solvents. In this work, the molar enthalpy of formation of the liquid 1-butyl-3-methylimidazolium dicyanamide, $206.2 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$, was measured by means of combustion calorimetry. The molar enthalpy of vaporization of 1-butyl-3-methylimidazolium dicyanamide, $157.2 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$, was obtained from the temperature dependence of the vapor pressure measured using the transpiration method. The latter method has been checked with measurements of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, where data are available from the effusion technique. The first experimental determination of the gaseous enthalpy of formation of the ionic liquid 1-butyl-3-methylimidazolium dicyanamide, $363.4 \pm 2.7 \text{ kJ}\cdot\text{mol}^{-1}$, from thermochemical measurements (combustion and transpiration) is presented. Ab initio calculations of the enthalpy of formation in the gaseous phase have been performed for 1-butyl-3-methylimidazolium dicyanamide using the G3MP2 theory. Excellent agreement with experimental results has been observed. The method developed opens a new way to obtain thermodynamic properties of ionic liquids which have not been available so far.

Introduction

Room-temperature ionic liquids (RTIL) are organic salts with melting points below $100 \text{ }^\circ\text{C}$. These substances have been suggested as potentially greener replacements for traditional molecular solvents since they are nonvolatile, nonflammable, thermally stable, and recyclable. While investigation of the synthesis and the application of ionic liquids in catalytic and separation processes, as well as in electrochemistry, have made remarkable progress during the last years, physicochemical properties have still not been studied systematically in the literature; this holds for mixtures containing ionic liquids and, in particular, for thermodynamic properties of pure RTIL.¹ Our interest in ionic liquids has been focused, so far, on providing systematic data on activity coefficients, phase equilibria, and heat of solution in mixtures of RTIL with organic solvents.^{2–4} These experimental studies are indispensable for testing modern methods of computational chemistry, such as molecular modeling or ab initio calculations, in order to understand the nature of interactions in ionic liquids and their mixtures and to predict physicochemical properties of new or not yet synthesized RTIL.

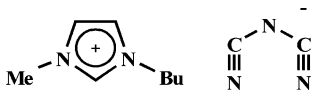
However, successful development of the computational chemistry methods toward ionic liquids is based on the availability of several fundamental properties of pure RTIL, such as enthalpy of formation, enthalpy of vaporization, and vapor pressure. As long as reliable experimental data of these important thermophysical properties of RTIL are missing, it is difficult to justify the attribution of intermolecular interaction parameters, including the role of electrostatic forces derived solely from quantum mechanical studies of isolated molecules.⁵ As a consequence, prediction of the formation and stabilities of ionic liquids using modern quantum chemical methods, which has become a popular endeavor in the recent literature,^{6,7} requires reliable values of the gaseous enthalpies of formation, $\Delta_f H_m^\circ(\text{g})$, for validation of the calculation procedure based on these methods.

RTIL are claimed to be environmentally benign due to their nonflammability. However, just recently, a series of specially designed energetic ionic liquids have turned out to be flammable due to their high nitrogen content and decomposition products.^{8,9}

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Interestingly, additional testing showed that a commercially available RTIL, not thought to be energetic, could be also ignited as a fine spray in air.¹⁰ Bomb calorimetry is the well-established and precise experimental technique to measure energies of combustion of organic compounds in oxygen.¹¹ However, the prerequisite of a reliable calorimetric experiment is the completeness of the combustion process and well-defined final products of reaction (e.g., CO₂ and H₂O). It is apparent that these requirements were hardly applicable to the first-generation ionic liquids (imidazolium–aluminate systems). With the discovery of second- and third-generation ionic liquids, the selection of the available structures has become more acceptable for the purpose of using combustion calorimetry. However, due to the presence of combinations of the elements F, Cl, P, and S in the common anions (e.g., hexafluorophosphate [PF₆]⁻ or bis(trifluoromethylsulfonyl) amide [NTf₂]⁻), the problem of defining the final degree of oxidation of heteroelements still remains challenging. At the same time, the current variety of available ammonium-, imidazolium-, pyridinium-, or pyrrolidinium-based cations with the anions, such as nitrate NO₃⁻, acetate CH₃CO₂⁻, dicyanamide N(CN)₂⁻, or tricyanomethanide C(CN)₃⁻, builds a promising collection of C-, H-, N-, and O-containing RTIL, where a combustion reaction occurs with very well-established final states,^{11,12} provided that completeness of combustion will be achieved. To realize this idea, we have launched our systematic investigation of the thermochemistry of the ionic liquids on the study of 1-butyl-3-methylimidazolium dicyanamide [BMIM][dca]



We present the first experimental determination of the gaseous enthalpy of formation, $\Delta_f H_m^\circ(\text{g})$, of liquid [BMIM][dca]. For that purpose, the following thermodynamic relationship has been used to obtain the gaseous enthalpy of formation of [BMIM][dca]:

$$\Delta_f H_m^\circ(\text{g}) = \Delta_f H_m^\circ(\text{l}) + \Delta_1^\circ H_m \quad (1)$$

where $\Delta_f H_m^\circ(\text{l})$ is the molar enthalpy of formation in the liquid state obtained in this work by high precision combustion calorimetry, and $\Delta_1^\circ H_m$ is the molar enthalpy of vaporization also obtained in this work from the temperature dependence of vapor pressure measured by using the transpiration method. Furthermore, ab initio calculations of the cation [BMIM]⁺, the anion [dca]⁻, and the neutral molecule [BMIM][dca] have been performed using density functional theory (DFT) calculations as well as the G3MP2 theory in order to determine the stability of gaseous ion pairs and to calculate $\Delta_f H_m^\circ(\text{g})$ by an independent, theoretical method, which allows one to perform a thermodynamic consistency test of both methods, the experimental and the theoretical one.

RTIL are also claimed to have negligible vapor pressures. Due to this fact, most of the chemical and technical applications

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of RTIL are indeed based on this remarkable property, and the scientific community has been faced with the continuously increasing challenge to measure the vapor pressure or at least to find other arguments, which allow the determination of the vapor pressure by an indirect but reliable method. In the literature, only a few serious attempts have been described to approach this goal in a, more or less, semiempirical way. The first attempt was made by Paulechka et al.¹³ using an attractive idea. Adiabatic calorimetric measurements of the molar heat capacity c_p as function of temperature starting at very low temperatures and covering the solid as well as the liquid state allow the estimation of the entropy and the enthalpy of the liquid at 298 K. The basis of this procedure is the assumption of the validity of Nernst's heat theorem and Debye's T^3 law for c_p at very low temperatures. Ab initio calculations of ion pairs in the gaseous state provide the corresponding values of the entropy and enthalpy in the (ideal) gaseous state. From differences of enthalpies and entropies in the liquid and gaseous states, respectively, the heat of vaporization and the entropy of vaporization can be calculated. Using this procedure to obtain the enthalpy and entropy of the liquid as well as the gaseous state, the vapor pressure p_{sat} has been calculated and was found to be ca. 10^{-10} Pa for [BMIM][PF₆] at 298 K. Knudsen effusion measurements have also been used to measure p_{sat} of [BMIM][PF₆] directly. However, the agreement with the indirectly determined data of p_{sat} was not satisfactory. The same group presented a more detailed series of c_p measurements of [BMIM][PF₆]¹⁴ without being able to remove this discrepancy. The discrepancy might have several reasons. A nonequilibrium situation in the liquid and solid states of [BMIM][PF₆] may lead to erroneous data of the enthalpy and entropy obtained from integrating over measured $c_p(T)$ and c_p/T values, respectively. The ab initio calculations of the gaseous species might not be accurate enough, considering the relatively low level of the calculation procedure.

Another approach to estimate at least the heat of vaporization was based on the rather crude assumption of the validity of Hildebrandt's solubility parameter,¹⁵ and recently, Rebelo et al.⁵ tried to make predictions of boiling temperatures of RTIL based on experimental surface tension and density data of RTIL, which were used to estimate hypothetical critical points from which finally boiling temperatures were obtained.

The possibility to distillate a number of RTIL at 300 °C has been demonstrated by Earl et al.;¹⁶ however, the first reliable data of vapor pressures directly measured as a function of temperature have been reported just recently using the well-established Knudsen cell effusion techniques. RTIL of the general formula [C_nMIM][NTf₂] with $n = 2, 4, 6$, and 8 have been studied, and from the temperature dependences of vapor pressures, their molar enthalpies of vaporization have been determined.¹⁷

In this work, we decided to study the vapor pressure of [C₂MIM][NTf₂] (or [EMIM][NTf₂]) and [BMIM][dca] using the

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transpiration method. The procedure of the transpiration method is well-established^{18–20} and offers two advantages compared to other techniques. First, possible traces of moisture are removed by flashing the sample with helium prior to the beginning of the transpiration experiment. The completeness of the moisture removal indicates the invariant vapor pressure measured at an arbitrary temperature. Second, the protection of the sample against oxidation and decomposition is provided by the inert helium used as a transporting gas. This holds especially for labile materials at higher temperatures. For these reasons, we decided to apply the transpiration method for studying the temperature dependence of the vapor pressure of ionic liquids. Comparison of the results obtained for [EMIM][NTf₂] from transpiration and from effusion, as already published earlier,¹⁷ will provide a check for the mutual consistency of the two methods.

Experimental Procedure and Methods of Ab Initio Calculations

Materials. The sample of [BMIM][dca] studied, C₁₀H₁₅N₅ (CAS 448245-52-1), was of commercial origin (Merck product 4.90015). It contained <1000 ppm of halide and <10 000 ppm of water, according to specifications stated by the suppliers. Such an amount of halide impurity does not impact vapor pressure measurements and combustion experiments. The sample of the [EMIM][NTf₂] was from the same batch as that described in our previous paper.²¹ Prior to experiments, all ionic liquid (IL) samples were subjected to vacuum evaporation at 333 K for more than 24 h to remove possible traces of solvents and moisture. The water concentration in [BMIM][dca] of 420 ppm was determined by Karl Fischer titration before starting experiments, and appropriate corrections were made for combustion results. The water concentration in [EMIM][NTf₂] was measured to be 150 ppm. Samples of the ILs were kept and handled under a nitrogen stream in a special glass device furnished with a septum for the sample extraction using a syringe.

Thermochemical Measurements: Combustion Calorimetry. An isoperibol bomb calorimeter was used for measuring the energy of combustion of [BMIM][dca]. The construction of the calorimeter and the detailed experimental procedure have been described previously.^{22,23} A first combustion experiment has revealed a scope of difficulties related to restricted flammability of ILs. A sample of [BMIM][dca] simply filled into the platinum crucible according to the common procedure burned with noticeable traces of soot. The usually successful procedure of increasing the mass of a sample for combustion failed. Furthermore, during weighing of the sample in the crucible, a remarkable increase in the weight was observed due to absorption of air moisture. The dynamics of the weight increase is presented in the Supporting Information. Thus, from a practical point of view, careful encapsulation of the IL sample is required due to its hygroscopic nature. In the present study, we used commercially available polyethylene bulbs (Fa. NeoLab, Heidelberg, Germany) of 1 cm³ volume as the sample container for the liquid samples. The liquid sample was transferred into the polyethylene bulb with a syringe under a nitrogen stream in a glovebox. The fine neck of the container was compressed with special tweezers and was sealed outside of the glovebox by heating the neck

in close proximity to a glowing wire. Then, the container was placed in the crucible and was burned in oxygen at a pressure of 3.04 MPa. As already mentioned, the stock of IL was kept in the special glass device under an inert atmosphere. In order to simplify sampling and also to avoid the use of a glovebox (handling of sample in a glovebox is very awkward), we have tested whether the dry sample of IL filled in the polyethylene bulb with a narrow neck still absorbs humidity. It turned out that the orifice of the neck was small enough to protect the IL from absorbing humidity, that is, no increase in the weight of the sample in the bulb was observed within 10 min. Thus, encapsulation and sealing of the sample could be performed without use of a glovebox, provided that the reservoir with the dry IL was kept under inert gas. Having established this encapsulation procedure, a series of subsequently still unsuccessful combustion experiments were performed due to abundant soot formation in the crucible. The completeness of the combustion of the sample was ensured only by using the combination of a small crucible in a large one. Apparently, such a combination produces a sufficiently higher temperature due to restricted heat exchange inside the small crucible, resulting in complete combustion. Ten successful experiments were carried out for [BMIM][dca]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none of these substances were detected. The energy equivalent of the calorimeter ϵ_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39i, NIST). The calorimeter was specially calibrated for the temperature increase of 2 degrees, which was specific for combustion experiments with the IL enclosed in the polyethylene bulb (at least half of the temperature increase is due to combustion energy of polyethylene). From nine experiments, ϵ_{calor} was measured to be $(14816.20 \pm 0.85) \text{ J}\cdot\text{K}^{-1}$. 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.²⁴ The sample masses were reduced to vacuum, taking into consideration the density value of $\rho(293 \text{ K}) = 1.0575 \text{ g}\cdot\text{cm}^{-3}$ for the liquid [BMIM][dca].²⁵ For converting the energy of the actual combustion process to that of the isothermal process and reducing to standard states, the conventional procedure²⁶ was applied. Results for combustion experiments with [BMIM][dca] are summarized in the Supporting Information. The total uncertainty of $\Delta_f H_m^\circ(\text{l})$ was calculated according to the guidelines presented by Olofsson.²⁷ The uncertainty assigned to $\Delta_f H_m^\circ(\text{l})$ is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and from the uncertainties of the enthalpies of formation of the reaction products H₂O and CO₂.

Thermochemical Measurements: Transpiration Method. Vapor pressures and enthalpies of vaporization, $\Delta_f^\circ H_m$, of [EMIM][NTf₂] and [BMIM][dca] were determined using the method of transference in a saturated stream of inert gas and applying the Clausius–Clapeyron equation. The method is especially applicable at low pressures. It has been described in detail before^{18–20} and has proven to give results in good agreement with other established techniques. A sample of approximately 0.5 g was mixed with glass beads and placed in a thermostated U-tube 10 cm long and 0.5 cm in diameter. A preheated helium stream was passed through the U-tube at constant temperature ($\pm 0.1 \text{ K}$). The flow rate of the helium stream was measured using a soap film bubble flow meter ($\pm 0.2\text{--}0.3\%$) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow, below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus,

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the contribution due to diffusion was negligible at flow rates down to $0.5 \text{ dm}^3 \cdot \text{h}^{-1}$. The upper limit for our apparatus was a flow rate of $12 \text{ dm}^3 \cdot \text{h}^{-1}$. Thus, we carried out the experiments using flow rates ranging from 7 to $10 \text{ dm}^3 \cdot \text{h}^{-1}$, which ensured that the carrier gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The material transported was condensed in a cold trap. The amount of condensed product in the trap was determined by weighing ($\pm 0.0001 \text{ g}$).

The saturated vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a definite period of time. Assuming the validity of Dalton's law of partial pressures applied to the helium stream saturated with the substance i of interest i , values of p_i^{sat} were calculated according to the ideal gas law. Experimental vapor pressures of both ILs have been measured by using the transpiration method in the temperature ranges of 499 – 538 K for [EMIM][NTf₂] and 449 – 480 K for [BMIM][dca]. The following equation

$$R \cdot \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_1^{\text{g}} C_p \cdot \ln \left(\frac{T}{T_0} \right) \quad (2)$$

was fitted to the experimental p , T data using a and b as adjustable parameters. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which, in this case, is 298.15 K). Values of $\Delta_1^{\text{g}} C_p$ represent the difference of molar heat capacities of the gaseous and liquid phase. The expression for the enthalpy of vaporization at temperature T has been derived according to the Clausius–Clapeyron equation

$$\Delta_1^{\text{g}} H_m(T) = -b + \Delta_1^{\text{g}} C_p \cdot T \quad (3)$$

Values of $\Delta_1^{\text{g}} C_p$, the difference of molar heat capacities of the gaseous and liquid phases, have been calculated according to a procedure developed by Chickos and Acree²⁸ using the experimental isobaric molar heat capacity of [BMIM][dca]²⁵ $C_p^{\text{l}} = 364.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (at 298.15 K). The value of $\Delta_1^{\text{g}} C_p = -105.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ of [BMIM][dca] estimated in this work is in excellent agreement with those determined for [C₄MIM][PF₆], $\Delta_1^{\text{g}} C_p = -105 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, from calorimetric data and statistical thermodynamic calculations.^{13,17} In order to keep consistency with our previous work,¹⁷ in this paper, the value $\Delta_1^{\text{g}} C_p = -100 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was applied for both of the studied ILs, [EMIM][NTf₂] and [BMIM][dca]. Experimental results and parameters a and b are listed in Table 1.

Stability of ILs in Transpiration Experiments. The thermal stability of RTIL is an important factor in any kind of measurements of the vapor pressure. Recent studies have shown that stability problems could arise already at ca. $200 \text{ }^\circ\text{C}$ with certain RTIL, which are believed to be stable up to 673 K .¹ According to studies using thermogravimetry (TGA), the ionic liquid [EMIM][NTf₂] starts to decompose at 673 K ²⁹ or 713 – 728 K .³⁰ The corresponding temperature of decomposition of [BMIM][dca] is reported²⁵ to be 513 K . In any case, the temperature ranges used for our transpiration experiments were distinctly below these temperatures for both of the ILs (see Table 1). ILs inside the saturation tube remained colorless for [EMIM][NTf₂] and became slightly yellow for [BMIM][dca]. The vapor phase condensed in the trap was visually controlled. In most cases, the condensate was colorless. In the cases where a faint color was observed, the experimental vapor pressures did not deviate significantly from the linear behavior of the $\ln p/(1/T)$ plot. A similar appearance of color was also observed in our previous study¹⁷ of the vapor pressure of [EMIM][NTf₂] using the Knudsen effusion method where IR spectra of [EMIM][NTf₂] have been recorded from samples in the effusion cell before and after the experiments. No traces arising from possible decomposition have been

Table 1. Experimental Results of the Vapor Pressure p Measurements of [EMIM][NTf₂] and [BMIM][dca] Using the Transpiration Method

T^a K	m^b mg	$V_{(\text{N}_2)}^c$ dm^3	gas flow dm^3/h	p^d Pa	$(p_{\text{exp}} - p_{\text{calc}})$ Pa	$\Delta_1^{\text{g}} H_m$ $\text{kJ} \cdot \text{mol}^{-1}$
[EMIM][NTf ₂]; $\Delta_1^{\text{g}} H_m(298.15 \text{ K}) = (136.7 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p) = \frac{369.8}{R} - \frac{166477.7}{RT} - \frac{100}{R} \ln \left(\frac{T}{298.15} \right)$						
499.2	9.0	358.95	10.99	0.157	-0.002	116.56
506.2	21.8	615.65	7.09	0.223	-0.012	115.86
509.2	13.4	299.96	10.76	0.282	0.005	115.56
516.2	12.5	198.28	7.09	0.396	-0.004	114.86
519.2	35.0	443.30	10.76	0.498	0.032	114.56
529.2	23.4	186.71	10.99	0.787	0.017	113.56
538.2	41.8	234.72	10.99	1.119	-0.063	112.66
[BMIM][dca]; $\Delta_1^{\text{g}} H_m(298.15 \text{ K}) = (157.2 \pm 1.1) \text{ kJ} \cdot \text{mol}^{-1}$						
$\ln(p) = \frac{443.9}{R} - \frac{186993.2}{RT} - \frac{100}{R} \ln \left(\frac{T}{298.15} \right)$						
448.7	18.0	1146.2	8.31	0.192	0.000	142.13
453.9	2.2	90.0	8.59	0.298	0.003	141.61
463.2	19.7	388.3	8.59	0.614	-0.013	140.68
474.2	12.6	106.9	8.59	1.436	-0.021	139.58
479.6	13.4	73.9	8.59	2.206	0.036	139.04

^a Temperature of saturation. ^b Mass of transferred sample, condensed at $T = 299 \text{ K}$. ^c Volume of nitrogen, used to transfer mass m of the sample. ^d Vapor pressure at temperature T , calculated from m and the residual vapor pressure at the cooling temperature $T = 299 \text{ K}$.

detected. The same experiences have been made with the condensate of our transpiration studies. Additionally, the samples of [EMIM][NTf₂] and [BMIM][dca] collected in the cold trap of the transpiration apparatus have been analyzed using the GC–MS technique. At all of the temperatures, no traces of a possible decomposition have been found.

Ab Initio Calculations. Standard ab initio molecular orbital calculations were performed using the Gaussian 03 rev.04 program package.³¹ Rotational conformers of the 1-*n*-butyl-3-methylimidazolium cation were studied at the RHF/3-21G* level at 0 K . Molecular structures and relative energies of all conformations for the cation formed by rotation of alkyl groups around N–C and C–C bonds of the butyl group (CCCN and CCNC dihedrals) by 360° have been studied with 10° steps starting from the coplanar conformation. It was found that the cation has seven stable conformations, and six of them (confs 1, 2, and 3) formed chiral pairs having identical energies (see Supporting Information). Energies and frequencies of normal modes were calculated for all of the stable conformers using the RB3LYP/6-31+G(d,p) basis set. Corresponding calculations have been performed for the molecular ionic pair [BMIM][dca] at the HF/3-21G*, HF/6-31G(d,p) level and fully optimized at the B3LYP/6-31+G(d,p) level. Starting from 20 to 30 initial geometries, the energy of formation of ion pairs from separated ions was calculated using by the supermolecule method at the B3LYP level. The basis set superposition error (BSSE) has been accounted for at the B3LYP/6-31+G(d,p) level using the counterpoise method. The optimized structure of the [BMIM][dca] ion pair is presented in Figure 1. Optimized structures and energies of the ionic pair were also obtained using the G3MP2 method. The G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second row of the periodic table based on ab initio molecular orbital theory. A modification of G3 theory that uses reduced orders of Møller–Plesset perturbation theory is the G3MP2 theory.^{32,33} This method saves considerable computational time compared to the G3 theory with limited loss in accuracy but is much more accurate than G2(MP2) theory. G3(MP2) theory uses geometries from second-order perturbation theory

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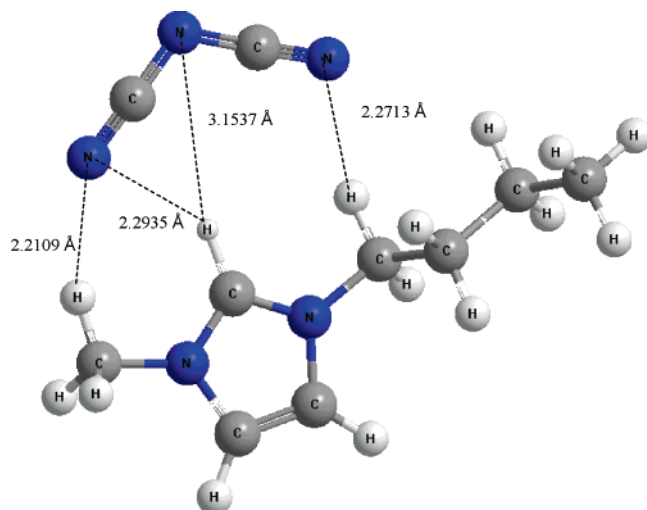
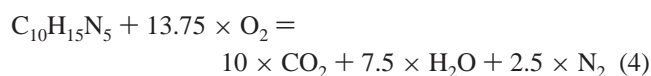


Figure 1. Optimized with B3LYP/6-31+G(d,p) structure of the [BMIM][dca].

and scaled zero-point energies from Hartree–Fock theory followed by a series of single-point energy calculations at the MP2(Full)/6-31G(d), QCISD(T)/6-31G(d), and MP2/GTMP2Large levels of theory (for details, see ref 32). Calculated values of the enthalpy and Gibbs enthalpy of ions and ion pairs are based on the electronic energy calculations obtained by the G3MP2 method using standard procedures of statistical thermodynamics.³⁴

Results and Discussion

Combustion Calorimetry. Results of combustion experiments on [BMIM][dca] are summarized in the Supporting Information. The value of the standard massic energy of combustion $\Delta_c u^\circ = -(30604.9 \pm 4.4) \text{ J}\cdot\text{g}^{-1}$ has been used to derive the standard molar enthalpy of combustion, $\Delta_c H_m^\circ = -(6285.1 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$, and the standard molar enthalpy of formation in the liquid state, $\Delta_f H_m^\circ(l) = (206.2 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$, based on the reaction



$\Delta_f H_m^\circ(l)$ of the [BMIM][dca] has been obtained from the enthalpic balance according to eq 4

$$\Delta_f H_m^\circ(l, [\text{BMIM}][\text{dca}]) = 10 \times \Delta_f H_m^\circ(\text{g}, \text{CO}_2) + 7.5 \times \Delta_f H_m^\circ(l, \text{H}_2\text{O}) - \Delta_c H_m^\circ \quad (5)$$

where molar enthalpies of formation of $\text{H}_2\text{O}(l)$ and $\text{CO}_2(\text{g})$ were taken from the literature, as assigned by CODATA.¹²

Vapor Pressure Measurements. Experimental vapor pressures of [EMIM][NTf₂] and [BMIM][dca] measured at different temperatures by using the transpiration method are presented in Table 1. Experiments with [EMIM][NTf₂] have been performed in the temperature range of 499–538 K. Comparison of the results obtained for [EMIM][NTf₂] with those obtained by the Knudsen technique measured in the T range of 442–484 K¹⁷ is shown in Figure 2. Both methods cover quite different temperature ranges. The transpiration method is able to measure vapor pressures at temperatures higher than those covered by the effusion technique. Indeed, in order to collect the measurable mass of sample [EMIM][NTf₂] at 499 K (lowest

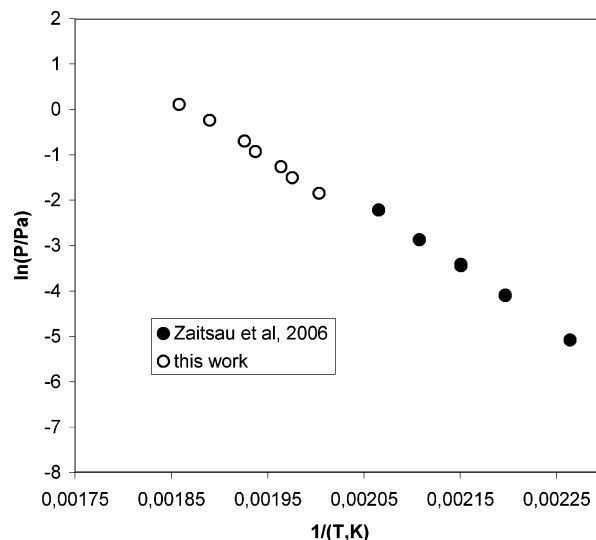


Figure 2. Plot of vapor pressure versus reciprocal temperature for [EMIM][NTf₂]. ○, this work; ●, Zaitsau et al.¹⁷

possible temperature for the present transpiration study), about 85 h was required. Further lowering of the temperature will extend the time in an exponential progression. The agreement of the two data sets is not exhilarating but still acceptable for this pioneering work, taking into account the very low vapor pressures of ILs at relatively high temperatures. However, it should be mentioned that discrepancies in absolute vapor pressures detected between the two methods suggest further improvement of the experimental and data treatment procedures. This holds especially for the Knudsen method, where several empirical parameters are involved in the calculation of absolute vapor pressures.²⁰ Vapor pressures of [BMIM][dca] have been obtained in the temperature range of 449–480 K. For this IL, the temperatures where measurements are possible are lower than in the case of [EMIM][NTf₂] since the volatility of [BMIM][dca] is somewhat higher.

Enthalpies of Vaporization $\Delta_1^g H_m$ of [EMIM][NTf₂] and [BMIM][dca]. Despite the slightly different absolute vapor pressures of [EMIM][NTf₂] obtained by the transpiration and the Knudsen methods, it is obvious that the slopes of both of the lines in Figure 2 are very similar, and enthalpies of vaporization derived from this data according to eq 3 are as follows

$$\text{Knudsen: } \Delta_1^g H_m(298 \text{ K}) = 135.3 \pm 1.3 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\text{Transpiration: } \Delta_1^g H_m(298 \text{ K}) = 136.7 \pm 3.4 \text{ kJ}\cdot\text{mol}^{-1}$$

It is apparent that the vaporization enthalpies of [EMIM][NTf₂] measured by different methods are indistinguishable within their experimental uncertainties. Thus, both methods could be recommended for measuring vaporization enthalpies of ionic liquids. The value of the enthalpy of vaporization of [BMIM][dca], $\Delta_1^g H_m(298 \text{ K}) = 157.2 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$, has also been obtained using eq 3. There exist no other experimental data for comparison. Hence, we have used an empirical correlation already applied in our previous work¹⁷ to verify this value of the enthalpy of vaporization of [BMIM][dca]. The experimental vaporization enthalpies of ionic liquids [C_nMIM][NTf₂] (with $n = 2-8$) correlate successfully with the surface tension (σ) and molar volume (V_m) of the ionic liquids.

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Table 2. G3MP2 Total Energies at 0 K and Enthalpies at 298 K (in Hartree) of the Molecules Appearing in Eqs 13–15

compounds	G3MP2		B3LYP/6-31+G(d,p)	Experimental
	E_0	H_{298}^a	H_{298}^b	$\Delta_f H_m^\circ$ (g, 298)
methane	-40.422100	-40.418284	-40.4791428	-74.40 ³⁸
hydrogen cyanide	-93.298948	-93.295483	-93.4113753	135.14 ³⁹
ethene	-78.434778	-78.430777	-78.5464950	52.50 ³⁸
ethane	-79.651199	-79.646714	-79.7652757	-83.80 ²⁴
ammonium	-56.470142	-56.466333	-56.5300129	-45.94 ¹²
1 <i>H</i> -imidazole	-225.867843	-225.863074	-226.1620731	132.90 ⁴¹
trimethylamine	-174.139755	-174.133223	-174.3708001	-23.60 ³⁸
ethylenediamine	-190.194682	-190.188105	-190.4293793	-17.00 ⁴⁰

^a Scaling factor, 0.8929. ^b Scaling factor, 0.9642; $H_{298} = E_0 + \text{ZPE} \cdot \text{scaling factor} + (\text{TCH} - \text{ZPE})$.

The correlation equation for the molar enthalpy of vaporization is given by

$$\Delta_f^\circ H_m(298 \text{ K}) = A(\sigma \cdot V_m^{2/3} \cdot N_A^{1/3}) + B \quad (6)$$

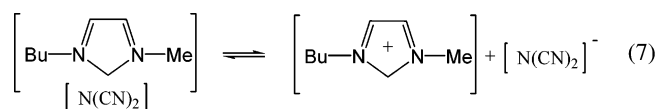
where N_A is Avogadro's constant. The parameters $A = 0.01121$ and $B = 2.4 \text{ kJ} \cdot \text{mol}^{-1}$ were calculated by a least-squares treatment.¹⁷ The molar enthalpy of vaporization for [BMIM][dca] calculated from eq 6 was found to be $142 \pm 3.0 \text{ kJ} \cdot \text{mol}^{-1}$. This value is in satisfactory agreement with experimental result, taking into account that only the experimental value of the surface tension, $\sigma = 44.4 \text{ mJ} \cdot \text{m}^{-2}$, for [EMIM][dca] was available in the literature.³⁵ Therefore, σ of [EMIM][dca] has been used in eq 6 assuming that this value is very close to the corresponding one of [BMIM][dca]. Such a procedure is justified by the fact that the surface tensions of [EMIM][NTf₂] ($\sigma = 34.9 \text{ mJ} \cdot \text{m}^{-2}$)¹⁷ and of [BMIM][NTf₂] ($\sigma = 31.8 \text{ mJ} \cdot \text{m}^{-2}$)¹⁷ are also close together. According to eq 6, the vaporization enthalpy is expected to increase with the surface tension. This trend is confirmed by our experiments because the surface tension of [EMIM][dca] (and apparently of [BMIM][dca]) is about $10 \text{ mJ} \cdot \text{m}^{-2}$ larger than those of the corresponding ILs [EMIM][NTf₂] and [BMIM][NTf₂]. As a consequence, the observed enthalpy of vaporization of [BMIM][dca], $\Delta_f^\circ H_m(298 \text{ K}) = 157.2 \pm 1.1 \text{ kJ} \cdot \text{mol}^{-1}$, derived in this work is distinctly larger than those reported¹⁷ for [EMIM][NTf₂], $\Delta_f^\circ H_m(298 \text{ K}) = 135.3 \pm 1.3 \text{ kJ} \cdot \text{mol}^{-1}$, and for [BMIM][NTf₂], $\Delta_f^\circ H_m(298 \text{ K}) = 136.2 \pm 1.7 \text{ kJ} \cdot \text{mol}^{-1}$.

Ab Initio Results and Thermodynamics in The Gaseous Phase. The DFT methods provide good predictions of normal frequencies of molecules, while the electronic energies of the molecules are not always calculated in a satisfying way. MP2 ab initio methods such as G3MP2 provide more reliable results concerning electronic energies and are, therefore, preferably used for calculating enthalpic quantities such as enthalpies of formation and enthalpies of reaction.³⁶ However, normal frequencies calculated by G3MP2 are often inferior to DFT results, and therefore, entropic quantities which do not depend directly on electronic energy values are often described better using normal frequencies and moments of inertia obtained from DFT methods. We have applied both techniques, G3MP2 as well as DFT, for predicting absolute thermodynamic properties (see Tables 2 and 3). Calculations for the free cation [BMIM]⁺, the free anion [dca]⁻, and the ion pair [BMIM]⁺[dca]⁻ have been performed. As a results of the electronic energy at 0 K,

Table 3. Comparison of the Calculated and Measured Standard Molar Enthalpy of Formation $\Delta_f H_m^\circ$ (g) for [BMIM][dca] in the Gaseous Phase at 298.15 K (in $\text{kJ} \cdot \text{mol}^{-1}$)

DFT			G3MP2				$\Delta_f H_m^\circ$ (g) exptl
reaction			reaction				
13	14	15	atomization	13	14	15	
336.7	363.5	336.3	360.1	361.6	360.8	356.4	363.4 ± 2.7
average = 345.5			average = 359.63				

the molecular structures in the lowest energetic state and all vibrational frequencies of each species have been obtained. Results of these data are available in the Supporting Information. The optimized structure of the ion pair is shown in Figure 1. On the basis of these quantum mechanical results, the molar Gibbs energy, the molar enthalpy, and the molar entropy have been calculated at 298.15 and 423.15 K using standard procedures of statistical thermodynamics. The purpose of this procedure was to obtain absolute values of the molar standard Gibbs energy of reaction $\Delta_r G^\circ$, the standard molar entropy reaction $\Delta_r S^\circ$, and the molar reaction enthalpy $\Delta_r H^\circ$ for the process of dissociation of the ion pair [BMIM]⁺[dca]⁻ in the gaseous phase according to



The results obtained are listed in Tables 4 and 5. From the calculated theoretical results, the chemical equilibrium constant K_p in the ideal gaseous state has been calculated according to

$$K_p = \exp[-\Delta_r G^\circ/RT] \quad (8)$$

from which the degree of dissociation of the ion pair α defined as

$$\alpha = \frac{p^+}{p_{\text{IP}} + p^+} = \frac{p^-}{p_{\text{IP}} + p^-} \quad (9)$$

can be calculated according to

$$K_p = \frac{\alpha^2}{1 - \alpha^2} \cdot p_{\text{sat}} \quad (10)$$

or

$$\alpha = \sqrt{\frac{K_p/p_{\text{sat}}}{1 + K_p/p_{\text{sat}}}} \quad (11)$$

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Table 4. B3LYP/6-31+G(d,p) Calculations of the Thermodynamic Properties of the Ions [dca]⁻, [BMIM]⁺, and the Ionic Pair [BMIM][dca] Used for Prediction of the Equilibrium Constant K_p of Dissociation of the Ionic Liquid According to the Reactions in Eqs 7 and 8

298.15			423.15		
components	Gibbs energy hartree	enthalpy hartree	components	Gibbs energy hartree	enthalpy hartree
[dca] ⁻	-240.5202395	-240.48873	[dca] ⁻	-240.5367541	-240.487713
[BMIM] ⁺	-423.0278391	-422.976914	[BMIM] ⁺	-423.0606495	-422.975991
[BMIM][dca]	-663.6558162	-663.588312	[BMIM][dca]	-663.7015716	-663.587965
$\Delta_f G^\circ$, kJ·mol ⁻¹		282.87	$\Delta_f G^\circ$, kJ·mol ⁻¹		273.49
$\Delta_f H^\circ$, kJ·mol ⁻¹		322.07	$\Delta_f H^\circ$, kJ·mol ⁻¹		326.25
$\Delta_f S^\circ$, J·mol ⁻¹ ·K ⁻¹		131.48	$\Delta_f S^\circ$, J·mol ⁻¹ ·K ⁻¹		124.67
K_p		2.8×10^{-50}	K_p		1.7×10^{-34}

Table 5. G3MP2 Calculations of the Thermodynamic Properties of the Ions [dca]⁻, [BMIM]⁺, and the Ionic Pair [BMIM][dca] Used for Prediction of the Equilibrium Constant K_p of Dissociation of the Ionic Liquid According to the Reactions in Eqs 7 and 8

298.15			423.15		
components	Gibbs energy hartree	enthalpy hartree	components	Gibbs energy hartree	enthalpy hartree
[dca] ⁻	-240.2152848	-240.183855	[dca] ⁻	-240.2293875	-240.180531
[BMIM] ⁺	-422.4478654	-422.39716	[BMIM] ⁺	-422.4710436	-422.386819
[BMIM][dca]	-662.7802475	-662.713061	[BMIM][dca]	-662.8122079	-662.698682
$\Delta_f G^\circ$, kJ·mol ⁻¹		307.44	$\Delta_f G^\circ$, kJ·mol ⁻¹		293.47
$\Delta_f H^\circ$, kJ·mol ⁻¹		346.69	$\Delta_f H^\circ$, kJ·mol ⁻¹		344.81
$\Delta_f S^\circ$, J·mol ⁻¹ ·K ⁻¹		131.64	$\Delta_f S^\circ$, J·mol ⁻¹ ·K ⁻¹		121.34
K_p		1.4×10^{-54}	K_p		5.9×10^{-37}

where $p^+ = p^-$ is the partial pressure of the cation and anion, respectively, p_{IP} is the partial pressure of the ion pair, and p_{sat} is the saturation pressure of the ionic liquid related to these partial pressures by

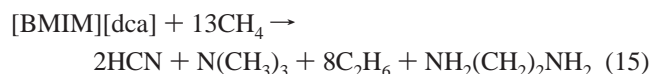
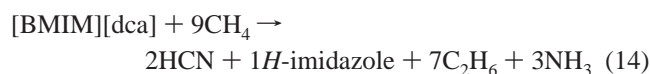
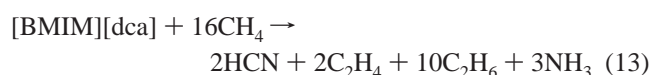
$$p_{sat} = p_{IP} + p^+ + p^- \quad (12)$$

The results presented in Table 4 show that K_p is very small even at temperatures between 400 and 500 K. The results of K_p obtained by the DFT method and the MP2 method differ by several orders of magnitude due to the difference of the $\Delta_f G^\circ$ values by ca. 23 kJ mol⁻¹, this is ca. 8%. However, even if the uncertainty of $\Delta_f G^\circ$ using such theoretical methods is estimated to be $\pm 10\%$, the K_p remains at such a low value that it can be concluded with high reliability that α is zero, that is, the ionic liquid [BMIM]⁺[dca]⁻ exists exclusively as an ion pair in the gaseous phase within the considered range of temperature.

Determination of the Gaseous Enthalpies of Formation of [BMIM][dca]. The enthalpy of formation, $\Delta_f H_m^\circ(l) = (206.2 \pm 2.5)$ kJ·mol⁻¹, of [BMIM][dca], derived from the combustion experiments together with the vaporization enthalpy, $\Delta_f^\# H_m = (157.2 \pm 1.1)$ kJ·mol⁻¹, derived from the vapor pressure measurements are referred to the reference temperature, $T = 298.15$ K. Using the equation $\Delta_f H_m^\circ(g) = \Delta_f H_m^\circ(l) + \Delta_f^\# H_m$, we calculated the value of the standard molar enthalpy of formation, $\Delta_f H_m^\circ(g) = (363.4 \pm 2.7)$ kJ·mol⁻¹, which is, to our knowledge, the first experimental determination of this key thermodynamic property of ionic liquids in the literature. This value has been used to check the validity of ab initio methods as follows.

Quantum Chemical Calculations for $\Delta_f H_m^\circ(g)$ of [BMIM][dca]. Results of the molar enthalpy of formation, $\Delta_f H_m^\circ(g)$, of ionic liquids obtained by using ab initio methods have not been reported in the literature so far. In standard Gaussian-n theories, theoretical enthalpies of formation in the gaseous state are calculated through atomization reactions.³²

Raghavachari et al.³⁷ have proposed using a set of isodesmic reactions, the “bond separation reactions”, to derive theoretical enthalpies of formation. Isodesmic reactions conserve the number of types of bonds and, therefore, should provide an improvement compared to simple atomization reactions. Further enhancement in the calculation of enthalpies of formation should be provided by isodesmic reactions, which, in addition to the types of bonds, also conserve the hybridization of the atoms in the bond. We have calculated the enthalpies of formation of [BMIM][dca] using G3MP2 and DFT methods with help from both standard atomization reactions as well as isodesmic reactions. For the latter method, we have chosen the following three reactions



Using standard enthalpies of reactions 13–15 calculated by G3MP2 or DFT and experimental enthalpies of formation, $\Delta_f H_m^\circ(g)$, for species involved in reactions 13–15 as recommended by Pedley et al.,³⁸ the enthalpy of formation of [BMIM][dca] has been calculated (see Tables 2 and 3). As shown in Table 3, the average value for $\Delta_f H_m^\circ(g)$ calculated by G3MP2 is in excellent agreement with the experimental values

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derived in this work. The enthalpy of formation of [BMIM][dca] derived by G3(MP2), with the help of the atomization procedure, is also in excellent agreement with the experimental results. Enthalpies of formation of [BMIM][dca] calculated by the DFT procedure are systematically (about 20 $\text{kJ}\cdot\text{mol}^{-1}$) less positive than the experimental value (see Table 3).

Conclusions

The first experimental determination of the gaseous enthalpy of formation, $\Delta_f H_m^\circ(\text{g})$, of 1-butyl-3-methylimidazolium dicyanamide has been reported based on experimental data of the enthalpy of vaporization, $\Delta_v^\circ H_m$, and the enthalpy of combustion, $\Delta_c^\circ H_m$, of this ionic liquid. Independently, quantum mechanical calculations of the gaseous enthalpy of formation give results very close to the experimental value, indicating thermodynamic consistency of the procedure. The method developed in this work opens a new way to obtain thermodynamic properties of ionic liquids, which have not been available so far and would provide indispensable data materials for testing

ab initio procedures and molecular dynamic simulation techniques in order to understand thermodynamic properties of ionic liquids on a molecular basis.

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Supporting Information Available: Results for typical combustion experiments; results from conformational analysis of the ionic liquid and optimized structures; geometry parameters for the cation, anion, and ionic pair; input data for calculation of the equilibrium constant of the dissociation process of the ionic liquid. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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