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Pyridinium based ionic liquids. N-Butyl-3-methyl-pyridinium dicyanoamide: Thermochemical measurement and first-principles calculations

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ABSTRACT

The standard molar enthalpy of formation $\Delta_f H_m{}^\circ(l)$ of the ionic liquid N-butyl-3-methylpyridinium dicyanamide has been determined at 298.15 K by means of combustion calorimetry. Vaporization of the ionic liquid into the nitrogen stream in order to obtain vaporization enthalpy has been attempted, but no vaporization was achieved. First-principles 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 quantum–chemical calculations allows estimation of the molar enthalpy of vaporization of the ionic liquid under study.

1. Introduction

Ionic liquids (ILs) are a route to volatile organic solvent replacement. ILs are currently attracting considerable attention as potentially benign solvents for many areas such as fuel cells, rechargeable batteries and "green solvents" [1]. Most frequently the imidazolium based ILs have been studied. Pyridinium based ILs has been investigated less intensively. A comprehensive thermophysical study of N-butyl-3-methyl-pyridinium tetrafluoroborate, N-butyl-4-methyl-pyridinium tetrafluoroborate, and N-butyl-3-methylpyridinium dicyanamide has been performed recently [2,3]. Physicochemical properties such as density, speed of sound, refractive index, surface tension, and kinematic viscosity of the pyridinium based ILs have been measured in a wide range of temperatures [2,3]. Here we present the first experimental and theoretical study of the enthalpy of combustion and enthalpies of formation, $\Delta_f H_m{}^\circ$, in the liquid as well as in the gaseous state of the ionic liquid N-butyl-1-methylpyridinium dicyanamide [B3MPYR][DCA] (see Fig. 1). We also report the enthalpy of vaporization, $\Delta_l^g H_m$, of this ionic liquid derived according to the general equation [4,5]:

$$\Delta_l^g H_m = \Delta_f H_m^\circ(g) - \Delta_f H_m^\circ(l) \quad (1)$$

where the standard molar enthalpy of formation of IL in the liquid phase, $\Delta_f H_m{}^\circ(l)$, was obtained from the calorimetrically measured energy of combustion and the molar enthalpy of formation, $\Delta_f H_m{}^\circ(g)$, was obtained by the high-level first-principles calculations.

2. Experimental procedure and methods of ab initio calculations

2.1. Materials

The sample of 1-butyl-3-methylpyridinium dicyanamide [B3MPYR][DCA], $C_{12}H_{16}N_4$, was of commercial origin (Solvent Innovation, 99.327-1) with purity 98% (HPLC, NMR) it contained 415.4 ppm of chloride according to specifications stated by the suppliers. Prior to experiments the IL samples were subjected to vacuum treatment at 333 K and 10^{-2} mbar for more than 24 h to reduce possible traces of solvents and moisture. The water concentration 644.5 ppm was determined by Karl Fischer titration shortly before combustion experiments and an appropriate correction was applied to the results.

2.2. Thermochemical measurements. combustion calorimetry

An isoperibol bomb calorimeter was used for the measurement of energy of combustion of [B3MPYR][DCA]. Five successful experiments were carried out for this compound (see Tables 1 and 2). In the present study, we used commercially available polyethy-

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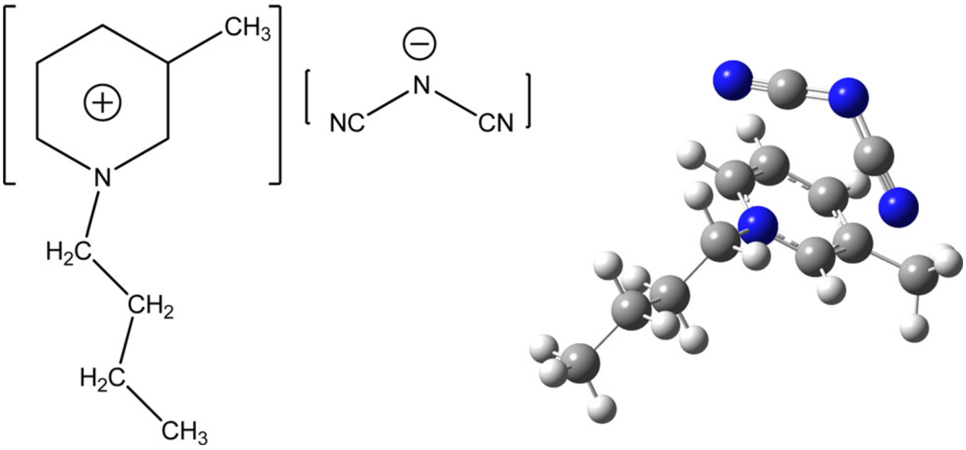

Fig. 1. Structure of [B3MPYR][DCA] and its most stable conformation.

Table 1
Results for typical combustion experiments at $T = 298.15$ K ($p^\circ = 0.1$ MPa) of the [B3MPYR][DCA][a].

m (substance) (g)[b]	0.421580	0.343080	0.363681	0.37176	0.331758
m'(cotton) (g)[b]	0.001033	0.000745	0.000776	0.000868	0.000872
m''(polyethen) (g)[b]	0.277813	0.287623	0.285298	0.295419	0.270668
ΔT_c (K)[c]	1.82032	1.67391	1.71359	1.76232	1.59536
$(\varepsilon_{calor})\cdot(-\Delta T_c)$ (J)	−26955.6	−24787.5	−25375.2	−26096.8	−23624.4
$(\varepsilon_{cont})\cdot(-\Delta T_c)$ (J)	−29.58	−26.9	−27.53	−28.47	−25.41
ΔU_{decomp} HNO_3 (J)	71.67	63.91	69.58	66.30	63.31
ΔU_{corr} (J)[d]	9.80	8.70	8.95	9.29	8.24
$-m'\cdot\Delta_c u'$ (J)	17.50	12.62	13.15	14.71	14.78
$-m''\cdot\Delta_c u''$ (J)	12877.88	13332.62	13224.85	13694	12546.68
$\Delta_c u^\circ$(liq)/(J g^{-1})	−33228.2	−33218.5	−33233.1	−33218.5	−33207.3
$\Delta_c u^\circ$(liq)/(J g^{-1})			−33221.1 ± 4.5		

[a] For the definition of the symbols see Ref. [8], macrocalorimeter: $T_h = 298.15$ K; V(bomb) = 0.320 dm^3; p^i(gas) = 3.04 MPa; $m^i(H_2O) = 1.00$ g.

[b] Masses obtained from apparent masses.

[c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\varepsilon_{cont})\cdot(-\Delta T_c) = (\varepsilon^i{}_{cont})\cdot(T^i - 298.15\ \text{K}) + (\varepsilon^f{}_{cont})\cdot(298.15\ \text{K} - T^f + \Delta T_{corr.})$.

[d] ΔU_{corr}, the correction to standard states, is the sum of items 81–85, 87–90, 93, and 94 in Ref. [8]; $^f\varepsilon = 14808.2 \pm 0.8$ J K^{-1}.

lene bulbs (Fa. NeoLab, Heidelberg, Germany) of 1 cm^3 as the sample containers. The sample was transferred from the stock bottle into the polyethylene bulb with a syringe and the sealed according to a procedure described previously [6]. The combustion 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 39j, N.I.S.T.). 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]. The sample masses were reduced to vacuum, taking into consideration the density value $\rho(293\ \text{K}) = 1.056$ g cm^{-3} for the liquid [B3MPYR][DCA] (from specification by Solvent Inovation). For converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states, the conventional procedure [8] was applied. Values of the standard specific energies of combustion $\Delta_c u^\circ$, together with the necessary auxiliary quantities, are given in Table 2. To derive $\Delta_f H_m{}^\circ(1)$ from $\Delta_c H_m{}^\circ$, molar enthalpies of formation of H_2O (l) and CO_2 (g) were taken, as assigned by CODATA [9]. Table 3 lists the derived standard molar enthalpy of combustion, and standard molar enthalpy of formation of the [B3MPYR][DCA]. 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 H_2O and CO_2.

Table 2
Formula, density $\rho(T = 293\ \text{K})$, mass heat capacity c_p ($T = 298.15$ K), and expansion coefficients $(\delta V/\delta T)_p$ of the materials used in the present study.

Compounds	Formula	ρ[b] (g cm^{-3})	c_p (J K^{-1} g^{-1})	$10^{-6}\cdot(\delta V/\delta T)_p$[c] (dm^3 K^{-1})
[B3MPYR][DCA]]	$C_{12}H_{16}N_4$	1.056	1.7	1.0
Polyethen[d]	$CH_{1.93}$	0.920	2.53[a]	0.1
Cotton[e]	$CH_{1.774}O_{0.887}$	1.500	1.67[a]	0.1

[a] From d.s.c. measurements.

[b] Measured with a pycnometer.

[c] Estimated.

[d] From 10 combustion experiments, $\Delta_c u^\circ = -(46351.6 \pm 3.5)$ J g^{-1}.

[e] From 10 combustion experiments, $\Delta_c u = -(16945.2 \pm 4.2)$ J g^{-1}.

2.3. Thermochemical measurements. Transpiration method

Vapor pressures and enthalpy of vaporization, $\Delta_l^g H_m$, of several ILs such as [BMIM][DCA] and [EMIM][NTf$_2$] have successfully been determined in the past using the method of transference in a saturated stream of an inert gas [6]. 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 nitro-

Table 3
Thermochemical data at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for [B3MPYR][DCA] in kJ mol^{-1}.

$\Delta_c H_m{}^\circ$ (l)	$\Delta_f H_m{}^\circ$ (l)	$\Delta_f H_m{}^\circ(g)_{g3MP2}$	$\Delta_l^g H_m$[a]
−7190.1 ± 2.5	181.3 ± 3.0	343.4 ± 2.8	162.1 ± 4.1

[a] The differences between the $\Delta_f H_m{}^\circ$(g) derived using the G3MP2 methods and the $\Delta_f H_m{}^\circ$(1) from the combustion experiments.

Table 4
Calculated total energies at 0 K and enthalpies at 298.15 K (in Hartree) of the molecules studied in this work.

Compounds	G3MP2		CBS-QB3		$\Delta_f H_m{}^\circ$ exp. gas (kJ mol^{-1})
	E_0	H_{298}	E_0	H_{298}	
[B3MPYR][DCA]	−684.737076	−684.717873	−684.635008	−684.616130	–
[B3MPYR]$^+$	−444.412895	−444.399822	−444.333166	−444.320377	–
[DCA]$^-$	−240.189032	−240.183854	−240.167200	−240.162042	–
Methane	−40.422100	−40.418284	−40.410000	−40.406185	−74.9 ± 0.4 [16]
Ethane	−79.651199	−79.646714	−79.630567	−79.626125	−83.8 ± 0.3 [16]
Propane	−118.885057	−118.879478	−118.855869	−118.850352	−104.7 ± 0.5 [16]
Ammonium	−56.470142	−56.466333	−56.460177	−56.456366	−45.9 ± 0.4 [18]
Pyridine	−247.867613	−247.862308	−247.830971	−247.825718	140.4 ± 0.7 [16]
Trimethylamine	−174.139755	−174.133223	−174.106348	−174.099913	−23.7 ± 0.7 [16]

gen 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 [B3MPYR][DCA] in the temperature range 393–443 K at a flow rate of 8.5 dm^3 h^{-1}. Such a flow rate is close to the upper limit of our apparatus 12 dm^3 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 colouration of the IL after heating. Clearly, neither the vapor pressure nor the enthalpy of vaporization of this IL could be determined using the transpiration method. Thus, an alternative indirect method has been applied for this purpose.

2.4. *First-principles calculations.*

Standard *ab initio* molecular orbital calculations were performed using the Gaussian 03 Rev.04 program package [11]. Conformation analysis of the IL was performed using B3LYP/6-31 + G(d,p) with help of the procedure developed in our previous work [6]. Optimized structures, and energies of the most stable conformer of the ionic pair was further obtained using the G3MP2 and CBS-QB3 composite-methods. 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. This method saves considerable computational time compared to the G3 theory with limited loss in accuracy. G3MP2 theory uses geometries from second-order perturbation theory 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. [12]). CBS-QB3 theory uses geometries from B3LYP/6-311G(2d,d,p) calculation, scaled zero-point energies from B3LYP/6-311G(2d,d,p) calculation followed by a series of single-point energy calculations at the MP2/6-311G(3df,2df,2p), MP4(SDQ)/6-31G(d(f),p) and CCSD(T)/6-31G† levels of theory [13]. Calculated values of the enthalpy and Gibbs energy of ions and ion pairs are based on the electronic energy calculations obtained by the CBS-QB3 and G3MP2 methods using standard procedures of statistical thermodynamics [14].

3. Results and discussion

3.1. *Combustion calorimetry*

Results of combustion experiments on [B3MPYR][DCA] are summarized in the Tables 1–3. The value of the standard specific energy of combustion $\Delta_c u^\circ = -(33221.1 \pm 4.5)\,\mathrm{J\,g^{-1}}$ has been used to derive the standard molar enthalpy of combustion $\Delta_c H_m{}^\circ = -(7190.1 \pm 2.5)\,\mathrm{kJ\,mol^{-1}}$ and the standard molar enthalpy of formation in the liquid state $\Delta_f H_m{}^\circ(\mathrm{l}) = (181.3 \pm 3.0)\,\mathrm{kJ\,mol^{-1}}$ based on the reaction:

$$C_{12}H_{16}N_4 + 16O_2 = 12CO_2 + 8H_2O + 2N_2 \qquad (2)$$

$\Delta_f H_m{}^\circ(1)$ of the [B3MPYR][DCA] has been obtained from the enthalpic balance according to Eq. (3):

$$\Delta_f H^\circ_m(l,\ [\mathrm{B3MPYR}][\mathrm{DCA}]) = 12\Delta_f H^\circ_m(g,\ CO_2) + 8\Delta_f H^\circ_m(l,\ H_2O) - \Delta_c H^\circ_m \qquad (3)$$

3.2. *Quantum chemical calculations for $\Delta_f H_m{}^\circ(g)$ of [B3MPYR][DCA]*

In our recent work [6] we have shown, that one of the aprotic ILs - [C4MIM][DCA] exists in the gaseous phase as contact ion pairs and not as a gas of separated ions. In order to justify such an assumption in case of [B3MPYR][DCA] we have assessed the equilibrium constant for the processes of dissociation of [B3MPYR][DCA] in two separated ions [B3MPYR]$^+$ and [DCA]$^-$. The chemical equilibrium constants K_p for this reactions in the ideal gaseous state have been calculated at 298.15 K and we have obtained the $K_p = 1.3 \times 10^{-55}$ from the G3MP2 and $K_p = 2.3 \times 10^{-55}$ from CBS-QB3 (see Table 6). Such extremely low values allow to conclude with high reliability that the degree of dissociation of the ion pair is zero for the [B3MPYR][DCA], i.e. this ILs exists exclusively as an ion pairs in the gaseous phase.

Results of the molar enthalpy of formation, $\Delta_f H_m{}^\circ(g)$, of [B3MPYR][DCA] obtained by using quantum chemical methods have not been reported in the literature so far. In standard G* or CBS* theories, theoretical enthalpies of formation in the gaseous state are calculated using atomization reactions or bond separation reactions [15]. We have calculated the enthalpies of formation of [B3MPYR][DCA] using G3MP2 method applying both, standard atomization reactions as well as bond separation reactions. For the latter method we have chosen the following two reactions:

$$[\mathrm{B3MPYR}][\mathrm{DCA}] + 32CH_4 = 4NH_3 + 22C_2H_6 \qquad (4)$$

$$[\mathrm{B3MPYR}][\mathrm{DCA}] + 16C_2H_6 = 3(CH_3)_3N + \mathrm{pyridine} + 10C_3H_8 \qquad (5)$$

Using enthalpies of these reactions calculated by G3MP2 and enthalpies of formation $\Delta_f H_m{}^\circ(g)$, for species involved in the reactions (4) and (5) recommended by Pedley et al. [16] the enthalpy of formation of [B3MPYR][DCA] has been calculated (see Tables 4 and 5). The results in Table 5 show that the $\Delta_f H_m{}^\circ(g)$ values calculated by G3MP2 using the atomization procedure, as well as using the Eqs. (4) and (5) are in good agreement, and we averaged them (see Table 3) for further discussion (Table 6).

Table 5
Results of calculation of the standard enthalpy of formation $\Delta_f H_m{}^\circ(g)$ for [B3MPYR][DCA] in the gaseous phase at 298.15 K in kJ mol^{-1}.

Method	Atomization	Bond separation		Average
		(1)	(2)	
G3MP2	345.7	343.6	340.9	343.4 ± 2.8

Table 6
Quantum chemical calculations of the thermodynamic properties of dissociation reactions of [B3MPYR][DCA] = [B3MPYR]$^+$ + [DCA]$^-$ in the ideal gas at 298 K ($\Delta_r G^\circ$ and $\Delta_r H^\circ$ in kJ mol^{-1}, $\Delta_r S^\circ$ in J mol^{-1} K^{-1}).

	G3MP2	CBS-QB3
$\Delta_r G^\circ$	313.3	311.9
$\Delta_r H^\circ$	352.3	351.1
$\Delta_r S^\circ$	130.9	131.2
K_p	1.3×10^{-55}	2.3×10^{-55}

3.3. *Enthalpy of vaporization* $\Delta_l^g H_m$ *of [B3MPYR][DCA]*

Enthalpies of vaporization of several ILs such as [BMIM][DCA] and [EMIM][NTf$_2$] have successfully been determined using the transpiration method [6]. However, in case of the ionic liquids [C$_2$MIM][NO$_3$] and [C$_4$MIM][NO$_3$] the ILs were not stable enough during the transpiration process for determining vaporization enthalpies [4]. In this work we also have failed applying this method and no experimental enthalpy of vaporization for [B3MPYR][DCA] could be determined using the transpiration technique. In our recent papers [4–6] we have developed an alternative procedure to estimate vaporization enthalpies of ILs in such cases using a combination of the traditional combustion calorimetry with the high-level quantum chemical calculations according to Eq. (1). In order to obtain the molar enthalpy of vaporization of [B3MPYR][DCA] at 298 K we have used the molar enthalpy of formation of [B3MPYR][DCA] in the liquid state, $\Delta_f H_m{}^\circ(1) = 181.3 \pm 3.0$ kJ mol^{-1} obtained by precision combustion calorimetry (see Table 3), and the gaseous enthalpy of formation, $\Delta_f H_m{}^\circ(g)$, of [B3MPYR][DCA] calculated by G3MP2. We already demonstrated good agreement between $\Delta_l^g H_m$ values derived from Eq. (1) using the G3MP2 with the experimental results in case of other systems [6]. Therefore, we have also applied this method in the present work to derive the vaporization enthalpy of [B3MPYR][DCA]. Using the averaged value of $\Delta_f H_m{}^\circ(g) = 343.4 \pm 2.8$ kJ mol^{-1} calculated by G3MP2 (Table 3) and applying Eq. (1) the enthalpy of vaporization $\Delta_l^g H_m[\text{B3MPYR}][\text{DCA}] = 162.1 \pm 4.1$ kJ mol^{-1} at 298.15 K has been obtained. Our result is consonant with the vaporization enthalpies of two another pyridinium based ionic liquids available in the recent literature [17]: N-butylpyridinium tetrafluoroborate $\Delta_l^g H_m([\text{C}_4\text{PYR}][\text{BF}_4]) = 167 \pm 2$ kJ mol^{-1} and n-hexylpyridinium bis[(trifluoromethyl)sulfonyl]imide $\Delta_l^g H_m([\text{C}_6\text{PYR}][\text{NTf}_2]) = 152 \pm 1$ kJ mol^{-1}.

4. Conclusions

Combination of combustion calorimetry with the first-principles calculations allows to estimate the molar enthalpy of vaporization of the ionic liquid [B3MPYR][DCA]. Our new results can be used as reference values for molecular modeling studies and validation for their quality.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.11.028.

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