



Thermochemistry of 1,1,3,3-tetramethylguanidine and 1,1,3,3-tetramethylguanidinium nitrate



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ARTICLE INFO

Article history:

Received 13 October 2013

Received in revised form 9 January 2014

Accepted 10 January 2014

Available online 22 January 2014

Keywords:

Ionic liquids

Thermochemistry

Standard molar enthalpy of formation

Enthalpy of vaporisation

DSC

Combustion calorimetry

X-ray diffraction

Ab initio calculations

ABSTRACT

Considerable efforts have recently been made to investigate how the structure of protic ionic liquids determines some of their most important properties for technological applications (e.g. low vapour pressure, conductivity). In contrast, the assessment of cohesive energies (which are also linked to those properties) based on thermodynamic results is still practically unexplored. This problem is addressed here for 1,1,3,3-tetramethylguanidinium nitrate, [Htmg][NO₃], through a combination of experimental and computational chemistry results at the reference temperature of 298.15 K. The standard molar enthalpies of formation, $\Delta_f H_m^\circ$ ([Htmg][NO₃], cr) = $-(311.8 \pm 2.3)$ kJ · mol⁻¹, and fusion, $\Delta_{fus} H_m^\circ$ ([Htmg][NO₃]) = 16.2 ± 3.8 kJ · mol⁻¹, of solid 1,1,3,3-tetramethylguanidinium nitrate (form I polymorph) were obtained by combustion and differential scanning calorimetry, respectively. From these results $\Delta_f H_m^\circ$ ([Htmg][NO₃], l) = $-(295.6 \pm 4.4)$ kJ · mol⁻¹ could be derived. Also determined were the standard molar enthalpies of formation, $\Delta_f H_m^\circ$ (tmg, l) = 7.7 ± 2.8 kJ · mol⁻¹, and vaporisation, $\Delta_{vap} H_m^\circ$ (tmg, l) = 50.0 ± 1.2 kJ · mol⁻¹, of 1,1,3,3-tetramethylguanidine, by reaction solution and Calvet-drop microcalorimetry, respectively, leading to $\Delta_f H_m^\circ$ (tmg, g) = 57.7 ± 3.0 kJ · mol⁻¹. This result is in excellent agreement with $\Delta_f H_m^\circ$ (tmg, g) = 58.4 ± 4.0 kJ · mol⁻¹, obtained from the *ab initio* calculation of the standard molar enthalpy of atomization of tmg using the W1-F12 procedure. From the above results, the cohesive energy of [Htmg][NO₃] (l) could be evaluated. Finally, the nature of a solid to solid phase transition observed for [Htmg][NO₃] at 221.4 ± 1.2 K using DSC was investigated by single crystal X-ray diffraction. The structural results indicate that complete proton transfer from HNO₃ to tmg only occurs above the phase transition temperature.

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1. Introduction

Protic ionic liquids (PILs) are a class of ionic liquids (IL) of general formula [BH⁺][A⁻], obtained by proton transfer from a Brønsted acid, HA, to a Brønsted base, B, according to [1–4]:



PILs have attracted a significant interest in recent years due to various important industrial applications (e.g. the Biphasic Acid Scavenging Utilising Ionic Liquids – BASIL processes from BASF [5,6]) and potential uses (e.g. chromatography [7,8], development

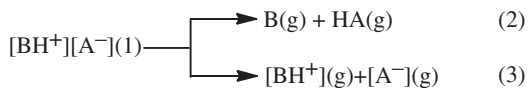
of new forms of active pharmaceutical ingredients [9–12], or electrolytes in fuel cells [13–17]). This also fostered considerable efforts to investigate how the nature of the HA and B precursors influences the cohesive energy of the [BH⁺][A⁻] species and how, in turn, the cohesive energy determines some of most relevant properties of PILs for technological applications (e.g. low vapour pressure, conductivity) [1,18]. All attempts to experimentally characterise the cohesive energies of PILs carried out up to now relied, however, on non-energetic data such as temperatures of glass transition, fusion, or boiling [1,18].

We have recently proposed a general strategy for the determination of standard molar enthalpies of formation of protic ionic liquids and analyse the energetics of their vaporisation [19]. Because the enthalpies of formation in the gaseous phase of many HA, B, A⁻ and BH⁺ species are available in the literature or can be

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experimentally measured, this strategy can also afford cohesive energies based on the enthalpies of reactions (2) or (3).



The procedure was tested for 1-methylimidazolium ethanoate, [Hmim][O₂CCH₃], which is generally regarded as a low ionicity PIL. Indeed, due to the weak nature of its base (1-methylimidazole) and acid (ethanoic acid) precursors, the equilibrium in equation (1) is likely to be shifted to the left. Thus, albeit formally designated as 1-methylimidazolium ethanoate [3], the ionic species [Hmim]⁺ and [O₂CCH₃]⁻ are probably not dominant in this system. Such conclusion is, for example, supported by the low conductivity of [Hmim][O₂CCH₃] compared to highly ionic ILs [3]. 1-Methylimidazolium ethanoate was nevertheless selected for validation of the method because its vaporisation mechanism, involving the formation of 1-methylimidazole and ethanoic acid, had been unequivocally demonstrated by different experimental techniques and for different pressure ranges [20–22].

The above summarized studies are extended here to 1,1,3,3-tetramethylguanidinium nitrate, [Htmg][NO₃], along with a structural analysis performed by single crystal X-ray diffraction. In contrast with [Hmim][O₂CCH₃], this compound is expected to be considerably ionic, since it results from the reaction of a strong acid (HNO₃) with a superbase (1,1,3,3-tetramethylguanidine). The present investigation also required the determination of the standard molar enthalpies of formation and vaporisation of 1,1,3,3-tetramethylguanidine, opening the way for a future systematic thermochemical study of guanidinium-based protic ionic liquids.

2. Materials and methods

2.1. General

All materials were stored and handled under an oxygen and water free (<10 ppm) nitrogen atmosphere, inside a glove-box or using standard Schlenk techniques. Elemental analyses (C, H, and N) were performed on a CE-Instruments EA-1110 CHNS-O automatic analyser. The Fourier-transform infrared spectrum (FTIR) of [Htmg][NO₃] was obtained with a Bruker Tensor 27 spectrophotometer (4000 to 200) cm⁻¹ calibrated with 0.05 mm polystyrene film, with the samples mounted as Nujol mulls between CsI plates. X-ray powder diffraction analyses of [Htmg][NO₃] were carried out on a Philips PW1730 diffractometer, with automatic data acquisition (APD Philips v.35B), operating in the $\theta - 2\theta$ mode, using a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$), with the tube amperage set to 30 mA and the tube voltage to 40 kV. The apparatus was equipped with a vertical goniometer (PW1820), a proportional xenon detector (PW1711), and a graphite monochromator (PW1752). The diffractograms were recorded at room temperature by continuous scanning in the 2θ range 5° to 80°, with 2θ step sizes of 0.03° and a scan speed of 0.02° · min⁻¹. The sample was mounted on an aluminium sample holder sealed with a polyethylene film to prevent the absorption of water vapour from the atmosphere. The indexation of the powder pattern was performed using the program Checkcell [23]. The ¹H NMR spectra of tmg and of [Htmg][NO₃] were obtained in CDCl₃ at ambient temperature, on Bruker Ultrashield 400 MHz and Varian Oxford NMR 300 spectrometers, respectively. In the case of tmg the CDCl₃ (Aldrich, 99.96 at.% D, containing 0.03% (v/v) TMS) was stored over molecu-

lar sieves (Aldrich, 4 Å, 8–12 mesh, activated in vacuum at ~0.1 Pa and ~493 K during at least 6 h). In the analysis of [Htmg][NO₃] CDCl₃ (Aldrich, 99.8 at.% D) distilled over P₂O₅ was used. Karl-Fischer titration of tmg was carried out with a Methrom 831 KF coulometer. GC-MS analysis of tmg was performed on a Thermo-Finnigan Trace-DSQ GC/MS. A Thermo 5-ms column (5% phenyl polypherrylene-siloxane; 30 m × 0.25 mm ID, 0.25 μm film thickness) was used. The sample was dissolved in dichloromethane (Sigma-Aldrich, mass fraction > 0.99), and the injection volume was 1 μL. The carrier gas was helium maintained at a constant pressure of 3 kPa and with a flow rate of 20 mL · min⁻¹. A programmed temperature vaporisation injector with a septumless sampling head having a baffled liner (Gerstel) operating in the splitless mode was employed. The inlet temperature was set to 533 K, and the oven temperature was programmed as follows: 343 K for 2 min, ramp at 5 K · min⁻¹ to 443 K, and finally ramp to 573 at 20 K · min⁻¹. The transfer line, ion source, and quadrupole analyser were maintained at $T = (573, 523, \text{ and } 523) \text{ K}$, respectively. A solvent delay of 4 min was selected. Electron ionisation mass spectra in the range m/z 50 to m/z 500 were recorded in the full-scan mode, with 70 eV electron energy. Data recording and instrument control were performed by using the Xcalibur Data System. The identity of the analysed compound was assigned by comparison of the mass-spectrometric results with data in the NIST reference spectral databank.

2.2. Materials

Two samples of 1,1,3,3-tetramethylguanidine (Sigma-Aldrich) were used in this work. They were stored as received in Schlenk tubes over molecular sieves (Aldrich, 4 Å, 8–12 mesh, that were activated under a reduced pressure of ~0.1 Pa and ~493 K during at least 6 h). Sample 1 was used in the Calvet-drop microcalorimetry experiments, and sample 2 was used in the solution calorimetry experiments and in the synthesis of [Htmg][NO₃]. The water content determined from Karl Fisher titration was 20.8 ppm for sample 1 and 72.3 ppm for sample 2. The results of the ¹H NMR analysis (400 MHz, CDCl₃) were as follows: for sample 1, $\delta/\text{ppm} = 2.62$ (s, CH, 12H), 4.90 (s, NH, 1H); for sample 2, $\delta/\text{ppm} = 2.63$ (s, CH, 12H), 4.85 (s, NH, 1H). No impurities were detected in the GC-MS analysis of both samples.

The [Htmg][NO₃] sample was synthesized by adding 5.6 cm³ (81 mmol) of aqueous HNO₃ (Panreac, mass fraction 0.65, $d = 1.395 \text{ g} \cdot \text{cm}^{-3}$) to a magnetically stirred solution of 10 cm³ (80 mmol) of tmg (sample 2) in 16 cm³ of 1-butanol (Lab Scan Analytical Sciences, mass fraction 0.99). The reaction mixture was kept under N₂ atmosphere inside a Schlenk tube immersed in an ice bath. Stirring was continued for 1.5 h after addition, and the solvent was removed in vacuum (~1 Pa), at ambient temperature (~296 K), during ~12 h to yield a white solid. The obtained product was washed four times with ~10 cm³ of diisopropyl ether (Merck, mass fraction 0.99; previously dried over calcium chloride from Acrös Organics, mass fraction 0.96), dried under reduced pressure at ambient temperature for two days, and stored in an oxygen and water free (<10 ppm) nitrogen atmosphere, inside a glove-box. Elemental analysis for C₅H₁₄N₄O₃ (mass percentage): expected C 33.70%, H 7.92%, N 31.44%; found C 34.38 ± 0.68%, H 7.73 ± 0.42%, N 31.92 ± 0.24%, where the assigned uncertainties correspond to the standard errors of the mean of four determinations. FTIR (Nujol, CsI plates, main peaks): $\tilde{\nu}/\text{cm}^{-1} = 3330, 3142$ (CH₃ asymmetric stretching); 1667 (CN₂ asymmetric stretching); 1091 (CH₃ rocking); 1061 (CH₃ rocking + CN₃ symmetric stretching); 876, 723 (NH₂ rocking + NC asymmetric stretching). The absence of water in the sample was indicated by the lack of the typical H—O—H bending frequency at 1644 cm⁻¹. The ¹H NMR (300 MHz, CDCl₃) δ/ppm : 3.01 (s, CH₃, 12H), 7.86 (s, NH, 2H). The

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