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Sulfur-Containing Ionic Liquids. Rotating-Bomb Combustion Calorimetry and First-Principles Calculations for 1-Ethyl-3-methylimidazolium Thiocyanate

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The standard molar enthalpy of formation, $\Delta_f H_m°(l)$, of the ionic liquid 1-ethyl-3-methylimidazolium thiocyanate has been determined at $T = 298.15$ K by means of rotating-bomb combustion calorimetry. The enthalpy of formation of this ionic liquid in the gaseous phase, $\Delta_f H_m°(g)$, was obtained using the value $\Delta_f H_m°(l)$ and the enthalpy of vaporization of 1-ethyl-3-methylimidazolium thiocyanate available from the literature. *First-principles* calculations of the ionic pair of the ionic liquid 1-ethyl-3-methylimidazolium thiocyanate have been performed using the G3MP2 theory. Close agreement of the molar enthalpy of formation, $\Delta_f H_m°(g)$, from experiment and from the high-level first-principles method G3MP2 allows us to conclude that this method seems to be suitable for calculation of the thermodynamic properties of sulfur-containing ionic liquids in the gaseous phase.

1. Introduction

Sulfur-containing ionic liquids (ILs) are promising solvents for deep desulfurization of diesel fuels.[1] The thiocyanate ILs also have a high extraction efficiency for hexane/thiophene and hexane/benzene mixtures.[2] ILs are currently attracting considerable attention as potentially benign solvents for many areas such as fuel cells, rechargeable batteries, and "green solvents".[3] Here we present the first experimental study of the enthalpy of combustion and enthalpy of formation, $\Delta_f H_m°$, in the liquid as well as in the gaseous state of the ionic liquid 1-ethyl-3-methylimidazolium thiocyanate ([C_2mim][SCN]; see Figure 1) and compare the results to theoretical calculations. In previous work[4−6] we have successfully demonstrated the ability of the composite first-principles method G3MP2 to calculate the enthalpies of C-, H-, N-, and O-containing ILs. In this work we have tested this method using our own experimental results for $\Delta_f H_m°(l)$ from rotating-bomb combustion calorimetry and the molar enthalpy of vaporization of [C_2mim][SCN] available from ultra-high-vacuum mass spectrometric measurements.[7]

2. Experimental Procedure and Methods of First-Principles Calculations

2.1. Materials. The sample of 1-ethyl-3-methylimidazolium thiocyanate, $C_7H_{11}N_3S$, used in our experiments was of commercial origin (Sigma-Aldrich, 07424) with a purity better than 99 %. It contained less than 0.1 % water according to specifications stated by the suppliers. Prior to the experiments the IL sample was subjected to vacuum treatment at 330 K and 10^{-2} mbar for 15 h to reduce possible traces of solvents and moisture. A water mass fraction of $6.402 \cdot 10^{-4}$ was determined by Karl Fischer titration immediately before the combustion experiments were started, and an appropriate correction was applied to the results.

2.2. Thermochemical Measurements. Rotating-Bomb Combustion Calorimetry. For the measurement of the energies of combustion, a calorimetric system with a constant-temperature jacket and a rotating bomb was used. This system was originally developed by S. Sunner at the University of Lund, Sweden.[8] The device was manufactured in Lund in the 1970s, and after successful work at the University of Freiburg, Germany (Prof. C. Rüchardt and Dr. H.-D. Beckhaus), it was modified at the University of Rostock in our working group. We have improved the temperature maintenance and control unit and the ignition circuit and updated the data acquisition system. The principle construction of the calorimeter is shown in Figure 2. The isothermal jacket consists of a thermostated bath with a cavity of exactly the same shape as the calorimeter. Water in the jacket is stirred, and a pump circulates water through the thermostated lid. The water jacket is maintained at a constant temperature of $T = (298.150 \pm 0.003)$ K. The calorimeter can is suspended in the jacket well and consists of a stainless-steel vessel containing a weighted amount of water and a closely fitting cover, a stirrer of the water, an electric heater, and the mechanism for bomb rotation. The bomb can be rotated simultaneously axially and end-over-end. The calorimeter and the well in the thermostated bath are separated by a 1 cm air gap on all sides. The stainless-

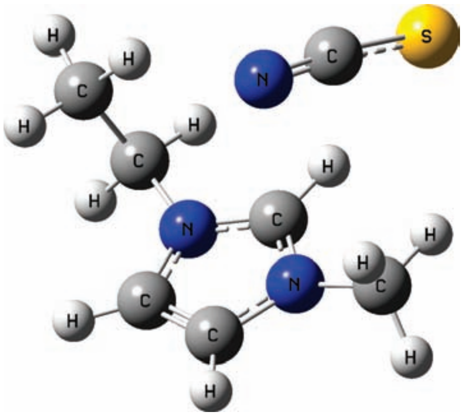

Figure 1. Structure of [C_2mim][SCN] and its most stable conformation.

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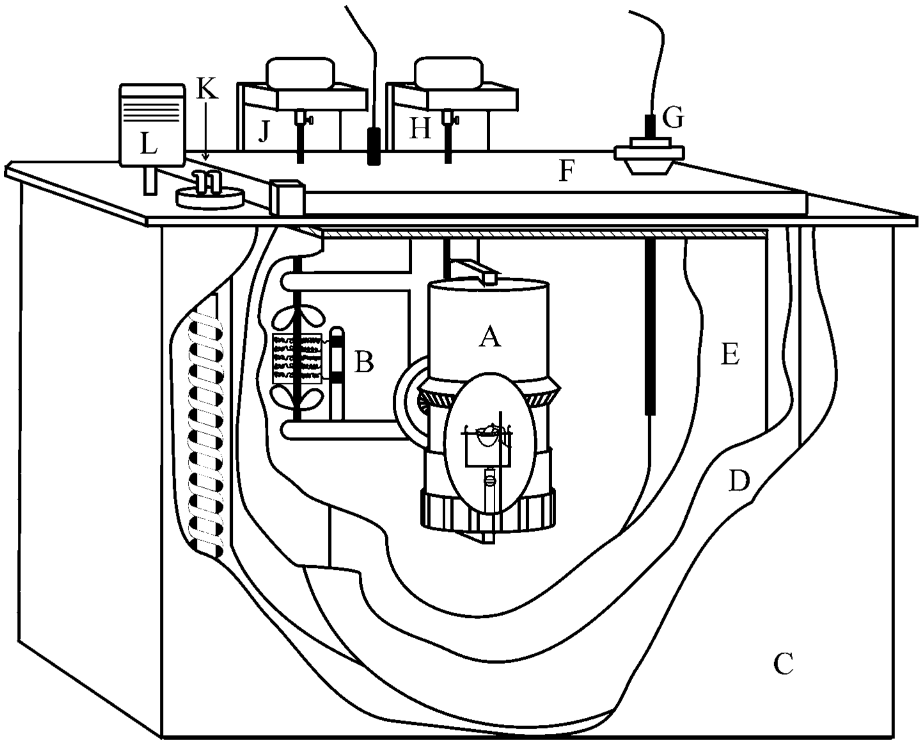

(A) Pt-lined stainless steel bomb with sample inside
(B) heater for the initial temperature adjustment
(C) thermostated container
(D) thermostat inner wall
(E) calorimeter vessel
(F) double-walled lid for circulation of thermostat water
(G) temperature sensor and the sleeve for it
(H) synchronous motor for bomb rotation
(J) synchronous motor for calorimeter stirrer
(K) heating-cooling unit for thermostat
(L) circulation pump for stirring in thermostat bath

Figure 2. Rotating-bomb combustion calorimeter.

steel combustion bomb has an internal volume of 0.2511 dm^3 and a wall thickness of ca. 1 cm. The bomb has a valve for charging it with oxygen, and the same valve serves also for discharging the bomb. The bomb is completely lined with platinum. All the internal fittings, electrodes, and crucible are fabricated from platinum. Calorimetric temperatures were measured to within $\pm 1 \cdot 10^{-5}$ K by means of a Hart Scientific 1006 Micro-Therm with a measuring time interval of 100 s. The electrical energy for ignition was assumed to be constant, and it was introduced into the calibration procedure. The bomb, which initially contains air at atmospheric pressure and 10 cm^3 of water, is assembled and charged with oxygen to a total pressure of $p = 3.0$ MPa at $T = 293.15$ K without previous flushing. This is the usual technique for the combustion experiments with compounds containing sulfur.[9]

Solid samples were pelleted before combustion. For mass determinations a Mettler AT-21 microbalance with a certified reproducibility $2 \cdot 10^{-6}$ g was used. A 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 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.[4]

The initial temperature of the combustion experiment was chosen to reach a final temperature close to $T = 298.15$ K. The energy of reaction was always referred to the final temperature, $T = 298.15$ K. Combustion is initiated by an electrical device connected to the computer which automatically fires the ignition circuit at the programmed time. The initial, main, and final periods were about 22 min. Rotation of the bomb was started 2 min after ignition and was ended after 12 min of rotation. The energy equivalent of the calorimeter, $\varepsilon_{calor} = (25045.6 \pm 1.6)$ $J \cdot K^{-1}$, was determined using benzoic acid (NIST standard reference sample 39j with the certified massic energy of combustion $\Delta_c u = (-26434 \pm 3)$ $J \cdot g^{-1}$) under the same conditions in which the experiments were done, with rotation and 10 cm^3 of water added to the bomb (see Table S1, Supporting Information).

After completion of the combustion experiments, the bomb was discharged and the liquid content of the bomb quantitatively transferred into a volumetric flask together with the rinsing water and diluted to a volume of 250 cm^3. An aliquot of 25 cm^3 of the bomb solution was boiled for 5 min to remove the dissolved carbon dioxide and the solution titrated with the 0.1 $mol \cdot dm^{-3}$ NaOH (aq) to determine the total amount of acid. The quantity of nitric acid was taken as the difference between the total acid and the theoretical quantity of sulfuric acid calculated from the mass of sample. The correction for the energy of formation of the nitric acid from $N_2(g)$, $O_2(g)$, and $H_2O(l)$ was based on the value of -59.7 $kJ \cdot mol^{-1}$ for the molar internal energy of formation of 0.1 $mol \cdot dm^{-3}$ $HNO_3(aq)$.[10] The combustion products were examined for carbon monoxide and SO_2 (Dräger tube, mass fraction sensitivity of $\sim 1 \cdot 10^{-6}$) and unburned carbon, but none was detected. Such experiments, where even small traces of soot were observed, were rejected. The sample masses were reduced to vacuum, using the densities of the sample and auxiliary compounds (Table S2, Supporting Information; ESI). The atomic weights used were those recommended by the IUPAC Commission in 2009.[11] For converting the energy of the actual combustion process to that of the isothermal process, and reducing to standard states, the conventional procedure was

Table 1. Results for Combustion Experiments at T = 298.15 K ($p°$ = 0.1 MPa) of Thianthrene[a]

m (substance)[b]/g	0.781187	0.742774	0.745597	0.767226	0.774701	0.76292	0.760138
m'(cotton)[b]/g	0.000802	0.000815	0.000821	0.000766	0.000782	0.0006	0.000671
ΔT_c[c]/K	1.045027	0.994336	0.998232	1.02675	1.035993	1.02076	1.016839
$\varepsilon_{calor}\cdot(-\Delta T_c)$/J	−26173.3	−24903.7	−25001.3	−25715.5	−25947	−25565.5	−25467.3
$\varepsilon_{cont}\cdot(-\Delta T_c)$/J	−52.79	−50.22	−50.44	−51.98	−52.23	−51.56	−51.47
$\Delta U_{decomp}(HNO_3)$/J	51.1	53.2	57.5	54.5	38.8	53.3	50.4
$\Delta U_{dil}(H_2SO_4)$/J	−3.24	−2.62	−2.66	−3.01	−3.13	−2.94	−2.90
ΔU_{corr}[d]/J	20.07	19.57	19.55	19.86	20.15	19.82	19.82
$-m'\cdot\Delta_c u'$/J	13.58	13.80	13.90	12.99	13.24	10.17	11.38
$\Delta_c u°(liq)/(J\cdot g^{-1})$	−33464.5	−33479.1	−33477.6	−33471.4	−33467.2	−33468.4	−33463.9
$\Delta_c u_{av}°(liq)/(J\cdot g^{-1})$				−33470.28 ± 2.3			

[a] For the definition of the symbols see ref 9. V(bomb) = 0.2511 dm^3, p^i(gas) = 3.00 MPa, and $m^i(H_2O)$ = 10.00 g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $\varepsilon_{cont}\cdot(-\Delta T_c) = \varepsilon^i_{cont}\cdot(T^i - 298.15\ K) + \varepsilon^f_{cont}\cdot(298.15\ K - T^f + \Delta T_{corr})$. [d] ΔU_{corr}, the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in ref 9. $\Delta_c u°$(polyethene) = (−46357.7 ± 3.5) J·g^{-1}.

Table 2. Results for Typical Combustion Experiments at T = 298.15 K ($p°$ = 0.1 MPa) of [C$_2$mim][SCN][a]

m (substance)[b]/g	0.443382	0.394665	0.376200	0.406405
m'(cotton)[b]/g	0.000756	0.000731	0.000821	0.000874
m''(polyethylene)[b]/g	0.283457	0.277799	0.285661	0.282033
ΔT_c[c]/K	1.046407	0.978968	0.971752	1.000881
$\varepsilon_{calor}\cdot(-\Delta T_c)$/J	−26207.6	−24518.6	−24337.8	−25067.4
$\varepsilon_{cont}\cdot(-\Delta T_c)$/J	−53.41	−49.86	−49.24	−50.70
$\Delta U_{decomp}(HNO_3)$/J	71.3	58.9	63.0	64.5
$\Delta U_{dil}(H_2SO_4)$/J	2.51	2.75	2.83	2.70
ΔU_{corr}[d]/J	24.27	23.32	23.30	23.66
$-m'\cdot\Delta_c u'$/J	12.82	12.39	13.90	14.80
$-m''\cdot\Delta_c u''$/J	13140.43	12878.11	13242.58	13074.38
$\Delta_c u°(liq)/(J\cdot g^{-1})$	−29380.2	−29400.5	−29387.5	−29400.7
$\Delta_c u_{av}°(liq)/(J\cdot g^{-1})$		−29392.2 ± 5.1		

[a] For the definition of the symbols see ref 9. V(bomb) = 0.2511 dm^3, p^i(gas) = 3.00 MPa, and $m^i(H_2O)$ = 10.00 g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $\varepsilon_{cont}\cdot(-\Delta T_c) = \varepsilon^i_{cont}\cdot(T^i - 298.15\ K) + \varepsilon^f_{cont}\cdot(298.15\ K - T^f + \Delta T_{corr})$. [d] ΔU_{corr}, the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in ref 9. $\Delta_c u°$(polyethene) = (−46357.7 ± 3.5) J·g^{-1}. Water content 640.3 ppm.

applied.[9] The physical properties of the compounds under study as well as the specific energies of combustion $\Delta_c u°$ of auxiliary compounds, are given in Table S2.

The total uncertainty of $\Delta_f H_m°$(l) was calculated according to the guidelines presented by Olofsson.[12] The uncertainty assigned to $\Delta_f H_m°$(l) is 2 times 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.

A second standard material is generally used in combustion calorimetry to verify the chemistry of the combustion process and to control the accuracy of the energy corrections involved in the data treatment. Thianthrene is commonly proposed as the reference material for combustion calorimetry of sulfur-containing compounds.[13] We used a sample of thianthrene (NIST standard reference sample SRM 1656) to check our experimental and calculation procedures. The results of the test combustion experiments are given in Table 1. The results for combustion experiments with [C$_2$MIM][SCN] are summarized in Table 2.

2.3. First-Principles Calculations. Standard ab initio molecular orbital calculations were performed using the Gaussian 03, revision B.04, program package.[14] Conformational analysis of the IL was performed using B3LYP/6-31+G(d,p) with the help of the procedure developed in our previous work.[4] The optimized structures and energies of the most stable conformer of the ionic pair were further obtained using the G3MP2 composite method.[15] The calculated values of the enthalpy of ion pairs are based on the electronic energy calculations obtained by the G3MP2 methods using standard procedures of statistical thermodynamics.[16]

3. Results and Discussion

3.1. Combustion Calorimetry. To test the procedure for the combustion experiments with sulfur-containing compounds, thianthrene was used as a reference material. The results of combustion with thianthrene are given in Table 1. They refer to the reaction

$$C_{12}H_8S_2(cr) + 17O_2(g) + 228H_2O(l) \rightleftarrows 12CO_2(g) + 2(H_2SO_4\cdot 115H_2O)(aq) \quad (1)$$

Our value for the massic energy of combustion, $\Delta_c u$ = (−33470.2 ± 2.3) J·g^{-1}, is in excellent agreement with the recommended value, $\Delta_c u$ = (−33468 ± 4.0) J·g^{-1}.[13] From these results, the standard molar energy and enthalpy of combustion and the standard molar enthalpy of formation of thianthrene in the condensed state were derived: $\Delta_c U_m°$(298.15 K) = (−7240.4 ± 1.6) kJ·mol^{-1}; $\Delta_c H_m°$(298.15 K) = (−7252.8 ± 1.6) kJ·mol^{-1}; $\Delta_f H_m°$(298.15 K) = (183.3 ± 2.2) kJ·mol^{-1}. The uncertainties of the standard molar energy and enthalpy of combustion are 2 times the overall standard deviation of the mean.[12] The values for the standard molar enthalpies of formation of H_2O(l) and CO_2(g) at T = 298.15 K, (−285.830 ± 0.042) kJ·mol^{-1} and (−393.51 ± 0.13) kJ·mol^{-1}, were taken as assigned by CODATA.[17] The value of the enthalpy of formation of the solution $H_2SO_4\cdot 115H_2O$, (−887.811 ± 0.042) kJ·mol^{-1}, was taken from ref 10.

In total, 17 combustion experiments with [C$_2$MIM][SCN] have been performed. However, the completeness of combustion was achieved only in the experiments which are summarized in Table 2. The calculation of the combustion energy was based on the reaction

$$C_7H_{11}N_3S(l) + 11.25O_2(g) + 110.5H_2O(l) \rightleftarrows 7CO_2(g) + 1.5N_2(g) + (H_2SO_4 \cdot 115H_2O)(aq) \quad (2)$$

and results for the standard molar energy of combustion, the standard molar enthalpy of combustion, and the standard molar enthalpy of formation are as follows: $\Delta_c U_m°(298.15\ K) = (-4974.6 \pm 2.1)\ kJ \cdot mol^{-1}$; $\Delta_c H_m°(298.15\ K) = (-4981.4 \pm 2.1)\ kJ \cdot mol^{-1}$; $\Delta_f H_m°(l,\ 298.15\ K) = (52.8 \pm 2.3)\ kJ \cdot mol^{-1}$.

Nowadays there are no literature data concerning the enthalpy of combustion for [C$_2$MIM][SCN]. Therefore, no direct comparison of the obtained experimental value can be carried out.

3.2. Quantum Chemical Calculations for $\Delta_f H_m°(g)$ of [C$_2$MIM][SCN]. The results of the molar enthalpy of formation, $\Delta_f H_m°(g)$, of [C$_2$MIM][SCN] obtained by using quantum chemical methods have not been reported in the literature so far. We have calculated the enthalpy of formation of [C$_2$MIM][SCN] using the G3MP2 method with the help of the atomization reaction (Table S3, Supporting Information). The enthalpy of formation of [C$_2$MIM][SCN] was found to be $\Delta_f H_m°(g,\ 298.15\ K) = (205.7 \pm 4.9)\ kJ \cdot mol^{-1}$ (see Table 3). This value agrees well with the experimental value:

$$\Delta_f H_m°(g) = \Delta_f H_m°(l) + \Delta_l^g H_m° = 52.8 + 151.0 = 203.8 \pm 3.1\ kJ \cdot mol^{-1} \quad (4)$$

where the standard molar enthalpy of formation of IL in the gaseous phase, $\Delta_f H_m°(g)$, has been obtained from rotating-bomb calorimetry combined with the molar enthalpy of vaporization, $\Delta_l^g H_m° = (151.0 \pm 2.0)\ kJ \cdot mol^{-1}$, measured by ultra-high-vacuum mass spectrometry reported recently.[7] Good agreement of the molar enthalpy of formation, $\Delta_f H_m°(g)$, from the experiment and from the high-level *first-principles* method G3MP2 has been observed (see Table 3). This enables us to conclude that this method seems to be suitable for calculating the thermochemical properties of the sulfur-containing ionic liquids in the gaseous phase.

Table 3. Thermochemical Data ($kJ \cdot mol^{-1}$) at $T = 298.15$ K ($p° = 0.1$ MPa) for [C$_2$mim][SCN]

$\Delta_c H_m°(l)$	$\Delta_f H_m°(l)$	$\Delta_l^g H_m°$ [a]	$\Delta_f H_m°(g)_{exptl}$	$\Delta_f H_m°(g)_{G3MP2}$
-4981.4 ± 2.1	52.8 ± 2.3	151.0 ± 2.0	203.8 ± 3.1	205.7 ± 4.9

[a] The value was taken from ref 7.

Supporting Information Available:

Results of the calibration of the combustion calorimeter with benzoic acid, properties of the substances obvious in combustion calorimetry, optimized geometry, and set of fundamentals. This material is available free of charge via the Internet at http://pubs.acs.org.

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