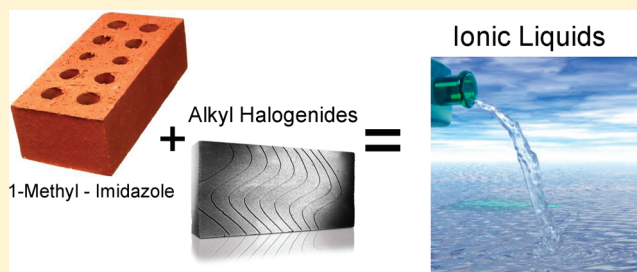


Thermodynamics of Ionic Liquids Precursors: 1-Methylimidazole

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S Supporting Information

ABSTRACT: The standard molar enthalpy of formation in the liquid state for 1-methylimidazole (MeIm) was obtained from combustion calorimetry. The enthalpy of vaporization of the compound was derived from the temperature dependence of the vapor pressure measured by the transpiration method. Additionally, the enthalpy of vaporization for MeIm was measured directly using Calvet-type calorimetry. In order to verify the experimental data, first-principles calculations of MeIm were performed. The enthalpy of formation evaluated at the G3MP2 level of theory is in excellent agreement with the experimental value. The heat capacity and parameters of fusion of MeIm were measured in the temperature range (5 to 370) K using adiabatic calorimetry. The thermodynamic functions for the compound in the crystal and liquid states were calculated from these data. Based on the experimental spectroscopic data and the results of quantum-chemical calculations, the ideal-gas properties for MeIm were calculated by methods of statistical thermodynamics.



1. INTRODUCTION

Alkylimidazoles are the building blocks for ionic liquids (ILs). ILs have gained large interest during the last years. They have no detectable vapor pressure at ambient temperatures, and therefore exhibit ideal systems which can be used as solvents for new catalytic reactions and other chemical production processes as well as separation processes referred to as “green chemistry.”¹ 1-Methylimidazole (MeIm) is one of the most often used precursors for the synthesis of ILs. However, thermodynamic data for this compound available in literature are insufficient. The available data on the enthalpies of vaporization are collected in Table 1, and they spread from 47 to 65 kJ·mol^{−1}. Two values of the standard molar enthalpy of formation $\Delta_f H_m^\circ$ (l) at $T = 298.15$ K reported in the literature^{2,3} differ by ca. 6 kJ·mol^{−1} (see Table 2). The heat capacity for the liquid MeIm was measured by DSC.² No thermodynamic data on crystalline MeIm or its enthalpy of fusion have been found. Thus, an additional study to provide a consistent data set for the MeIm is required.

In this work we report results of comprehensive study of thermodynamic properties for MeIm. The standard molar enthalpy of formation in the liquid state for MeIm was obtained from combustion calorimetry. The enthalpy of vaporization of the compound was derived from the temperature dependence of the vapor pressure measured by the transpiration method. Additionally, the enthalpy of vaporization for MeIm was measured directly using Calvet-type calorimetry. In order to verify the experimental data, first-principles calculations of MeIm were performed. The enthalpy of formation evaluated at the G3MP2 level of theory is in excellent agreement with

the experimental value. The heat capacity and parameters of fusion of MeIm were measured in the temperature range (5 to 370) K using adiabatic calorimetry. The thermodynamic functions for the compound in the crystal and liquid states were calculated from these data. Based on the experimental spectroscopic data and the results of quantum-chemical calculations, the ideal-gas properties for MeIm were calculated by methods of statistical thermodynamics.

2. EXPERIMENTAL SECTION

2.1. Materials. The samples of MeIm used for the combustion experiments, the vapor pressure measurements, and the vaporization enthalpy determinations were of commercial origin (Aldrich, with purity $\geq 99\%$). Prior to experiments the samples were purified by repeated vacuum distillation. The degree of purity of the samples was determined using a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 cm³·s^{−1}. A capillary column HP-5 (stationary phase cross-linked 5% phenyl methyl silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 mm. The standard temperature program of the GC was $T = 333.15$ K for 180 s followed by a heating rate of 0.167 K·s^{−1} to $T = 523.15$ K. No impurities

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Table 1. Compilation of Data on Enthalpies of Vaporization $\Delta_f^{\circ}H_m(298.15\text{ K})$ for MeIm

technique ^a	T range, K	$\Delta_f^{\circ}H_m(T_{av})$, ^b kJ·mol ^{−1}	$\Delta_f^{\circ}H_m(298.15\text{ K})$, kJ·mol ^{−1}	ref
DC	371	71.9	64.7 ± 1.3	2
C		-	47.2 ± 0.1	3
estimated		-	54.0	4
C	298	54.5	54.5 ± 0.5	5
GC			54.6 ± 1.9	6
C	305.2	55.2	55.6 ± 0.6	this work
T	278.5–318.3	55.2	55.2 ± 0.5	this work
			55.0 ± 0.3	average

^a DC = drop microcalorimetry; C = calorimetry; T = transpiration; GC = gas-chromatography correlation. ^b Enthalpy of vaporization at the average temperature of measurements.

Table 2. Thermochemical Results for MeIm at $T = 298.15\text{ K}$ ($p^{\circ} = 0.1\text{ MPa}$), kJ·mol^{−1}

$\Delta_f^{\circ}H_m(l)$	$\Delta_f^{\circ}H_m$	$\Delta_f^{\circ}H_m(g)$ experiment	$\Delta_f^{\circ}H_m(g)$ (G3MP2)
73.1 ± 3.8 [2]			
66.9 ± 0.6 [3]			
70.7 ± 1.1 [this work]	55.0 ± 0.3	125.7 ± 1.1	126.0

(greater than mass fraction 0.001) could be detected in the samples used for the thermochemical measurements. Water content in these samples was determined either by Karl Fischer titration or using a gas chromatograph equipped with a katharometer.

For adiabatic calorimetry measurements a commercial sample of MeIm from Fluka (with purity according to certificate >0.99%) was used without further purification. The mole-fraction purity of this sample was determined by the fractional melting technique in an adiabatic calorimeter to be 0.9975.

2.2. Combustion Calorimetry. The enthalpy of combustion of MeIm was measured in two laboratories. In Rostock, for measurements of the enthalpy of combustion of MeIm an isoperibol calorimeter with a static bomb ($V = 320\text{ cm}^3$) and a stirred water bath was used. The samples were placed (under an inert atmosphere in a glovebox) in polyethylene ampules and burned in oxygen at 3.04 MPa pressure. The detailed procedure has been described previously.^{7,8} The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter $\varepsilon_{\text{calor}} = (14807.1 \pm 2.1)\text{ J} \cdot \text{K}^{-1}$ was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). The working procedure has been tested with combustion experiments on further two reference materials – nicotinic acid and 3-methoxy benzoic acid successfully.

In Minsk, the enthalpy of combustion for MeIm was obtained in the homemade isoperibol calorimeter with a static bomb ($V = 95.6\text{ cm}^3$) and an air bath. The calorimetric container was equipped with a vacuum shell.⁹ The energy equivalent of the calorimeter $\varepsilon_{\text{calor}} = (9826.4 \pm 2.9)\text{ J} \cdot \text{K}^{-1}$ was obtained in a series of 16 calorimetric experiments with benzoic acid (K-2 grade, mass-fraction purity of 0.99993) having a certified value of the combustion energy under standard conditions, $\Delta_c u^{\circ}(\text{cr}, 298.15\text{ K}) = -(26414 \pm 5)\text{ J} \cdot \text{g}^{-1}$ for mass in vacuum. The combustion of MeIm was carried out in the polyethylene bags.

For the reduction of the data to standard conditions, conventional procedures¹⁰ were used. Corrections for nitric acid formation were based on titration with $0.1\text{ mol} \cdot \text{dm}^{-3}$ NaOH (aq). We used the

value $-59.7\text{ kJ} \cdot \text{mol}^{-1}$ for the molar energy of formation of $0.1\text{ mol} \cdot \text{dm}^{-3}$ HNO_3 from N_2 , O_2 , and H_2O (l).¹¹ The auxiliary quantities required for the data treatment are listed in Table S1 (Supporting Information).

2.3. Vapor Pressures and Enthalpy of Vaporization from the Transpiration Method. Vapor pressures were determined using the method of transpiration in a saturated nitrogen stream,^{12,13} and enthalpy of vaporization of MeIm was obtained from the temperature dependence of saturated vapor pressure. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with diameter of 1 mm provide surface which was sufficient for the vapor–liquid equilibration. At constant temperature ($\pm 0.1\text{ K}$), a nitrogen stream was passed through the U-tube, and the transported amount of gaseous material was collected in a cooling trap. The mass of compound collected within a certain time interval was determined by dissolving it in a suitable solvent with certain amount of external standard (undecane). This solution was analyzed using a gas chromatograph equipped with autosampler. Uncertainty of the sample amount determined by GC analysis was assessed to be within (1 to 3)%. The peak area of the compound related to the peak of the external standard ($n\text{-C}_{11}\text{H}_{24}$) is a direct measure of the mass of the compound condensed into the cooling trap, provided that a calibration of the system has been made. The saturation 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 that Dalton law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated

$$p_i^{\text{sat}} = m_i \cdot R \cdot T_a / V \cdot M_i; V = V_{\text{N}_2} + V_i; (V_{\text{N}_2} \gg V_i) \quad (1)$$

where $R = 8.314472\text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N_2} is the volume of transporting gas, and T_a is the temperature of the soap bubble meter. The volume of transporting gas V_{N_2} was determined from the flow rate and time measurements. Data of p_i^{sat} were obtained as a function of temperature and fitted using following equation¹²

$$R \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_f^{\circ}C_{p,m} \cdot \ln\left(\frac{T}{T_0}\right) \quad (2)$$

where a and b are adjustable parameters, and $\Delta_f^{\circ}C_{p,m}$ is the difference of the molar heat capacities of the gaseous and the liquid phases. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from eq 2 the expression for the vaporization enthalpy at

Table 3. Results from Measurements of the Vapor Pressure p^{sat} Using the Transpiration Method

$T, ^\circ\text{K}$	$m, ^b\text{mg}$	$V_{(\text{N}_2)}, ^c\text{dm}^3$	gas-flow, dm^3/h	$p^{\text{sat}}, ^d\text{Pa}$	$(p_{\text{exp}} - p_{\text{calc}}), \text{Pa}$	$\Delta_f^{\text{g}}H_m, \text{kJ}\cdot\text{mol}^{-1}$
$\Delta_f^{\text{g}}H_m^{\text{c}}(298.15\text{ K}) = 55.15 \pm 0.46 \text{ kJ}\cdot\text{mol}^{-1}$						
$\ln(p/\text{Pa}) = (279.41/R) - (73631.93/(R \cdot (T/\text{K}))) - (62.0/R)(\ln((T/\text{K})/298.15))$						
278.5	1.89	5.65	3.00	10.35	0.3	56.37
281.5	1.60	3.76	3.01	13.02	0.0	56.18
284.5	1.69	3.01	3.01	17.12	0.3	56.00
285.2	1.75	3.00	3.00	17.49	−0.3	55.95
287.4	1.79	2.55	3.06	21.30	−0.1	55.82
290.3	1.53	1.78	3.06	26.00	−1.0	55.64
293.3	1.82	1.63	3.06	33.77	−0.3	55.45
296.3	2.04	1.43	3.06	43.06	0.1	55.26
298.3	1.72	1.04	3.13	49.58	−0.3	55.14
299.4	1.49	0.820	3.28	54.88	0.7	55.07
302.4	1.83	0.820	3.28	67.31	−0.1	54.89
303.3	1.91	0.784	3.13	73.35	1.4	54.83
306.2	2.46	0.820	3.28	90.04	1.7	54.65
308.3	2.61	0.784	3.13	99.91	−2.3	54.52
309.2	2.95	0.814	3.25	109.1	0.4	54.46
312.3	3.63	0.814	3.25	134.2	0.0	54.27
313.3	3.79	0.784	3.13	145.3	1.8	54.21
315.3	4.42	0.814	3.25	163.1	−0.5	54.09
318.3	5.37	0.814	3.25	197.9	−0.8	53.90

^a Temperature of saturation. ^b Mass of transferred sample condensed at $T = 243.15\text{ K}$. ^c Volume of nitrogen, used to transfer mass m of sample. ^d Vapor pressure at temperature T . Calculated from m and the residual vapor pressure at the cooling temperature $T = 243.15\text{ K}$.

Table 4. Results of Calorimetric Determination of MeIm Vaporization Enthalpy

m, g	T, K	$(\int_{\tau=0}^{\tau} \Delta E \cdot d\tau), \text{V}\cdot\text{s}$	$\Delta H, \text{J}$	$(\Delta_f^{\text{g}}H_m), ^a\text{kJ}\cdot\text{mol}^{-1}$
0.08987	304.85	11.69	61.53	55.47
0.04159	305.65	5.320	28.00	54.53
0.11075	305.25	14.22	74.86	54.74
0.12465	305.10	16.34	86.01	55.90
average:	305.2			55.2 ± 0.6

$$\Delta_f^{\text{g}}H_m^{\text{c}}(298.15\text{ K}) = 55.6 \pm 0.6 \text{ kJ}\cdot\text{mol}^{-1}$$

^a Water content in the sample 3750 ppm was determined by gas chromatography. The enthalpy of vaporization was corrected using $\Delta_f^{\text{g}}H_m^{\text{c}}(\text{H}_2\text{O}; 298.15\text{ K}) = 44.0 \text{ kJ}\cdot\text{mol}^{-1}$.²⁰

temperature T is derived

$$\Delta_f^{\text{g}}H_m(T) = -b + \Delta_f^{\text{g}}C_{p,m} \cdot T \quad (3)$$

The value of $\Delta_f^{\text{g}}C_{p,m} = -62 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was calculated using the heat capacities of gas and liquid at $T = 298.15\text{ K}$ obtained in this work. The uncertainties in the enthalpies of vaporization were calculated as twice the standard deviation. The uncertainties in values of $\Delta_f^{\text{g}}C_{p,m}$ were not taken into account. We have checked experimental and calculation procedure with measurements of vapor pressures of n-alkanols.¹² It turned out that vapor pressures derived from the transpiration method were reliable within (1 to 3)%, and their accuracy was governed by reproducibility of the GC analysis.

2.4. Direct Measurements of Vaporization Enthalpy Using Calorimetry. For direct determination of the enthalpy of vaporization for MeIm a differential Calvet type microcalorimeter MID–200

was used. The instrument and the used technique was described in refs 14 and 15. The sample of MeIm was placed into the hermetic cell made of the stainless steel and covered with the nickel foil. After preliminary thermostating of the cell, the foil was punctured with a special rod, and the thermal flow caused by the evaporation of the sample was recorded. The calorimeter was calibrated by experiments with standard reference samples of naphthalene and n-undecane. The uncertainty of measurements of the enthalpies of vaporization was estimated to be within $\pm 1\%$.

The molar enthalpy of vaporization was obtained according to the equation

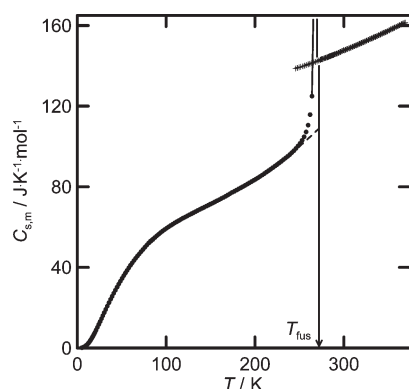
$$\Delta_f^{\text{g}}H_m = K^{-1} \cdot M \cdot m^{-1} \cdot \int_{\tau=0}^{\tau} \Delta E \cdot d\tau \quad (4)$$

where m is the mass of the sample corrected for buoyancy; $K = (190.0 \pm 1.1) \text{ mV}\cdot\text{s}\cdot\text{J}^{-1}$ is the calorimetric constant of the cell; ΔE is the difference of the potentials of thermocouples, which corresponds to the temperature imbalance between the cell and the thermostat of the calorimeter at the time τ ; $\int_{\tau=0}^{\tau} \Delta E \cdot d\tau$ is the total signal value recorded during the experiment; M is the molar mass of MeIm.

2.5. Adiabatic Calorimetry. Heat capacity of MeIm under saturated vapor pressure (C_s) in the temperature range from 5 to 370 K and its fusion enthalpy were determined in a TAU-10 adiabatic calorimeter (Termis, Moscow). The apparatus and experimental procedures were described elsewhere.¹⁶ The uncertainty of the heat capacity measurements did not exceed $\pm 4 \times 10^{-3} C_s$ in the main temperature interval of measurements above 20 K. The sample was loaded into the calorimetric container in a glovebox. The mass of the sample corrected for the buoyancy was 0.7806 g. Since the saturated vapor pressure of the compound under study is about

Table 5. Results of Calculation of the Standard Enthalpy of Formation $\Delta_f H_m^\circ(g)$ for Imidazole Derivates and Pyrazole in the Gas Phase at 298.15 K in $\text{kJ} \cdot \text{mol}^{-1}$

compounds	bond separation		$\Delta_f H_m^\circ(g)$ G3MP2	$\Delta_f H_m^\circ(g)$ experiment
	(6)	(7)		
1	2	3	4	5
imidazole	133.5	---	133.5	132.9 ± 0.6 [21]
pyrazole	179.5	---	179.5	179.4 ± 0.8 [21]
1-methylimidazole	126.3	125.7	126.0 ^a	125.7 ± 1.1 this work
2-methylimidazole	91.3	90.7	91.0 ^a	89.8 ± 1.1 [22]
2-ethylimidazole	71.3	70.7	71.0 ^a	68.3 ± 1.3 [22]

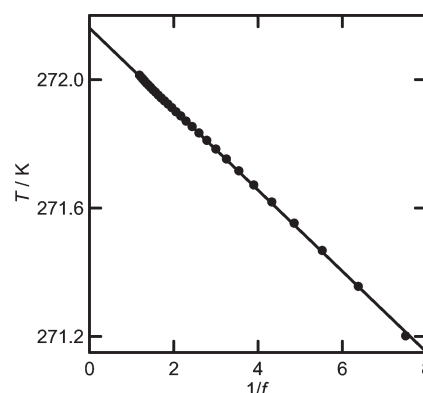
^a Average of values from columns 2 and 3.**Figure 1.** Experimental heat capacities of MeIm in the crystal (●) and liquid (+) states.

$P = 3$ kPa at $T = 370$ K, the correction for the vaporization of the sample was negligibly small compared to the uncertainty of the obtained values and was ignored.

2.6. Computations. Standard first-principles molecular orbital calculations were performed with the Gaussian 03 Rev.04 series of programs.¹⁷ Energies were obtained at the G3MP2 level of theory. G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second row of the periodic chart based on *ab initio* molecular orbital theory. A modification of G3 theory that uses reduced orders of Møller–Plesset perturbation theory is G3(MP2) theory.¹⁸ For all the species included in this study, full geometry optimizations were carried out at the HF/6-31G(d) level. All the minima found at the HF/6-31G(d) level were again fully reoptimized at the MP2(full)/6-31G(d) level. The 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), QCISD(T), and MP2/GTMP2 Large levels of theory (for details see ref 18). The enthalpy value of studied compound at $T = 298$ K was evaluated using the Gaussian software.¹⁷ The molecular parameters required for the statistical thermodynamic calculations were obtained from the geometry of MeIm optimized at the B3LYP/6-31+G(2df,p) theory level. The basic procedures of the statistical thermodynamic calculations were described in ref 19.

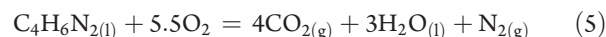
3. RESULTS AND DISCUSSION

Considerable activity has taken place with respect to the thermochemical properties measurements on the MeIm. However, the

**Figure 2.** Fractional melting results for MeIm.

mutual consistency of the data sets available from the literature (see Tables 1 and 2) is less than desired. Additional thermodynamic studies performed in this work should help us to provide a consistent data set for MeIm.

3.1. Enthalpy of Formation in the Liquid State. Results of combustion experiments on MeIm performed in Rostock (see Table S2) and in Minsk (see Table S3) were indistinguishable within the boundaries of their experimental uncertainties, and they were treated together and summarized in Table 2. The value of the standard specific energy of combustion $\Delta_c u^\circ = -(30461 \pm 12)$ $\text{J} \cdot \text{g}^{-1}$ was used to derive the standard molar enthalpy of combustion $\Delta_c H_m^\circ = -(2502.2 \pm 1.0)$ $\text{kJ} \cdot \text{mol}^{-1}$ and the standard molar enthalpy of formation in the liquid state $\Delta_f H_m^\circ(l) = (70.7 \pm 1.1)$ $\text{kJ} \cdot \text{mol}^{-1}$ based on the reaction



The value of the standard molar enthalpy of formation of the compound under study has been obtained from the enthalpic balance for reaction 5 according to the Hess's law using the molar enthalpies of formation of $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ as assigned by CODATA.²⁰ The uncertainties assigned to $\Delta_f H_m^\circ$ are twice the overall standard deviation of the mean and include 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 .

Previous determinations of the standard molar enthalpy of formation $\Delta_f H_m^\circ(l)$ of MeIm were reported by Mo et al.² and Kostikova et al.³ from combustion calorimetry. It should be mentioned that no experimental details were reported in ref 3. Our result

Table 6. Determination of Enthalpy of Fusion for MeIm

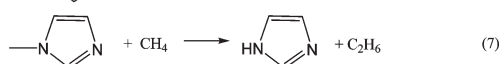
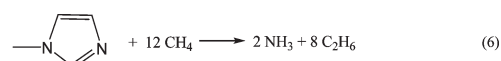
T_i , K	T_f , K	Q , $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{T_i}^{T_f} H_m(\text{cr})$, $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{T_{\text{fus}}}^{T_f} H_m(1)$, $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{cr}}^1 H_m^{\circ}(T_{\text{fus}})$, $\text{kJ} \cdot \text{mol}^{-1}$
240.00	273.10	15.54	3.30	0.13	12.11
240.00	272.83	15.50	3.30	0.09	12.11
240.00	272.75	15.46	3.30	0.08	12.08
240.00	273.67	15.63	3.30	0.21	12.12
240.00	274.82	15.81	3.30	0.38	12.13
240.00	280.80	16.68	3.30	1.24	12.14
average:					12.11 ± 0.02

$\Delta_f H_m^{\circ}(1) = (70.7 \pm 1.1) \text{ kJ} \cdot \text{mol}^{-1}$ is in agreement within the boundaries of experimental uncertainties with those $\Delta_f H_m^{\circ}(1) = (73.3 \pm 3.8) \text{ kJ} \cdot \text{mol}^{-1}$ reported by Mo et al.;² however, our new result is substantially more reliable because it was obtained in two laboratories independently as well as our result is more accurate.

3.2. Thermodynamics of Vaporization. The extended vapor pressures measurements on MeIm were performed in this work in the temperature range possibly close to the reference temperature $T = 298.15 \text{ K}$ (Table 3). The standard molar enthalpy of vaporization $\Delta_f^{\circ} H_m^{\circ}(298.15 \text{ K}) = (55.2 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$ for this compound was obtained from the temperature dependence of the vapor pressure. This value is in very good agreement with the direct calorimetric result $(55.6 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$ measured in this work (Table 4) as well as with another calorimetric result $(54.5 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$ reported by Catalan et al.⁵ The latter three values were selected, and the weighted average value $\Delta_f^{\circ} H_m^{\circ}(298.15 \text{ K}) = (55.0 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$ could be recommended for further calculations. This value also fulfills an expectation suggested by semiempirical estimation in ref 4 and the recent GC-correlation study by Lipkind et al.⁶ (see Table 1).

3.3. Enthalpy of Formation in the Gaseous State. The recommended vaporization enthalpy of MeIm combined with the results from our combustion experiments has provided the value of the standard enthalpy of formation of MeIm in the gas state, $\Delta_f H_m^{\circ}(g) = (125.7 \pm 1.1) \text{ kJ} \cdot \text{mol}^{-1}$ at $T = 298.15 \text{ K}$. This experimental value can now be compared with the results from quantum chemical calculations.

We calculated the total energies E_0 at $T = 0 \text{ K}$ and enthalpies H_{298} at $T = 298.15 \text{ K}$ (Table S4, Supporting Information). In this work we applied the following bond separation reactions for calculation enthalpy of formation of MeIm and the parent 2-methylimidazole (these species are isomeric and the same bond separation reactions 6 and 7 can be used for both)



The results of calculations are given in Table 5. To check the validity of the G3MP2 method for imidazoles we additionally calculated enthalpies of formation of the four similar heterocyclic compounds (imidazole, 2-methylimidazole, pyrazole, and 2-ethylimidazole) where recent experimental data (Table 5) were available.^{21,22} For these compounds the G3MP2 composition method with reactions listed in the Supporting Information is able to predict their enthalpies of formation as well as for MeIm within the experimental uncertainties of $1\text{--}3 \text{ kJ} \cdot \text{mol}^{-1}$ (Table 5). Thus, the results of first principles calculations helped us to establish thermodynamic consistency of the experimental result from the transpiration, the vaporization

calorimetry, and from the combustion calorimetry. The G3MP2 method combined with the both bond separation reactions 6 and 7 could be recommended for reliable calculations of $\Delta_f H_m^{\circ}(g, 298 \text{ K})$ of another parent alkylimidazoles and alkylpyrazoles widely used as precursors for IL synthesis.

3.4. Heat Capacity and Parameters of Fusion. The experimental heat capacities for MeIm are presented in Figure 1 and in Table S5 (Supporting Information) When cooling the sample from 370 K, the spontaneous crystallization of the supercooled liquid began at only about 240 K. This allowed us to measure heat capacity of liquid MeIm above 245 K. The heat capacities of liquid MeIm reported in ref 2 are (21 to 25)% higher than those obtained here.

When crystallization began the sample temperature was allowed to rise to about (1 to 3) K below the temperature of fusion. The sample was kept at those temperatures for at least 3 h before the measurements of the crystalline phase. Then, the sample was cooled to the required temperature.

The triple-point temperature $T_{\text{fus}} = 272.16 \pm 0.01 \text{ K}$ was determined by the fractional melting method (Figure 2). The results were fitted by the van't Hoff equation

$$T_{\text{fus}} - T = \frac{RT_{\text{fus}}^2(1-x)}{\Delta_{\text{cr}}^1 H_m^{\circ}} \frac{1}{f} \quad (8)$$

where f is a fraction melted at temperature T , x is a mole fraction of the main component in a sample, and $\Delta_{\text{cr}}^1 H_m^{\circ}$ is a standard molar enthalpy of fusion for a pure compound. The enthalpy of fusion $\Delta_{\text{cr}}^1 H_m^{\circ} = 12.11 \pm 0.02 \text{ kJ} \cdot \text{mol}^{-1}$ was determined from a series of six experiments (Table 6). The following equation was used to calculate $\Delta_{\text{cr}}^1 H_m^{\circ}$

$$\begin{aligned} \Delta_{\text{cr}}^1 H_m^{\circ} &= Q - \Delta_{T_i}^{T_{\text{fus}}} H_m(\text{cr}) - \Delta_{T_{\text{fus}}}^{T_f} H_m(1) \\ &= Q - \int_{T_i}^{T_{\text{fus}}} C_{p,m}(\text{cr}) dT - \int_{T_{\text{fus}}}^{T_f} C_{p,m}(1) dT \end{aligned} \quad (9)$$

where Q is the energy needed to heat 1 mol of MeIm from T_i to T_f . The initial T_i and final T_f temperatures lay outside the premelting region. In all the experiments, T_i was assumed to be equal to 240.00 K, and the values of Q and $\Delta_{T_i}^{T_{\text{fus}}} H_m(\text{cr})$ were adjusted to this temperature using the experimental heat capacities. The heat capacities of the crystalline $C_{p,m}(\text{cr})$ and liquid $C_{p,m}(1)$ compound were calculated from the following equations

$$\begin{aligned} C_{p,m}(\text{cr}) / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} &= \\ 72.76 - 0.1662(T/\text{K}) + 11.01 \cdot 10^{-4}(T/\text{K})^2 \end{aligned} \quad (10)$$

$$\begin{aligned} C_{p,m}(1) / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} &= 136.6 - 0.1675(T/\text{K}) \\ &+ 8.692 \cdot 10^{-4}(T/\text{K})^2 - 6.313 \cdot 10^{-7}(T/\text{K})^3 \end{aligned} \quad (11)$$

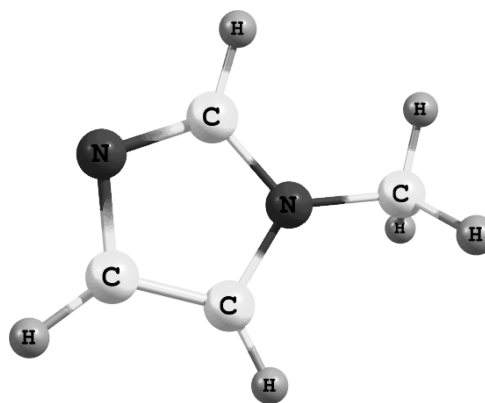
Table 7. Molar Thermodynamic Functions of MeIm in the Condensed State

T, K	$C_{p,m}^{\circ}$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	S_m° $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_0^T H_m^{\circ}/T$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Phi_m^{\circ,a}$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Crystal				
0	0	0	.	.
5	0.158 ^b	0.053	0.040	0.013
10	1.256	0.421	0.316	0.105
15	3.923	1.382	1.031	0.351
20	7.855	3.026	2.225	0.801
25	12.43	5.264	3.803	1.461
30	17.21	7.952	5.639	2.314
35	21.89	10.96	7.628	3.331
40	26.29	14.17	9.689	4.484
45	30.41	17.51	11.76	5.745
50	34.25	20.91	13.82	7.091
60	41.10	27.78	17.81	9.967
70	46.93	34.57	21.57	13.00
80	51.84	41.16	25.05	16.11
90	55.92	47.51	28.26	19.25
100	59.29	53.58	31.20	22.38
110	62.15	59.37	33.89	25.48
120	64.66	64.89	36.35	28.54
130	66.98	70.16	38.62	31.54
140	69.22	75.20	40.73	34.48
150	71.44	80.06	42.70	37.36
160	73.71	84.74	44.57	40.17
170	76.08	89.28	46.35	42.93
180	78.51	93.69	48.07	45.63
190	81.01	98.01	49.74	48.27
200	83.60	102.2	51.36	50.86
210	86.39	106.4	52.96	53.41
220	89.46	110.5	54.55	55.91
230	92.75	114.5	56.14	58.37
240	96.27	118.5	57.74	60.79
250	100.0 ^b	122.5	59.35	63.18
260	103.9 ^b	126.5	60.99	65.54
270	108.1 ^b	130.5	62.66	67.87
272.16	109.1 ^b	131.4	63.02	68.37
Supercooled Liquid				
250	139.2	163.9	104.6	59.4
260	140.8	169.4	105.9	63.5
270	142.4	174.8	107.3	67.5
Liquid				
272.16	142.7	175.9	107.5	68.4
280	144.0	180.0	108.5	71.4
290	145.8	185.1	109.8	75.3
298.15	147.2	189.1	110.8	78.3
300	147.6	190.0	111.0	79.0
310	149.5	194.9	112.2	82.7
320	151.4	199.7	113.4	86.3
330	153.3	204.4	114.6	89.8
340	155.4	209.0	115.8	93.2
350	157.4	213.5	116.9	96.6
360	159.5	218.0	118.1	99.9
370	161.7 ^b	222.4	119.2	103.1

^a $\Phi_m^{\circ} = -((C_m^{\circ}(T) - H_m^{\circ}(0))/T) = S_m^{\circ} - ((\Delta_0^T H_m^{\circ})/T)$. ^b Extrapolated values.

These equations were derived from the experimental heat capacities in the temperature ranges (201 to 239) K and (246 to 369) K, respectively.

3.5. Thermodynamic Properties in the Crystal and Liquid States. For calculation of entropy and enthalpy of the phases the experimental heat capacities have to be extrapolated below $T = 5$ K. The extrapolation was performed by the Debye function for three

**Figure 3. Geometry of MeIm molecule.****Table 8. Vibrational Wavenumbers of MeIm**

$w_{\text{exp}},^a \text{cm}^{-1}$		$w_{\text{calc}}, \text{cm}^{-1}$	IR intensity, $\text{km} \cdot \text{mol}^{-1}$	selected w, cm^{-1}
ref 24	ref 23			
		76	0.1	
	214 ^b	209	0.8	214
	352 ^b	349	0.6	352
609	610	626	5.9	609
659	659	676	15.3	659
		676	3.9	659
719	718	729	32.7	719
806	805	818	37.0	806
849	849	871	2.7	849
902	903	916	8.8	902
1027	1027	1042	8.3	1027
1062	1062	1074	11.6	1062
1076	1075	1096	11.7	1076
1102/1120	1110 ^c	1138	18.8	1110
		1149	0.2	1126
1233	1232	1265	19.2	1233
1286	1286	1306	23.5	1286
	1336 ^c	1374	3.0	1336
1357	1357	1383	1.1	1357
1424	1423	1453	19.0	1424
	1451	1486	9.0	1451
	1463	1509	7.8	1463
1512	1512	1534	35.1	1512
		1537	32.3	1512
2915	2914	3024	51.0	2915
2957	2958	3079	16.3	2957
	3011	3115	8.7	3011
	3113 ^d	3223	2.7	3111
		3228	3.2	3116
3155	3155	3252	2.3	3155

^a IR gas-phase frequencies unless otherwise noted. ^b In cyclohexane solution. ^c In CS₂ solution. ^d In CCl₄ solution.

degrees of freedom. The characteristic temperature $\theta_D = 115.4$ K was determined by the least-squares fit of the experimental heat capacities in the temperature range (5.6 to 10.5) K. The smoothed

Table 9. Thermodynamic Properties of MeIm in the Ideal-Gas State

<i>T</i> , K	<i>C</i> _{p,mv} ^o , J·K ^{−1} ·mol ^{−1}	<i>S</i> _m ^o , J·K ^{−1} ·mol ^{−1}	$\Delta_0^T H_m^o/T$, J·K ^{−1} ·mol ^{−1}	Φ_m^o , ^a J·K ^{−1} ·mol ^{−1}	$\Delta_f H_m^o$, kJ·mol ^{−1}	$\Delta_f G_m^o$, kJ·mol ^{−1}
0	0	0	0	0	147.7	147.7
100	45.9	245.0	39.4	205.6	139.5	161.6
150	51.9	264.7	42.5	222.1	136.0	173.4
200	60.8	280.8	45.9	234.8	132.4	186.4
298.15	85.1	309.4	54.7	254.7	125.7	214.3
400	112.6	338.2	65.9	272.3	119.8	245.6
500	136.6	366.0	77.7	288.3	115.3	277.6
600	156.5	392.8	89.3	303.5	111.9	310.3
700	172.8	418.1	100.1	318.1	109.4	343.6
800	186.3	442.1	110.0	332.1	107.7	377.4
900	197.6	464.7	119.2	345.6	106.7	411.0
1000	207.2	486.1	127.5	358.6	106.2	444.8

$$^a \Phi_m^o = -((C_m^o(T) - H_m^o(0))/T) = S_m^o - ((\Delta_0^T H_m^o)/T).$$

values of the heat capacity and the derived thermodynamic functions are presented in Table 7. The standard thermodynamic functions of liquid MeIm at *T* = 298.15 K are as follows

$$\begin{aligned} C_{p,m}^o &= (147.2 \pm 0.6) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}, \\ S_m^o &= (189.1 \pm 0.8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ \Delta_0^T H_m^o/T &= (110.8 \pm 0.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}, \\ \Phi_m^o &= (78.3 \pm 0.9) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

3.6. Ideal-Gas Thermodynamic Properties. The results obtained in this work made it possible to calculate the standard molar ideal-gas entropy *S*_m^o(*g*; *T*) for the studied compound according to the equation

$$S_m^o(g; T) = S_m^o(l; T) + \frac{\Delta_f^g H_m^o(T)}{T} + R \ln \frac{p^{\text{sat}}(T)}{p^o} \quad (12)$$

where *p*^o = 1 bar. The resulting value at *T* = 298.15 K is *S*_m^o(*g*) = 310.3 ± 1.3 J·K^{−1}·mol^{−1}.

Thermodynamic properties of MeIm, including entropy, in a wide temperature range can also be calculated by the method of statistical thermodynamics. In this method, the property (for example, entropy *S*(*g*; *T*, *P*)) is represented as a sum of translational *S*_{tr}(*T*, *P*), rotational *S*_{rot}(*T*), vibrational *S*_{vib}(*T*), and conformational *S*_{conf}(*T*) contributions

$$S(g; T, P) = S_{tr}(T, P) + S_{rot}(T) + S_{vib}(T) + S_{conf}(T) \quad (13)$$

To calculate the translational contribution to the thermodynamic functions only the molar mass of the compound *M* = 82.104 g·mol^{−1} was required. Geometrical parameters of the MeIm molecule, which were used for calculation of the rotational contribution, were obtained from the quantum-chemical calculations and presented in Table S6 (Supporting Information). The molecule was found to belong to the *C_s* point group (Figure 3) and, therefore, its symmetry number *σ* is 1. The product of principal moments of inertia of the molecule was calculated to be *I_AI_BI_C* = 6.74 × 10^{−135} kg³·m⁶.

To find the vibrational contribution, one has to know all 3*n* − 6 = 30 frequencies of normal vibrations of the molecule, where *n* = 12 is the number of atoms in it. The complete set of frequencies of normal vibrations of MeIm (Table 8) was compiled based on the

IR spectra of MeIm reported in refs 23 and 24 and the results of DFT calculations. A scaling factor *k* is equal to the ratio of the experimental vibrational wavenumber *w*_{exp} to the calculated one *w*_{calc}. The scaling factors were found to be 0.965 ± 0.004 for C–H and N–H stretching vibrations and 0.980 ± 0.003 for the other vibrations. These values were obtained from *w*_{exp} and *w*_{calc} reported in Table 8 in the wavenumber range 600 to 1500 cm^{−1} and above 2900 cm^{−1}, respectively. The wavenumbers of the vibrations not identified in the experimental spectra were calculated from the *w*_{calc} values using the above-mentioned scaling factors. Those values are printed in italics in Table 9.

Internal rotation of the methyl top attached to the imidazole ring occurs in MeIm. The barrier to the internal rotation was found from B3LYP/6-31+G(2df,p) calculations to be *V*₀ = 2.26 kJ·mol^{−1}. The corresponding potential energy curve was approximated by the equation

$$V(\varphi)/\text{kJ} \cdot \text{mol}^{-1} = 1.13 + 1.13 \cos 3\varphi \quad (14)$$

where *φ* is a phase angle. The reduced moment of inertia was calculated according to the procedures described in ref 25 to be 4.97 × 10^{−47} kg·m². The contribution of internal rotation was found from the energy levels of a hindered rotator.

The thermodynamic properties of MeIm in the ideal-gas state are presented in Table 9. The calculated entropy value *S*_m^o(*g*; 298 K) = 309.4 J·K^{−1}·mol^{−1} is in very good agreement with the value 310.3 ± 1.3 J·K^{−1}·mol^{−1} obtained from the experimental data. The difference between the values is −0.3% and does not exceed the uncertainty of the latter value. A good agreement of the gas-phase entropies obtained from experiment and theory confirms validity of the parameters used for the statistical thermodynamic calculations.

■ ASSOCIATED CONTENT

Supporting Information. Auxiliary quantities for the combustion calorimetry (Table S1); results from combustion calorimetry (Tables S2 and S3); G3MP2 total energies at 0 K and enthalpies at 298.15 K of the molecules studied in this work (Table S4); experimental molar heat capacities of MeIm at saturated vapor pressure (Table S5); geometrical parameters of MeIm molecule from B3LYP/6-31+G(2df,p) calculations

(Table S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH Verlag, GmbH & Co. KGaA: Weinheim, 2008.
- (2) Mo, O.; Yanez, M.; Roux, M. V.; Jimenez, P.; Davalos, J. Z.; Ribeiro da Silva, M. A. V.; Ribeiro da Silva, M. D. M. C.; Matos, M. A. R.; Amaral, L. M. P. F.; Sanchez-Migallon, A.; Cabildo, P.; Claramunt, R.; Elguero, J.; Liebman, J. F. *J. Phys. Chem. A* **1999**, *103*, 9336–9344.
- (3) Kostikova, L. M.; Miroshnichenko, E. A.; Matyushin, Y. N.; Vorob'ev, A. B.; Inozemtsev, J. O. *Book of Abstracts*, 33rd International Annual Conference of ICT, Fraunhofer-Institut für Chemische Technologie ICT, 2002; pp 86/1–86/8.
- (4) Benoit, R. L.; Frechette, M. *Thermochim. Acta* **1988**, *126*, 155–164.
- (5) Catalan, J.; Cabildo, P.; Elguero, J.; Gómez, J.; Laynez, J. J. *Phys. Org. Chem.* **1989**, *2*, 646–52.
- (6) Lipkind, D.; Plienrasri, C.; Chickos, J. S. *J. Phys. Chem. B* **2010**, *114*, 16959–16967.
- (7) Emel'yanenko, V. N.; Verevkin, S. P.; Heintz, A. *J. Am. Chem. Soc.* **2007**, *129*, 3930–3937.
- (8) Beckhaus, H.-D.; Kratt, G.; Lay, K.; Geiselman, J.; Rüchardt, C.; Kitschke, B.; Lindner, H. J. *Chem. Ber.* **1980**, *113*, 3441–3455.
- (9) Bazyleva, A. B.; Blokhin, A. V.; Kabo, A. G.; Kabo, G. J.; Emel'yanenko, V. N.; Verevkin, S. P. *J. Chem. Thermodyn.* **2008**, *40*, 509–522.
- (10) Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*; Interscience Publishers: New York, 1956; pp 75–127.
- (11) Wagman, D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamics Properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, Supplement no. 2.
- (12) Kulikov, D. V.; Verevkin, S. P.; Heintz, A. *Fluid Phase Equilib.* **2001**, *192*, 187–202.
- (13) Verevkin, S. P. *Experimental Thermodynamics. Vol. 7. Measurement of the thermodynamic properties of multiple phases*; Elsevier: 2005; pp 6–30.
- (14) Sevruck, V. M.; Simirsky, V. V.; Kabo, G. J.; Kozyro, A. A.; Krasulin, A. P. *Zh. Fiz. Khim.* **1990**, *64*, 3402–3404.
- (15) Zaitsau, D. H.; Paulechka, Y. U.; Blokhin, A. V.; Yermalayeu, A. V.; Kabo, A. G.; Ivanets, M. R. *J. Chem. Eng. Data* **2009**, *54*, 3026–3033.
- (16) Blokhin, A. V.; Kabo, G. J.; Paulechka, Y. U. *J. Chem. Eng. Data* **2006**, *51*, 1377–1388.
- (17) Frisch, M. J. et al. *Gaussian 03, Revision B.04*; Gaussian, Inc.: Pittsburgh PA, 2003.
- (18) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703–4709.

- (19) McQuarrie, D. A. *Statistical Mechanics*; Harper & Row: New York, 1976.
- (20) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.
- (21) Jimenez, P.; Roux, M. V.; Turrion, C. *J. Chem. Thermodyn.* **1987**, *19*, 985–992.
- (22) Jimenez, P.; Roux, M. V.; Turrion, C. *J. Chem. Thermodyn.* **1992**, *24*, 1145–1149.
- (23) Perchard, C.; Novak, A. *Spectrochim. Acta* **1967**, *23A*, 1953–1968.
- (24) Chowdhury, A.; Thynell, S. T. *Thermochim. Acta* **2006**, *443*, 159–172.
- (25) Pitzer, K. S. *J. Chem. Phys.* **1946**, *14*, 239–243.