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Thermodynamics of Ionic Liquid Precursors. 1-Bromobutane and Its Isomers

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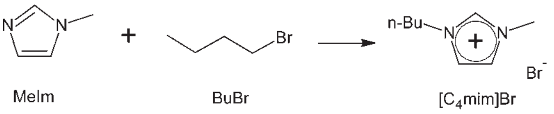
S *Supporting Information*

ABSTRACT: The heat capacity and parameters of fusion of 1-bromobutane (BuBr) 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. On the basis of the experimental spectroscopic data and the results of quantum-chemical calculations, the ideal-gas properties for BuBr were calculated by methods of statistical thermodynamics. The obtained entropy S°_{m}(g; 298.15 K) = 366.9 $J \cdot K^{-1} \cdot mol^{-1}$ is in excellent agreement with the value 367.0 ± 1.2 $J \cdot K^{-1} \cdot mol^{-1}$ obtained from the experimental data. The ideal-gas thermodynamic properties were also calculated for isomeric bromobutanes and 1-butyl-3-methylimdiazolium bromide ionic liquids that allowed us to find the changes of thermodynamic properties in the reactions of synthesis of 1-butyl-3-methylimidazolium bromide isomers. The literature data on the enthalpies of formation for isomeric bromobutanes were collected, and the recommended values were developed. It was demonstrated that the synthesis of ionic liquids from bromoalkanes and 1-methylimidazole in the gas phase, unlike the liquid-phase reaction, is not a thermodynamically favorable process. It possesses more positive enthalpy changes and more negative entropy changes compared to the synthesis in the liquid phase.

INTRODUCTION

1-Bromobutane (BuBr) is a key reagent in many organic syntheses. Nowadays, it is widely used for the synthesis of ionic liquids,[1] particularly, a prototype ionic liquid 1-butyl-3-methylimidazolium bromide ($[C_4mim]Br$):



(r1)

We have studied thermodynamic properties of $[C_4mim]Br$[2] and 1-methylimidazole (MeIm)[3] and determined the enthalpy of reaction r1.[4] To get the complete thermodynamic description of reaction r1, thermodynamic properties of BuBr are required.

The heat capacity of BuBr has been measured in limited temperature ranges.[5−9] The obtained results do not allow one to calculate the entropy for this compound in the condensed state. The enthalpies of fusion for BuBr determined by Timmermans[10] and Deese[8] differ by almost 1.5 times. The consistency of the enthalpies of vaporization[11−14] and the saturated vapor pressures[14−16] is good enough to use them for the evaluation of the standard entropy of vaporization for this compound at T = 298.15 K and, if the liquid-state entropy is known, the standard entropy of gaseous BuBr.

In this work we report the results of a thermodynamics study for BuBr. The heat capacity and parameters of fusion of BuBr 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. On the basis of the experimental spectroscopic data and the results of quantum-chemical calculations, the ideal-gas properties for BuBr and its isomers were calculated by methods of statistical thermodynamics. The changes of thermodynamic properties in the reactions of synthesis of ILs isomeric to $[C_4mim]Br$ were analyzed.

EXPERIMENTAL SECTION

A commercial sample of BuBr from Acros Organics with the GC purity according to the certificate of 0.997 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 0.9987.

The heat capacity of BuBr 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.[17] The uncertainty of the heat capacity measurements did not exceed $\pm 4 \cdot 10^{-3} C_s$ 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 samples corrected for the buoyancy was 1.0691 g for series 1 and 1.0025 g for series 2. The experimental heat capacities above T_{fus} were corrected for vaporization of the liquid into the free volume of the container according to the procedures described by Hoge[18] using the recommended data on density[19] and the saturated vapor pressure of BuBr.[14,15]

Quantum-chemical calculations were performed using the Firefly QC package[20] for calculations on bromoalkanes and the GAMESS[21] software for calculations on ionic liquids and

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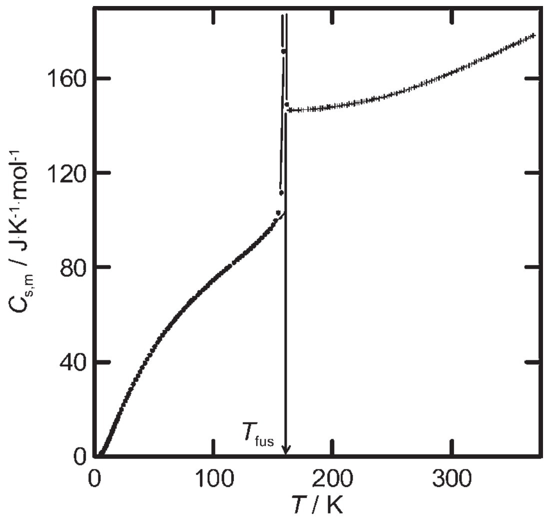

Figure 1. Experimental heat capacities of BuBr in the crystal (●) and liquid (+) states.

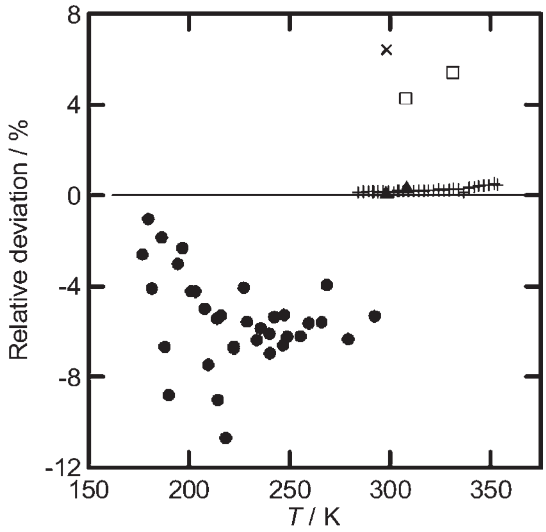

Figure 2. Relative deviation of the heat capacity of liquid BuBr from literature from the results of this work: ▲, DSC, ref 5; +, DSC, ref 6; □, isoperibol drop calorimeter, ref 7; ●, adiabatic calorimeter with continuous heating, ref 8; ×, isoperibol calorimeter, ref 9.

G3MP2 calculations. The optimization of geometry for the conformers and calculation of frequencies of normal vibrations were performed at the B3LYP/6-31+G(2df,p) theory level. In the calculations of the enthalpies of formation for ILs and the enthalpies of reactions of their synthesis the total energies were calculated by the G3MP2 method. The zero-point vibrational energies were found from the B3LYP/6-31+G(2df,p) scaled frequencies. The $\Delta_0^T H_m$ values were calculated by the method of statistical thermodynamics as described below or in ref 3. The basic procedures of the statistical thermodynamic calculations were described in refs 22 and 23. The reduced moments of inertia were found according to Pitzer.[24] We estimate the uncertainty of the calculations of thermodynamic functions to be < ± 1 % for molecular compounds and < ± 2 % for ILs.

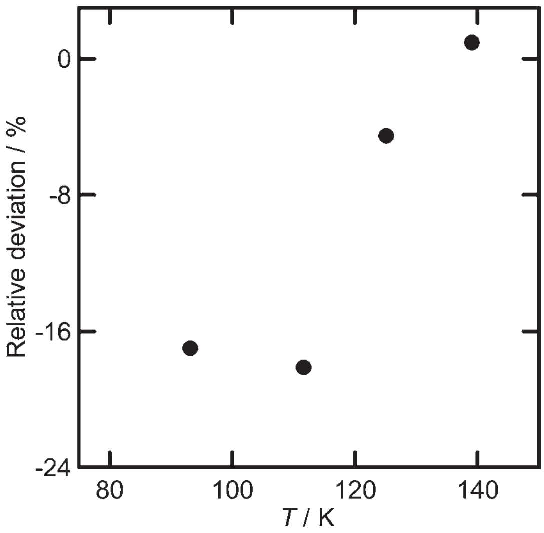

Figure 3. Relative deviation of the heat capacity of crystalline BuBr from ref 8 (●) from the results of this work.

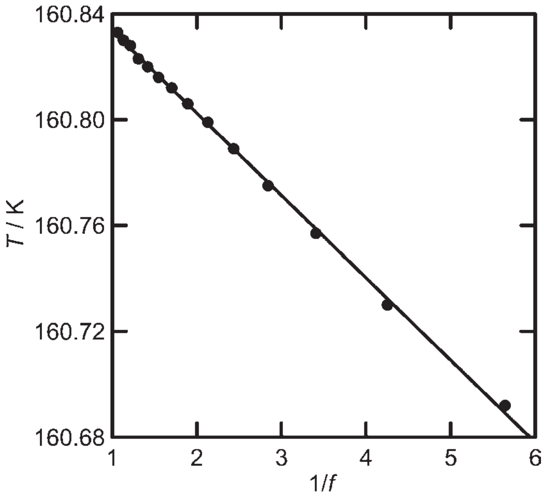

Figure 4. Fractional melting results for BuBr.

■ RESULTS AND DISCUSSION

Heat Capacity and Parameters of Fusion. The experimental heat capacities for BuBr are presented in Figure 1 and in the Supporting Information.

The heat capacity of liquid BuBr was determined in a number of works by different methods.[5−9] Deviations of the literature data from the results obtained in this work are presented in Figure 2. The results from refs 5 and 6 agree with the data from adiabatic calorimetry within 0.55 %. The deviation for the older works[7−9] reaches 10.7 %. The heat capacity of crystalline BuBr was earlier determined only by Deese.[8] Those data significantly deviate from the results obtained here (Figure 3).

The triple-point temperature T_{fus} = 160.86 ± 0.01 K was determined by the fractional melting method (Figure 4). The results were fitted by the van't Hoff equation:

$$T_{fus} - T = \frac{R{T_{fus}}^2(1-x)}{\Delta_{cr}^{l}H_m^\circ}\,\frac{1}{f} \qquad (1)$$

Table 1. Determination of the Enthalpy of Fusion for BuBr

T_i	T_f	Q	$\Delta_{T_i}^{T_{fus}} H_m(cr)$	$\Delta_{T_{fus}}^{T_f} H_m(l)$	$\Delta_{cr}^{l} H_m^o(T_{fus})$
K	/K	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
149.16	162.72	10576	1174	272	9131[a]
148.53	165.83	11087	1235	729	9123
147.86	163.13	10747	1300	332	9115
147.09	162.39	10711	1374	224	9113
147.61	162.87	10735	1324	295	9116
				Average:	9120 ± 6

[a] Fractional-melting series.

Table 2. Molar Thermodynamic Functions of BuBr at Saturation Pressure

T	$C_{s,m}$	S_m	$\Delta_0^T H_m/T$	$(\Phi_m)^a$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
		Crystal		
0	0	0	.	.
5	0.549	0.183	0.137	0.046
10	4.21	1.47	1.10	0.37
15	10.16	4.27	3.10	1.17
20	16.26	8.04	5.64	2.40
25	22.01	12.29	8.35	3.95
30	27.40	16.79	11.08	5.71
35	32.41	21.40	13.77	7.62
40	37.01	26.03	16.39	9.63
45	41.44	30.64	18.93	11.71
50	45.64	35.23	21.40	13.83
60	53.02	44.23	26.07	18.15
70	59.23	52.87	30.37	22.50
80	64.86	61.16	34.34	26.82
90	69.82	69.09	38.01	31.08
100	74.50	76.69	41.43	35.26
110	78.95	84.00	44.64	39.36
120	83.18	91.05	47.68	43.38
130	87.39	97.87	50.57	47.31
140	92.14	104.5	53.36	51.16
150	97.45[b]	111.1	56.12	54.93
160	103.3[b]	117.5	58.88	58.64
160.86	103.8[b]	118.1	59.12	58.96
		Liquid		
160.86	146.7	174.8	115.8	58.96
170	146.8	182.9	117.5	65.41
180	147.0	191.3	119.1	72.17
190	147.4	199.2	120.6	78.65
200	148.0	206.8	121.9	84.87
210	148.7	214.1	123.2	90.85
220	149.6	221.0	124.4	96.61
230	150.7	227.7	125.5	102.2
240	151.9	234.1	126.6	107.5
250	153.3	240.3	127.6	112.7
260	154.9	246.4	128.6	117.7
270	156.6	252.3	129.6	122.6
280	158.5	258.0	130.6	127.3
290	160.4	263.6	131.6	131.9
298.15	162.1	268.0	132.4	135.6
300	162.5	269.1	132.6	136.4
310	164.7	274.4	133.6	140.8
320	166.9	279.7	134.6	145.1
330	169.2	284.9	135.6	149.2
340	171.6	289.9	136.7	153.3
350	173.9	294.9	137.7	157.3
360	176.2	299.9	138.7	161.1
370	178.5[b]	304.7	139.8	165.0

[a] $\Phi_m^o = -[G_m^o(T) - H_m^o(0)]/T = S_m^o - (\Delta_0^T H_m^o)/T$. [b] Extrapolated values.

where f is a fraction melted at temperature T, x is a mole fraction of the main component in a sample, and $\Delta_{cr}^{l} H_m^o$ is a standard molar enthalpy of fusion for a pure compound. The enthalpy of fusion $\Delta_{cr}^{l} H_m^o = 9.120 \pm 0.006\ kJ \cdot mol^{-1}$ was determined from a series of five experiments (Table 1). The following equation was used to calculate $\Delta_{cr}^{l} H_m^o$:

$$\begin{aligned}\Delta_{cr}^{l} H_m^o &= Q - \Delta_{T_i}^{T_{fus}} H_m(cr) - \Delta_{T_{fus}}^{T_f} H_m(l) \\ &= Q - \int_{T_i}^{T_{fus}} C_{p,m}(cr)\ dT - \int_{T_{fus}}^{T_f} C_{p,m}(l)\ dT \qquad (2)\end{aligned}$$

where Q is the energy needed to heat 1 mol of BuBr from T_i to T_f. The initial T_i and final T_f temperatures lay outside the premelting region. The heat capacities of the crystalline $C_{p,m}(cr)$ and liquid $C_{p,m}(l)$ compound were calculated from the following equations:

$$C_{p,m}(cr)/J \cdot K^{-1} \cdot mol^{-1} = 76.15 - 0.2744(T/K) + 27.76 \cdot 10^{-4}(T/K)^2 \qquad (3)$$

$$\begin{aligned}C_{p,m}(l)/J \cdot K^{-1} \cdot mol^{-1} &= 153.0 \\ &+ 0.02930(T/K) - 13.20 \cdot 10^{-4}(T/K)^2 \\ &+ 6.862 \cdot 10^{-6}(T/K)^3 - 8.122 \cdot 10^{-9}(T/K)^4 \qquad (4)\end{aligned}$$

These equations were derived from the experimental heat capacities in the temperature ranges (120 to 148) K and (164 to 368) K, respectively.

The enthalpy of fusion $\Delta_{cr}^{l} H_m^o(160.4\ K) = 9.27 \pm 0.06\ kJ \cdot mol^{-1}$ reported by Deese[8] satisfactorily agrees with the value $9.120 \pm 0.006\ kJ \cdot mol^{-1}$ obtained in this work. The value found by Timmermans[10] from the solid−liquid two-phase diagrams, $\Delta_{cr}^{l} H_m^o(160.8\ K) = 6.7\ kJ \cdot mol^{-1}$, is too low.

Thermodynamic Properties in the Crystal and Liquid States. For the calculation of entropy and enthalpy of the phases, the experimental heat capacities are to be extrapolated below $T = 5$ K. The extrapolation of heat capacity was performed using the emipirical function:

$$C_{p,m} = D_3(\theta_D/T) + 3E(\theta_E/T) \qquad (5)$$

where $D_3(\theta_D/T)$ is the Debye heat-capacity function for three degrees of freedom and $E(\theta_E/T)$ is the Einstein heat capacity function for one degree of freedom. The corresponding characteristic temperatures $\theta_D = 76.3$ K and $\theta_E = 66.7$ K were determined by the least-squares fit of the experimental heat capacities in the temperature range (5.1 to 8.4) K. The values of S_m and $\Delta_0^T H_m$ for the compound at $T = 5$ K were obtained by integration of $C_{p,m}/T$ and $C_{p,m}$ calculated using eq 5 from $T = 0$ K

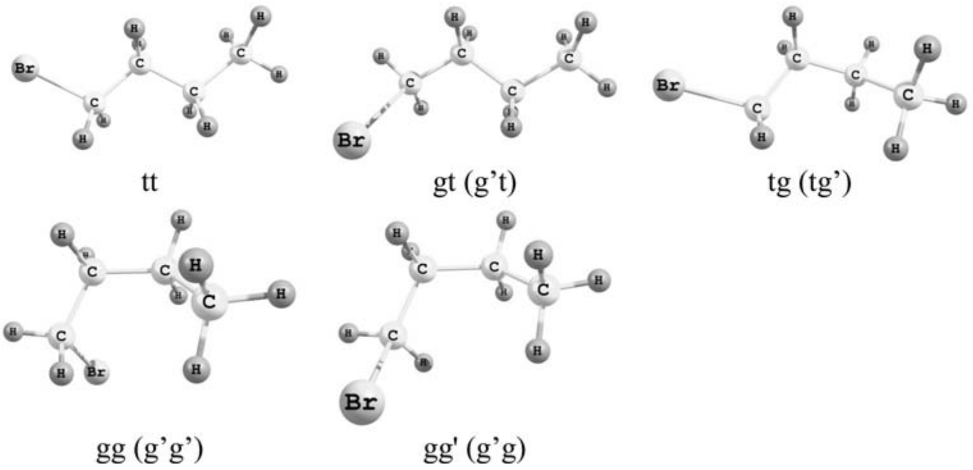

Figure 5. BuBr conformers.

to $T = 5$ K. The smoothed values of the heat capacity and the derived thermodynamic functions are presented in Table 2. The standard thermodynamic functions of liquid BuBr at $T = 298.15$ K are as follows: $C^{\text{o}}_{p,\text{m}} = (162.1 \pm 0.6)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $S^{\text{o}}_{\text{m}} = (268.0 \pm 1.1)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $\Delta_0^T H^{\text{o}}_{\text{m}}/T = (132.4 \pm 0.6)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $\Phi_{\text{m}}{}^{\text{o}} = (135.6 \pm 1.3)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Ideal Gas Thermodynamic Properties. The standard molar ideal gas entropy $S^{\text{o}}_{\text{m}}(\text{g};\ T)$ for the studied compound can be calculated from the equation:

$$S^{\text{o}}_{\text{m}}(\text{g};\ T) = S^{\text{o}}_{\text{m}}(\text{l};\ T) + \frac{\Delta_{\text{l}}^{\text{g}} H^{\text{o}}_{\text{m}}(T)}{T} + R \ln \frac{p^{\text{sat}}(T)}{p^{\text{o}}} \tag{6}$$

where $p^{\text{o}} = 1$ bar. The standard entropy of the liquid $S^{\text{o}}_{\text{m}}(\text{l};\ T)$ at $T = 298.15$ K was obtained from the calorimetric results obtained in this work. The enthalpy of vaporization for the compound is $\Delta_{\text{l}}^{\text{g}} H^{\text{o}}_{\text{m}}(T) = 36.7 \pm 0.1\ \text{kJ}\cdot\text{mol}^{-1}$ (see below); the saturated vapor pressure is $p_{\text{sat}}(T) = 5.5 \pm 0.1$ kPa,[15] and the resulting entropy value was found to be $S^{\text{o}}_{\text{m}}(\text{g};\ T) = 367.0 \pm 1.2\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

The ideal gas thermodynamic properties of BuBr in a wide temperature range were also calculated by the method of statistical thermodynamics. When a thermodynamic property of an ideal gas (for example, entropy S) is calculated, it is usually represented as a sum of translational $S_{\text{tr}}(T, P)$, rotational $S_{\text{rot}}(T)$, vibrational $S_{\text{vib}}(T)$, and conformational $S_{\text{conf}}(T)$ contributions:

$$S(\text{g};\ T, P) = S_{\text{tr}}(T, P) + S_{\text{rot}}(T) + S_{\text{vib}}(T) + S_{\text{conf}}(T) \tag{7}$$

To calculate the translational contribution to the thermodynamic functions only the molar mass of the compound $M = 137.02\ \text{g}\cdot\text{mol}^{-1}$ was required. Normally, the rotational and vibrational contributions are calculated for one or several of the most stable conformers of the gas species. To calculate the thermodynamic properties, the following procedure has been applied:

(a) Identifying possible conformers of the BuBr molecules, determination of their geometries, and relative energies;
(b) Obtaining the complete set of frequencies of normal vibrations;
(c) Calculating the thermodynamic properties.

Table 3. Relative Enthalpies of BuBr Conformers

conformer	$\Delta^i_{\text{tt}}H_{298}$[a] kJ·mol^{-1}	$\Delta^i_{\text{tt}}H_{291}$[b] kJ·mol^{-1}	$\Delta^i_{\text{tt}}H_{225}$[c] kJ·mol^{-1}	accepted for calculations
tt	0.0	0.0	0.0	0.0
gt	1.0	0.5	−1.2 ± 0.4	−1.2
tg	4.8	4.3	1.7 ± 0.6[d]	1.7
gg	2.4	−0.2	−0.6 ± 0.5[d]	−0.6
gg′	10.8			10.8

[a] This work, B3LYP/6-31+G(2df,p) calculations. [b] Reference 25, evaluated using the entropies for the conformers calculated by the method of statistical thermodynamics in this work; the uncertainty of the presented values is ca. ± 3 kJ·mol^{-1}. [c] Reference 26. [d] Evaluated from $\Delta^{\text{tg}}_{\text{gt}}H = 2.9 \pm 0.4\ \text{kJ}\cdot\text{mol}^{-1}$ and $\Delta^{\text{gg}}_{\text{gt}}H = -0.5 \pm 0.3\ \text{kJ}\cdot\text{mol}^{-1}$ reported in the original paper.

The internal rotation of CH_3-, C_2H_5-, and $-CH_2Br$ tops is possible in the BuBr molecule. The barriers to internal rotation of methyl tops $V(0)$ and their reduced moments of inertia I_{r} were found for all of the conformers and reported in Table S2 of the Supporting Information. The potential functions for the internal rotation were approximated by the functions:

$$V(\varphi) = V(0)/2 \cdot (1 + \cos 3\varphi) \tag{8}$$

where φ is the corresponding dihedral angle. The contributions of the internal rotation of methyl tops were calculated from the energy levels of the hindered rotor. The wavenumbers of the corresponding torsional vibrations were excluded from the complete set of frequencies of normal vibrations used in calculation of the vibrational contributions.

The rotation of two other tops results in the formation of a number of conformers presented in Figure 5. Here the first letter characterizes conformation (trans or gauche) of the C1−C2 bond next to the C−Br bond, and the second letter characterizes conformation of the C2−C3 bond. All of the conformers except tt have chiral counterparts. According to the gas-electronographic study by Aarset et al.,[25] at $T = 291$ K the composition of the gaseous equilibrium mixture is as follows: 21 % tt, 33 % gt, 8 % tg, and 38 % gg. The enthalpy differences corresponding to this content of the conformers are presented in Table 3. The enthalpy differences between the conformers in the liquid state were also determined from the temperature dependence of the

Raman spectra (Table 3).[26] The results of earlier studies were considered in refs 25 and 26. The enthalpy differences among the gt, tg, and gg conformers obtained from quantum-chemical calculations in this work are in satisfactory agreement with the results from ref 26; however, the relative enthalpy of the tt conformer is too high. In the subsequent calculations the enthalpy differences[26] possessing lower uncertainties compared to the gas diffraction values[25] were accepted. For the $\Delta_{\mathrm{tt}}^{\mathrm{gg}'}H$ value unavailable from experimental data, the value from the quantum-chemical calculations was accepted. The contributions to the thermodynamic functions related to the mixing of these conformers were calculated as the contributions of the corresponding vibrations corrected for the existence of multiple conformers in the equilibrium mixture.[23]

Geometrical parameters of the BuBr conformers, which were used for calculation of the rotational contribution, were obtained from the quantum-chemical calculations. Symmetry numbers for all of the conformers are equal to one. The products of principal moments of inertia for the conformers are presented in Table 4.

To find the vibrational contribution, one has to know all $3n - 6 = 36$ frequencies of normal vibrations of the molecule, where $n = 14$ is the number of atoms in it. A partial assignment of frequencies in the vibrational spectra of the compound was made by Ogawa et al.[26] The complete assignment of frequencies in the observed spectra for BuBr is very difficult due to the presence of a large number of conformers in the equilibrium mixture. We calculated the frequencies of normal vibrations for the conformers by the methods of quantum chemistry (Table S3 of the Supporting Information). The scaling factors for the calculated frequencies were found with the use of the gas-phase frequencies of normal vibrations for 1-bromopropane obtained in the experiment[27] and calculated in this work as well as the experimental and calculated frequencies for 1-methylimidazole (MeIm).[3] In the range of frequencies of C−H stretching vibrations the ratio of the experimental w_{exp} and calculated w_{calc} wavenumbers is

$$(w_{\mathrm{exp}}/w_{\mathrm{calc}}) = 0.967 \pm 0.002 \tag{9}$$

For the other vibrations, the following equation was derived:

$$(w_{\mathrm{exp}}/w_{\mathrm{calc}}) = 0.996 - 1.2710^{-5}(w_{\mathrm{calc}}/\mathrm{cm}^{-1}) \tag{10}$$

It should also be noted that eqs 9 and 10 can be used in the calculations of vibrational frequencies for isomers and homologues of BuBr as well as ILs in the gas state.

Table 4. Products of Principal Moments of Inertia of BuBr Conformers

conformer	$I_AI_BI_C \cdot 10^{135}$ $\mathrm{kg \cdot m^2}$
tt	46.43
gt	55.55
tg	50.29
gg	49.63
gg′	49.58

The thermodynamic properties of BuBr in the ideal gas state are presented in Table 5. The calculated entropy value $S_{\mathrm{m}}^{\mathrm{o}}$(g; 298 K) = 366.9 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ is in an excellent agreement with the value obtained from the experimental data. A good agreement of the gas-phase entropies obtained from experiment and theory confirms validity of the parameters used for the statistical thermodynamic calculations.

Ideal Gas Thermodynamic Functions of Isomeric Bromobutanes. Thermodynamic properties of isomeric bromobutanes presented in Table 6 were calculated similarly to BuBr. As seen from Table 6, the maximal differences between heat capacities and reduced enthalpies of the isomers are about 6 %. The differences for the entropy are much higher. At the same time, the symmetry-less entropy is defined as

$$S_{\mathrm{m}}^{*\mathrm{o}} = S_{\mathrm{m}}^{\mathrm{o}} + R \ln \sigma \tag{11}$$

where σ is the total symmetry number of overall and internal rotation, which remains almost unchanged for BuBr, 2-bromobutane (2BuBr), and 1-bromo-2-methylpropane (iBuBr). The difference for 2-bromo-2-methylpropane (tBuBr) is about 2 %.

Enthalpies of Formation of Isomeric Bromobutanes. *BuBr.* The literature data on the enthalpies of formation and vaporization for BuBr and its isomers are presented in Table 7. The enthalpy of formation of BuBr in the liquid state was determined

Table 5. Thermodynamic Properties of BuBr in the Ideal Gas State

T	$C_{p,\mathrm{m}}^{\mathrm{o}}$	$S_{\mathrm{m}}^{\mathrm{o}}$	$\Delta_0^T H_{\mathrm{m}}^{\mathrm{o}}/T$	$(\Phi_{\mathrm{m}}^{\mathrm{o}})^a$	$\Delta_f H_{\mathrm{m}}^{\mathrm{o}}$	$\Delta_f G_{\mathrm{m}}^{\mathrm{o}}$
K	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
0	0	0	0	0	−73.8	−73.8
100	61.3	280.0	47.2	232.8	−84.2	−63.8
150	72.4	307.0	53.8	253.2	−88.6	−52.7
200	83.1	329.3	59.8	269.5	−92.9	−40.0
298.15	107.7	366.9	71.4	295.5	−107.1	−11.6
400	135.5	402.4	84.2	318.3	−129.5	25.3
500	160.3	435.4	97.0	338.4	−135.0	64.6
600	181.5	466.5	109.3	357.2	−139.2	105.0
700	199.4	495.9	121.0	374.9	−142.3	145.9
800	214.8	523.6	131.8	391.8	−144.4	187.6
900	228.0	549.7	141.7	407.9	−145.7	228.8
1000	239.4	574.3	151.0	423.3	−146.2	270.5

[a] $\Phi_{\mathrm{m}}^{\mathrm{o}} = -[G_{\mathrm{m}}^{\mathrm{o}}(T) - H_{\mathrm{m}}^{\mathrm{o}}(0)]/T = S_{\mathrm{m}}^{\mathrm{o}} - (\Delta_0^T H_{\mathrm{m}}^{\mathrm{o}})/T$.

Table 6. Thermodynamic Functions of Isomeric Bromobutanes at T = 298.15 K

	$C^o_{p,\mathrm{m}}$	S^o_m	$(S^{*o}_\mathrm{m})^a$	$\Delta_0^T H^o_\mathrm{m}/T$	$\Delta_f H^o_\mathrm{m}$	$\Delta_f G^o_\mathrm{m}$
isomer	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
BuBr	107.7	366.9	376.0	71.4	−107.1	−11.6
S-2BuBr	111.7	356.9	375.2	73.3	−120.3	−21.8
2BuBr[b]	111.7	362.7	380.9	73.3	−120.3	−23.5
*i*BuBr	109.8	356.9	375.2	69.9	−116.7	−18.2
*t*BuBr	114.5	331.0	367.5	69.2	−129.9	−23.7

[a] Symmetry-less entropy. [b] Racemate.

Table 7. Enthalpies of Formation and Vaporization of BuBr and Its Isomers at T = 298.15 K[a]

	$\Delta_f H^o_{,\mathrm{m}}(\mathrm{l})$		$\Delta_l^g H^o_\mathrm{m}$		$\Delta_f H^o_\mathrm{m}(\mathrm{g})$	
isomer	$\mathrm{kJ \cdot mol^{-1}}$	ref	$\mathrm{kJ \cdot mol^{-1}}$	ref	$\mathrm{kJ \cdot mol^{-1}}$	ref
BuBr	−143.8 ± 1.3*	28, 29	36.7 ± 0.1*	11		
	−144.9 ± 4.9	30, 31	36.6 ± 0.1*	12		
			36.9	13		
			36.9 ± 0.1*	14		
			36.9 ± 0.1[b]	15		
			37.9 ± 0.6[b]	16		
			34.0 ± 0.3[b]	32		
	−143.8 ± 1.3		**36.7 ± 0.1**		**−107.1 ± 1.3**	
2BuBr	−154.9 ± 1.3*	29, 33	34.4 ± 0.1*	11, 12	−120.8 ± 1.0*	34
	−153.7 ± 4.9	30, 31			−120.6 ± 1.4*	34
					−119.1 ± 1.2*	34
	−154.7 ± 0.6		**34.4 ± 0.1**		**−120.3 ± 0.6**	
iBuBr	−151.6 ± 4.9*	30, 31	34.9 ± 0.1*	12		
			34.9 ± 0.1*	14		
			35.8 ± 0.2[b]	14		
	−151.6 ± 4.9		**34.9 ± 0.1**		**−116.7 ± 4.9**	
tBuBr	−162.1 ± 4.9	30, 31	31.8 ± 0.1*	12	−130.7 ± 3.6	36
			31.4 ± 0.1[b]	35	−126.4 ± 5.8	37
	−161.7 ± 2.6		**31.8 ± 0.1**		**−129.9 ± 2.6**	

[a] The recommended values are printed in bold. The values used in their calculations are marked by an asterisk. [b] Derived from the temperature dependence of saturated vapor pressure.

was determined by Bjellerup[28] and later reanalyzed by Cox and Pilcher.[29] This value was used in the following calculations. The enthalpy of vaporization for this compound was determined by calorimetry,[11,12,14] from the temperature dependence of the saturated vapor pressure,[14−16,32] and by correlation-gas chromatography.[13] When the $\Delta_l^g H^o_\mathrm{m}$(298.15 K) values were calculated from the vapor pressure data, the original $p^\mathrm{sat}(T)$ data were fitted with the Clarke−Glew equation:[38]

$$-RT \ln\left(\frac{p^\mathrm{sat}}{p^o}\right) = AT/\theta - B[(T/\theta) - 1] - C[\theta - T + T\ln(T/\theta)] \qquad (12)$$

where θ = 298.15 K and p^o = 1 bar. For the pressures much lower than 1 bar, the A, B, and C coefficients are equal to the changes of the Gibbs energy $\Delta_l^g G^o_\mathrm{m}(\theta)$, enthalpy $\Delta_l^g H^o_\mathrm{m}(\theta)$, and heat capacity $\Delta_l^g C^o_{p,\mathrm{m}}(\theta)$ when going from liquid to gas in the standard state. The value $\Delta_l^g C^o_{p,\mathrm{m}}(\theta) = -55\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ was obtained in this work from the results of statistical thermodynamic calculations and the calorimetric measurements. It was also used for the adjustment of the experimental $\Delta_l^g H^o_\mathrm{m}$ values from calorimetric measurements to T = 298.15 K. The recommended value of the enthalpy of vaporization is the weight-averaged value of the calorimetric results. The enthalpy of formation in the gas state was found as a sum of $\Delta_f H^o_\mathrm{m}$ and $\Delta_l^g H^o_\mathrm{m}$.

2BuBr. The enthalpy of formation for this compound was also determined by Bjellerup[33] and later reanalyzed by Cox and Pilcher.[29] Lacher et al.[34] measured the enthalpies of hydrobromination of isomeric butenes in the gas phase. The $\Delta_f H^o_\mathrm{m}(\mathrm{g})$ values found from these data are presented in Table 7. In these calculations, the enthalpies of formation for alkenes,[39] their heat capacity,[40] enthalpy of formation, and heat capacity of HBr,[41] and the heat capacity of gaseous 2BuBr obtained in this work was used.

The enthalpy of vaporization for this compound was measured by Wadsö.[11,12] The mutually consistent results[11,12,33,34] were used for the determination of the recommended values of thermodynamic properties for 2BuBr (Table 7).

iBuBr. Holm[30,31] carried out measurements of the enthalpies of the reactions

$$\mathrm{RBr(l) + Mg(cr) = RMgBr(Et_2O\ solution)} \qquad (\mathrm{r2})$$

$$\mathrm{RMgBr(Et_2O\ solution) + HBr(g) = RH(Et_2O\ solution) + MgBr_2(Et_2O\ solution)} \qquad (\mathrm{r3})$$

where R = Bu, 2Bu, *i*Bu, and *t*Bu. $\Delta_f H^o_\mathrm{m}(\mathrm{RBr})$ is equal to

$$\Delta_f H^o_\mathrm{m}(\mathrm{RBr}) = \Delta_f H_\mathrm{m}(\mathrm{MgBr_2(Et_2O\ solution)}) + \Delta_f H_\mathrm{m}(\mathrm{RH(Et_2O\ solution)}) - \Delta_f H^o_\mathrm{m}(\mathrm{HBr(g)}) - \Delta_r H_\mathrm{m}(\mathrm{r2}) - \Delta_r H_\mathrm{m}(\mathrm{r3}) \qquad (13)$$

The value of $\Delta_f H_\mathrm{m}(\mathrm{MgBr_2(Et_2O\ solution)}) + \Delta_f H_\mathrm{m}(\mathrm{RH(Et_2O\ solution)})$ is unknown; however, if one supposes that

$$\Delta_f H_\mathrm{m}(\mathrm{BuH(Et_2O)}) - \Delta_f H_\mathrm{m}(\mathrm{BuH(l)}) = \Delta_f H_\mathrm{m}(i\mathrm{BuH(Et_2O)}) - \Delta_f H_\mathrm{m}(i\mathrm{BuH(l)}) \qquad (14)$$

the enthalpy of formation for *i*BuBr can be found:

$$\Delta_f H^o_\mathrm{m}(\mathrm{RBr}) = A - \Delta_r H_\mathrm{m}(\mathrm{r2}) - \Delta_r H_\mathrm{m}(\mathrm{r3}) \qquad (15)$$

Here $A = -678.0\ \mathrm{kJ \cdot mol^{-1}}$ was determined using $\Delta_r H_\mathrm{m}(\mathrm{r2})$ and $\Delta_r H_\mathrm{m}(\mathrm{r3})$ for BuBr and 2BuBr from the original paper, $\Delta_f H^o_\mathrm{m}(\mathrm{l})$ for BuBr and 2BuBr reported in Table 7, and $\Delta_f H^o_\mathrm{m}(\mathrm{HBr(g)})$.[41] The obtained $\Delta_f H^o_\mathrm{m}(\mathrm{l})$ for iBuBr (Table 7) was used in the following calculations.

Table 8. Thermodynamic Functions of 1-Alkyl-3-methylimidazolium Bromides at T = 298.15 K

	$C^\circ_{p,m}$	S°_m	$(S^{*\circ}_m)^a$	$\Delta_0^T H^\circ_m/T$	$\Delta_f H^\circ_m$	$\Delta_f G^\circ_m$
alkyl	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
butyl	205.9	544.3	562.6	134.6	−5.2	218.2
S-1-methylpropyl	212.4	524.2	551.6	135.3	−23.6	205.8
1-methylpropyl[b]	212.4	530.0	557.4	135.3	−23.6	204.1
2-methylpropyl	209.2	524.1	551.5	131.5	−16.7	212.8
1,1-dimethylethyl	211.7	513.2	558.9	130.0	−30.1	202.6

[a] Symmetry-less entropy. [b] Racemate.

Table 9. Changes of Thermodynamic Functions on Gas-Phase 1-Alkyl-3-methylimidazolium Bromide Synthesis at T = 298.15 K

	$\Delta_r C^\circ_{p,m}$	$\Delta_r S^\circ_m$	$\Delta_r(\Delta_0^T H^\circ_m/T)$	$\Delta_r H^\circ_m$	$\Delta_r G^\circ_m$
reaction[a]	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
BuBr(g) + MeIm(g) = [C_4mim]Br(g)	13.1	−132.0	8.5	−23.8	15.6
S-*s*BuBr(g) + MeIm(g) = *S*-[*s*C_4mim]Br(g)	15.6	−142.1	7.3	−29.0	13.4
*s*BuBr(g) + MeIm(g) = [sC_4mim]Br(g)[b]	15.6	−142.1	7.3	−29.0	13.4
*i*BuBr(g) + MeIm(g) = [*i*C_4mim]Br(g)	14.3	−142.2	6.9	−25.1	17.3
*t*BuBr(g) + MeIm(g) = [*t*C_4mim]Br(g)	12.1	−127.2	6.1	−25.9	12.0

[a] *S*-[*s*C_4mim]Br, *S*-1-(1-methylpropyl)-3-methylimidazolium bromide; [*i*C_4mim]Br, 1-(2-methylpropyl)-3-methylimidazolium bromide; [*t*C_4mim]Br, 1-(1,1-dimethylethyl)-3-methylimidazolium bromide. [b] Racemate.

The enthalpy of vaporization for this compound was determined in a calorimeter[12,14] and from the temperature dependence of saturated vapor pressure.[14] The $\Delta_l^g C^\circ_{p,m} = -54 \ J \cdot K^{-1} \cdot mol^{-1}$ value used for the adjustment of the experimental $\Delta_l^g H^\circ_m$ to T = 298.15 K was found as a difference of the heat capacities of gas obtained in this work and liquid.[5] The value obtained in calorimetric measurements was used for calculation of the ideal gas enthalpy of formation for this compound.

tBuBr. The enthalpy of formation of tBuBr determined from the results by Holm[30,31] is presented in Table 7. The enthalpy of vaporization for this compound was measured in a calorimeter[12] and found from the temperature dependence of the saturated vapor pressure.[35] The $\Delta_l^g C^\circ_{p,m} = -51 \ J \cdot K^{-1} \cdot mol^{-1}$ value used in the processing of the data[35] with eq 12 was found as the difference of heat capacities of gas obtained in this work and liquid.[5] The calorimetric enthalpy of vaporization was used in the subsequent calculations.

The enthalpy of formation for gaseous *t*BuBr was found[36,37] from the temperature dependence of the equilibrium constant for the gas-phase reaction

$$t\mathrm{BuBr} = (\mathrm{CH_3})_2\mathrm{C} = \mathrm{CH_2} + \mathrm{HBr}$$

In the calculations the following values of thermodynamic properties were used in addition to the results of this work: $\Delta_f H^\circ_m$ and $C^\circ_{p,m}$ of $(CH_3)_2C{=}CH_2$,[39,40] as well as $\Delta_f H^\circ_m$ $C^\circ_{p,m}$ for HBr.[41] The mutually consistent results[12,30,31,36,37] were used to derive the recommended values of thermodynamic properties for *t*BuBr (Table 7).

Nesterova and Rozhnov[42] detemined that the enthalpy of the liquid-phase isomerization

$$i\mathrm{BuBr} = t\mathrm{BuBr}$$

is equal to $\Delta_r H_m(367 \ K) = -16.0 \pm 0.7 \ kJ \cdot mol^{-1}$ Taking into account $\Delta_r C_{p,m}(298.15 \ K) = 2.0 \ J \cdot K^{-1} \cdot mol^{-1}$,[5] $\Delta_r H_m(298.15 \ K) = -16.1 \pm 0.7 \ kJ \cdot mol^{-1}$ can be obtained which is in satisfactory agreement with the results of other works.

Thermodynamic functions of formation for gaseous bromobutanes are presented in Tables 5 and 6.

Ideal Gas Thermodynamic Functions of Isomeric 1-Butyl-3-methylimidazolium Bromides. One of primary problems existing in the thermodynamics of ILs is the search of regularities in thermodynamic properties of these compounds and changes of thermodynamic properties in their reactions. The calculation of ideal gas thermodynamic properties for the isomers of [C_4mim]Br seems to be a step toward solution of this problem.

Geometries of all possible configurations of the ionic pairs with the bromide anion near the C2 atom of the cations were considered. The products of the principal moments of inertia and the vibrational spectra were calculated for the most stable configuration at the B3LYP/6-31+G(2df,p) theory level. The frequencies of normal vibrations were scaled with the use of eqs 9 and 10. The contributions from the internal rotation of methyl tops were calculated using the energy levels of hindered rotors. The contributions for the other tops were calculated as a sum of a harmonic vibrational contribution from the corresponding torsional frequency plus the correction for the existence of the equilibrium mixture of the conformers. The enthalpy differences between the conformers were evaluated in this work from the B3LYP/6-31+G(d,p) quantum-chemical calculations for the corresponding cations, while the parameters of the potential functions of internal rotation and the enthalpy differences between the configurations were found from the calculations for the ionic pairs at the same theory level. As seen from Table 8, the dependences in thermodynamic properties for the considered ILs are similar to those for parent bromobutanes.

Thermodynamic functions of formation for ILs were calculated from the enthalpies of reactions listed in Table 9 calculated by the G3MP2 method and the experimental $\Delta_f H^\circ_m$ for MeIm[3] and isomeric bromoalkanes (Table 7).

Thermodynamics of Ionic Liquid Synthesis. The changes of thermodynamic functions in the reactions of the gas-phase synthesis of [Rmim]Br from bromobutanes and MeIm calculated using the results of this work and ref 3 are presented in Table 9. For all of these reactions, the changes of entropy are equal to the changes of the symmetryless entropy. As seen from Table 9, the changes of thermodynamic properties for the all reactions are in a good agreement, and this fact can be used for estimation of the thermodynamic parameters of synthesis for isomeric ILs. It is also worth noting that the synthesis of the considered ILs in the gas phase is not a thermodynamically favorable process. This happens because the enthalpies of the considered reactions in the gas phase are about 65 kJ·mol^{-1} more positive than in the liquid phase, while the entropy changes are about 30 J·K^{-1}·mol^{-1} more negative.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental molar heat capacities of BuBr at saturated vapor pressure (Table S1); parameters of internal rotation of methyl tops for BuBr conformers (Table S2); vibrational wavenumbers of BuBr conformers (Table S3); molecular parameters used for statistical thermodynamic calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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