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ARTICLES

The Kinetics of Thermal Decomposition of 1-Butyl-3-methylimidazolium Hexafluorophosphate

Dzmitry H. Zaitsau,* Yauheni U. Paulechka, and Gennady J. Kabo

Belarusian State University, Chemistry Faculty, Leningradskaya 14, 220030 Minsk, Belarus

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It is demonstrated that 1-butyl-3-methylimidazolium hexafluorophosphate decomposes in a vacuum in the temperature interval of $T = (410 \text{ to } 505)$ K according to zero-order kinetics with the activation energy $E_A = 68.0 \pm 2.8$ kJ·mol^{-1}.

Introduction

Hexafluorophosphate ionic liquids (ILs) are nonhygroscopic materials possessing thermal stability up to $T < 400$ K. All these properties stimulate investigation of their thermodynamic properties.[1−3] Previously, the authors studied thermodynamic properties for 1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6]:[4,5] measured heat capacities for crystalline, liquid, and glassy [C_4mim][PF_6] in the range from (5 to 550) K, determined the enthalpy and the temperature of fusion, and the temperature dependence of the density for the IL in the interval from (298 to 353) K. The endothermic effect at $T > 473$ K due to decomposition was found by DSC. The latter experiment was carried out in an aluminum pan under air pressure of 1 atm. Additionally, the fact of decomposition at these temperatures was confirmed by the integral Knudsen method.

Recently, vapor pressures for 1-alkyl-3-methylimidazolium-bis-(trifluoromethanesulfonyl)imide ILs[6,7] have been determined. It was demonstrated in ref 7 that the vaporization of the compounds is not accompanied by their decomposition. The correlation scheme for calculation of the enthalpies of vaporization $\Delta_l^g H_m^\circ = A\sigma\cdot\sqrt[3]{V_m^{\ 2}}\cdot\sqrt[3]{N_A} + B$ (σ is the surface tension; V_m is the molar volume) was also presented in ref 7. Until now, no vapor pressure data for [C_4mim][PF_6] have become available. However, Earle et al.[8] distilled [C_4mim][PF_6] in a glass bulb, and only 0.05 mole fraction of the sample was decomposed.

The authors made another attempt to determine vapor pressure for [C_4mim][PF_6], and the results are reported in this work.

Experimental Section

Sample. A commercial sample of [C_4mim][PF_6] (Covalent Associates, Inc.) was used. The sample was additionally degassed in a vacuum ($p \approx 10^{-3}$ Pa) by successive heating for 5 h at temperatures 370, 390, and 410 K.

Measuring Technique. The apparatus and the technique of effusion experiments were described in detail earlier.[7] In contrast to the previous investigation,[5] [C_4mim][PF_6] in the liquid phase was in contact only with the stainless steel walls of the effusion cell. The inner surface of the thermostating block was covered with a high-temperature silicon seal to prevent contact of the IL vapor with catalytically active copper and nickel, the materials of the block. The stainless steel membrane of 2.10 ± 0.05 mm thickness with an orifice of 3.10 ± 0.05 mm diameter was used. The temperature was maintained to within ±0.02 K.

The IR spectra in NaCl pellets were recorded on a Bruker Vertex 70 spectrometer with a resolution of 4 cm^{-1}.

Results

The results of the effusion experiments are listed in Table 1 in chronological order and shown in Figure 1. To estimate the reproducibility of the results, the experiments at 458.3 and 505.6 K were repeated. The deviation of the experimental data from the smoothing curve is less than ±5% and does not exceed the maximum uncertainty of the effusion measurements.[9]

The liquid in the effusion cell remained colorless below 487 K, but it became dark brown above this temperature. The IR spectrum of the [C_4mim][PF_6] residue taken from the effusion cell after the experiment at $T = 505.6$ K is shown in Figure 2b. Although the IL at those conditions was dark and nontransparent, its spectrum is close to that of the initial sample of [C_4mim]-[PF_6] (Figure 2). Only the increase in the relative intensity of the weak band at 1302 cm^{-1} and the appearance of the bands of low intensity at 1140 and 498 cm^{-1} were observed.

After every experiment, the condensate collected on a coldfinger was a light yellow mixture of liquid and crystal near 290 K. The IR spectrum of the condensate was recorded after a 2-h experiment at 477 K. This spectrum differs essentially from that of the initial sample (Figure 2).

The main differences of the IR spectra of the initial sample of [C_4mim][PF_6] and that of the condensate are described below.

3600 to 2800 cm^{-1}. The wide band at 3500 cm^{-1} is caused by condensation of water from the air on the coldfinger. The intensity of the bands related to the C−H stretching vibrations in the aromatic ring (3165 and 3118 cm^{-1}) is much lower than in the case of the initial sample. Probably, this is caused by the destruction of the imidazolium aromatic system. Below 3000 cm^{-1}, in the region of the alkyl C−H stretching vibrations, the band at 2858 cm^{-1} appears. This is caused by the condensation of oil vapors on the coldfinger as described in ref 7.

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* To whom correspondence should be addressed. Phone: +375-17-209-5197. E-mail: ZaitsevD@bsu.by.

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TABLE 1: Results of the Effusion Experiments for 1-Butyl-3-methylimidazolium Hexafluorophosphate[a]

T/K	10^6 Δm/kg	τ/s	10^{12} $(\mathrm{d}m/\mathrm{d}\tau)$/kg·s^{-1}	10^7 k/mol·m^{-2}·s^{-1}
410.11	0.10	13400	7.5	3.3
429.46	0.27	16320	16.5	7.4
448.65	0.65	16260	40.0	17.9
458.27	0.71	14820	47.9	21.5
458.27	0.86	18300	47.0	21.1
477.24	2.27	18000	126.1	56.5
486.88	2.50	16800	148.8	66.7
496.34	3.57	14400	247.9	111.1
505.63[b]	7.39	11640	634.9	284.4
505.61[b]	10.86	16320	665.4	298.1

[a] $M = 0.284$ kg·mol^{-1}; $S_{\mathrm{orifice}} = 7.85\cdot10^{-5}$ m^2. [b] These data were not used to calculate the activation energy of the process taking place in the effusion cell.

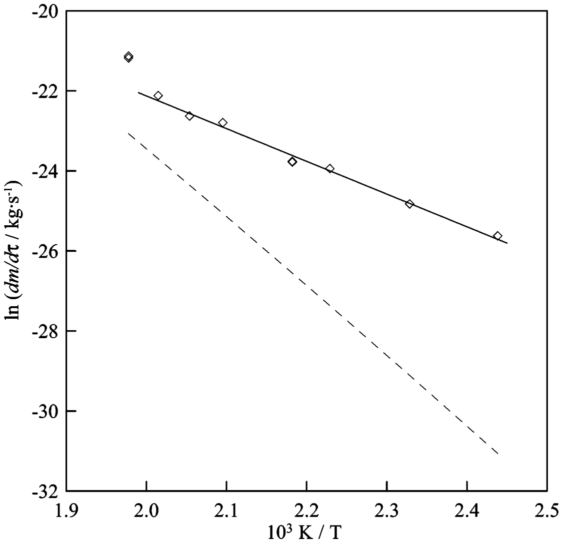

Figure 1. The temperature dependence of the mass-loss rate of the sample. The dashed line corresponds to the mass-loss rate due to the possible vaporization of the IL with $\Delta_l^g H_m^\circ = 161$ kJ·mol^{-1}.

1800 to 1500 cm^{-1}. The strong band at 1672 cm^{-1} appears, which is probably connected with the stretching vibrations of nonconjugated C═C or C═N bonds. The intensity of the band at 1572 cm^{-1} corresponding to the stretching vibrations of the C−N bonds in the aromatic system of imidazole and its derivatives decreases greatly.

1500 to 1000 cm^{-1}. A great increase in the IR intensity of the band at 1302 cm^{-1} is observed. The appearance of the strong narrow band at 1263 cm^{-1} corresponding to the C−N stretching vibrations is accompanied by a decrease in the intensity of the band at 1171 cm^{-1} (the stretching vibration in the imidazole ring). The spectrum of the condensate contains two intensive bands at 1097 and 1028 cm^{-1}, which, in contrast, have low intensity in the spectrum of initial [C$_4$mim][PF$_6$].

1000 to 490 cm^{-1}. The band of P−F stretching vibrations (837 cm^{-1}) decreases greatly in intensity and is split into two bands at 845 and 806 cm^{-1} in the spectrum of the condensate. The bands of the cation at 754 cm^{-1} and of the anion at 559 cm^{-1} also become weaker. Moreover, the band at 498 cm^{-1} appears.

Therefore, from the IR spectra one can conclude that the mass loss of [C$_4$mim][PF$_6$] in the effusion cell at $T = (410$ to $505)$ K is mainly caused by the decomposition of the compound. Imidazoles are not the main products of the decomposition as may be expected from the literature data.[10] The presence of other products of the destruction reaction—butenes, fluorobutanes, PF$_5$, CH$_3$F—was not established explicitly.

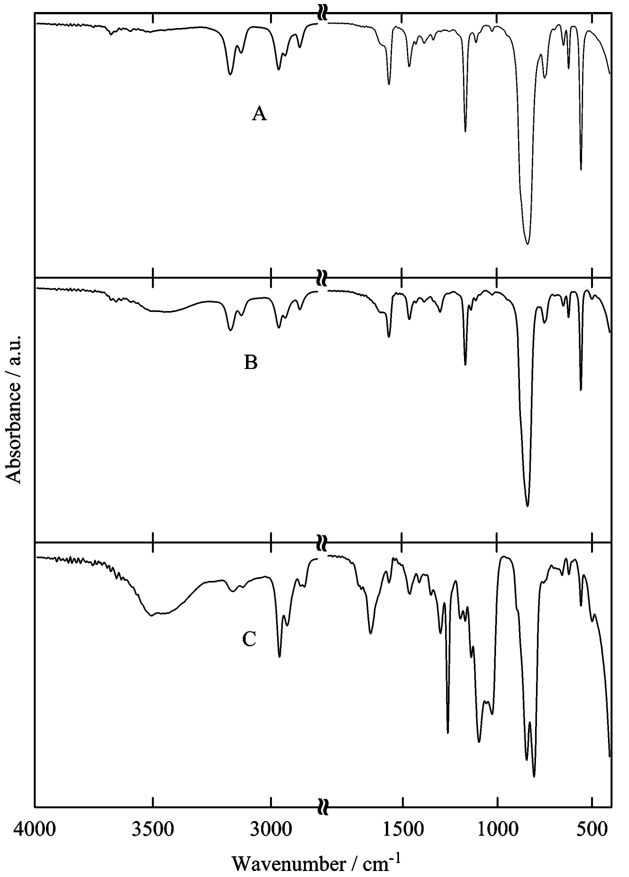

Figure 2. The IR spectra for 1-butyl-3-methylimidazolium hexafluorophosphate: (a) the spectrum of the initial sample of the IL; (b) the spectrum for the residue in the effusion cell; (c) the spectrum of the condensate on the coldfinger.

Discussion

As was shown in the experiments at 458 and 505 K, the mass-loss rate does not depend on the exposition time of the experiment. Therefore, two ways of the studied process are possible: (1) vaporization of the sample with the subsequent decomposition in the gaseous phase; (2) decomposition in the condensed phase according to zero-order kinetics.

In case of vaporization, the vapor pressure is described by the following equation:

$$p_{\mathrm{sat}} = \frac{\Delta m}{\tau}\sqrt{T}\cdot\mathrm{const} \tag{1}$$

where const is the constant depending on the parameters of the effusion orifice, the molar mass of the sample, and the vaporization surface. Provided that the enthalpy of vaporization $\Delta_l^g H_m$ is weakly dependent on temperature, the next equation will hold

$$\ln\left(\frac{\Delta m}{\tau}\right) = A - \frac{\Delta_l^g H}{RT} + \frac{1}{2}\ln T \tag{2}$$

where A is a parameter independent of temperature.

If the decomposition occurs according to zero-order kinetics on the surface of the IL, the mass-loss rate is proportional to the reaction rate

$$w = \frac{dm}{S d\tau} = k \tag{3}$$

where w is the reaction rate, S is the vaporization area, and k is the rate constant. The temperature dependence of the process rate should be described by the Arrhenius equation

$$\ln\left(\frac{\Delta m}{\tau}\right) = A - \frac{E_A}{RT} \tag{4}$$

where E_A is the activation energy.

From the temperature dependence of the mass-loss rate (Figure 1), it is impossible to establish unambiguously whether the decomposition takes place in the condensed or vapor phase. The value of the activation energy for the $[C_4mim][PF_6]$ decomposition evaluated from eq 4 using the experimental mass-loss rates in the temperature interval of (410 to 496) K was $E_A = 68.0 \pm 2.8$ kJ·mol^{-1} at $T = 456.5$ K. The apparent enthalpy of vaporization calculated from the identical experimental data according to eq 2 was $\Delta_l^g H_m = 69.8 \pm 2.8$ kJ·mol^{-1}. Earlier, the enthalpy of vaporization for $[C_4mim][PF_6]$ was estimated to be $\Delta_l^g H_m(298.15\ K) = 161$ kJ·mol^{-1}, based on its cohesion energy obtained from the molecular-dynamic simulation,[11] and $\Delta_l^g H_m(298.15\ K) = 154.8$ kJ·mol^{-1} according to the correlation scheme[7] $\Delta_l^g H_m^\circ = A(\sigma \cdot V_m{}^{2/3} \cdot N_A{}^{1/3}) + B$. Such a large difference in ΔH values show that process 2 prevails.

To determine the possible contribution of process 1 to the overall process, the vapor pressure was estimated for this IL, and the corresponding mass-loss rate for $[C_4mim][PF_6]$ was calculated (Figure 1). The vapor pressure was estimated using the equation

$$\Delta_l^g G_m^\circ = \Delta_l^g H_m^\circ - T\Delta_l^g S_m^\circ = -RT \ln\left(\frac{p_{sat}}{p^\circ}\right) \tag{5}$$

where p° is the standard pressure (10^5 Pa). The standard entropies of vaporization for the IL were calculated previously[5] to be $\Delta_l^g S_m^\circ$ (298.15 K) = 200 J·K^{-1}·mol^{-1} based on the results of statistical thermodynamic calculations and calorimetric measurements. The value of the enthalpy of vaporization from ref 11 was applied. The values of the enthalpy and the entropy of vaporization were adjusted to the temperature of each effusion experiment with the use of the heat-capacity differences for the gaseous and liquid phases.[5] It is seen from Figure 1 that vaporization is not the major process occurring in the effusion cell, and this is in agreement with the conclusion above.

Thus, one may state that decomposition of $[C_4mim][PF_6]$ takes place mainly in the condensed phase and that the products of the reaction leave the effusion cell through the orifice. The calculated rate constants for the $[C_4mim][PF_6]$ decomposition are shown in Table 1. In the calculations, the surface area of the liquid was taken to be equal to the cross-sectional area of the effusion cell. The possible uncertainty in the surface area was estimated to be 30%.

The sharp increase in the mass-loss rate at 505 K can be attributed to the change of the mechanism of the decomposition process; for this reason, these data were not treated for calculation of the activation energy.

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