Volatilization mechanism of 1-ethyl-3-methylimidazolium bromide ionic liquid

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Although molten salts, more recently known as ionic liquids (ILs), have been known for almost a century (for instance, ethylammonium nitrate, mp =12 °C, was discovered in 1914),[1] the rapid development of ionic liquid chemistry has only occurred within the last decade. In 2000, only 217 papers were published on the subject, whereas in 2010, over 6,000 papers appeared in the literature.[2] The number of possible ILs has been estimated at 10^{18}.[3] Detailed studies of ILs offer insight into new and more complex fundamental chemistry, as well as allow for an assessment for their potential application in emerging technologies such as in solar cells, fuel electrolytes, bio- or nano-catalysts, high-energy-density propellants, and green solvents.

In order to better understand the volatilization process for ILs, the vapor evolved from heating the ionic liquid 1-ethyl-3-methylimidazolium bromide ($EMIM^+Br^-$) was analyzed via tunable vacuum ultraviolet photoionization time of flight mass spectrometry (VUV-PI-TOFMS) and thermal gravimetric analysis mass spectrometry (TGA-MS). For this ionic liquid, the experimental results indicate that vaporization takes place via the evolution of alkyl bromides and alkylimidazoles, presumably through alkyl abstraction via an S_N2 type mechanism, and that vaporization of intact ion pairs or the formation of carbenes is negligible.

Activation enthalpies for the formation of the methyl and ethyl bromides were evaluated experimentally, $\Delta H^{\ddagger}(CH_3Br)$ = 116.1±6.6 kJ/mol and $\Delta H^{\ddagger}(CH_3CH_2Br)$ = 122.9±7.2 kJ/mol, and the results are found to be in agreement with calculated values for the S_N2 reactions. Comparisons of product photoionization efficiency (PIE) curves with literature data are in good agreement, and *ab initio* thermodynamics calculations are presented as further evidence for the proposed thermal decomposition mechanism. Estimates for the enthalpy of vaporization of 1-ethyl-3-methylimidazolium bromide and, by comparison, 1-butyl-3-methylimidazolium bromide ($BMIM^+Br^-$) from molecular dynamics calculations and their gas phase enthalpies of formation obtained by G4 calculations yield estimates for the ionic liquids' enthalpies of formation in the liquid phase: ΔH_{vap}(298 K) ($EMIM^+Br^-$) = 168±20 kJ/mol, $\Delta H_{f,\,gas}$(298 K) ($EMIM^+Br^-$) = 38.4±10 kJ/mol, $\Delta H_{f,\,liq}$(298 K) ($EMIM^+Br^-$) = -130±22 kJ/mol, $\Delta H_{f,\,gas}$(298 K) ($BMIM^+Br^-$) = -5.6±10 kJ/mol, and $\Delta H_{f,\,liq}$(298 K) ($BMIM^+Br^-$) = -180±20 kJ/mol.

References

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