Thermal Resilience of Imidazolium based Ionic Liquids – Studies on Short- and Long-Term Thermal Stability and Decomposition Mechanism of 1-Alkyl-3-Methylimidazolium Halides by Thermal Analysis and Single-Photon Ionization Time-of-Flight Mass Spectrometry

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Abstract

Ionic liquids are often considered as green alternatives of volatile organic solvents. The thermal behavior of the ionic liquids is relevant for a number of emerging large-scale applications at elevated temperature. Knowledge about the degradation products is indispensable for treatment and recycling of the used ionic liquids. The objective of this paper was an investigation of the short- and long-term stability of several 1-alkyl-3-methylimidazolium halides, determination of the degradation products, and the elucidation of their decomposition patterns and structure-stability relations.

Short-term stability and mechanism of thermal degradation were investigated by a self-developed, innovative thermal analysis single-photon ionization time-of-flight mass spectrometry device with skimmer coupling. The applied technology provides real-time monitoring of the forming species and allows to trace their change during the course of the decomposition. Therein, the almost fragment-free soft ionization with VUV photons plays a crucial role. We have detected unfragmented molecules whose formation was only assumed by electron ionization. Nevertheless, the main decomposition products of the selected ionic liquids were alkylimidazoles, alkenes, alkyl halides, and hydrogen halides. From the decomposition products we have deduced the fragmentation patterns and discussed their interrelation with the length of the alkyl chain and the type of the halide anion. Our results did not suggest evaporation of the investigated ionic liquids prior to their decomposition under atmospheric conditions.

Long term thermal stability and applicability were determined based on thermogravimetric analysis evaluated with a kinetic model. Thus, the time-dependent maximum operation temperature (MOT) for the respective ionic liquids has been calculated. As a rule, the short-term stability overestimates the long-term decomposition temperatures; the calculated maximum operation temperatures (MOT) are significantly lower (at least 100 K) than the standardly obtained decomposition temperatures.

Introduction

Ionic liquids (ILs) are perspective green alternatives to volatile organic solvents and are being intensively researched nowadays due to their high potential for industrial applications, e. g. as solvents for organic reactions1–3 and for cellulose,4–8 lubricants,9–12 propellants,13,14 etc. They are employed in other fields like engineering, electrochemistry15 and analytical chemistry. Selected examples include an extraction medium for liquid-liquid extraction,16–19 stationary or mobile phases in separation sciences20–22 and matrices in matrix-assisted-laser-desorption/ionization-time-of-flight mass-spectrometry (MALDI-TOF)23. Their steadily increasing relevance is also reflected in the growing number of publications.24,25 Since high-temperature applications (as high-temperature solvents, heat transfer and storage medium,26 high-temperature lubricants) represent a sizeable share, it is of great importance to study their thermal behavior and amass information about the correct and safe operation temperatures.

Thanks to such advantages as low melting temperatures and simplicity of handling and preparation, 1-alkyl-3-methylimidazolium halide ILs, which are under consideration in the present article, are frequently used as reaction media, including applications at elevated temperatures.27 Thermoanalytical (TA) methods such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are applied for investigation of their thermal stability. Combined analytical techniques such as TGA-gas chromatography-mass spectrometry (TGA-GC/MS),28–30 thermal desorption mass spectrometry (TDMS),32 simultaneous thermal analysis (STA) coupled with either Fourier transform infrared spectroscopy (STA-FTIR)31,32 or mass spectrometry (STA-MS)26,33–36 are required for detection of breakdown products. Another interesting aspect is highlighted by comparison of the quantum-chemistry-based predictions31,34–37 of possible mechanisms and temperatures of thermal decomposition for ionic liquids with experimental data.

Short-term thermal stability

In the following, we discuss experimental results obtained for 1-alkyl-3-methylimidazolium halides by TGA-MS. Generally, there are two options for coupling of TGA and MS. The most widely used is based on the capillary coupling so that the gases released in the course of a thermal process are transferred via a deactivated silica capillary. In *Efimova et al.*33,38 thermal degradation of 1-ethyl-3-methylimidazolium halides and 1-butyl-3-methylimidazolium halides was investigated by means of TGA-MS with the quartz glass capillary coupling. Two main decomposition scenarios were suggested, whereas the formation of 1-methylimidazole and ethyl halide is preferred over the formation of 1-ethylimidazole and methyl halide. However, the unambiguous identification of these gas species was not possible due to the applied standard electron ionization (EI) with the energy of 70 eV. The main disadvantage of the capillary coupling is an enhanced wall contact during transfer. The emitted molecules often undergo decomposition or interact with each other during the transfer from TA to MS. Since the temperature of the transfer line usually approaches 300 °C, it is impossible to transfer low-volatile compounds.

The nozzle skimmer fragmentation is another approach to hyphenate TGA with MS that enables *in situ* characterization of thermal-decomposition products.34 They are being transferred through a divergent nozzle and a conically distended aperture (skimmer) that is placed in the middle of the release gas effusion. The intermediate space between the TGA and the high-vacuum of the mass spectrometer is pumped by a further vacuum pump. The nozzle and the skimmer are either made of refractory metals for applications up to 800 °C, of alumina for applications up to 1450 °C or of glass carbon for applications up to 2000 °C39,40. *Hao et al*.34 used a TGA-Skimmer-MS setup for the investigation of 1-butyl-3-methylimidazolium chloride ([C4mim]Cl) and 1-allyl-3-methylimidazolium chloride. The applied standard ionization energy of 70 eV could have been the reason why the assumed degradation products, 1-butylimidazole and butyl chloride, were not detected upon decomposition of [C4mim]Cl.

Soft ionization techniques help to circumvent the limitations of electron ionization. One of them is photoionization with the energies of ionizing photons lying usually in the range of 7-12 eV. These energies correspond to typical ionization energies of organic molecules leading to molecular radical cations as characteristic high-mass fragments in the often fingerprint-like-mass spectra. This method is especially beneficial for TGA-MS studies of complex matrices,41,42 eventually with an additional GC step (TGA-GC-MS).43,44 The applied single photon ionization (SPI) is based on a one-photon absorption/ionization process; photon generation is realized with different lamps (e.g. discharge lamps, electron beam pumped excimer light sources (EBEL)) or lasers,45 emitting in the vacuum ultraviolet (VUV) wavelength region. *Chambreau et al.*35 applied tunable synchrotron photoionization for the investigation of degradation products of 1-ethyl-3-methylimidazolium bromide ([C2mim]Br) at 183 °C.

The Maximum Operation Temperature

According to user experience acquired over a long time, stability of ILs changes over time: decomposition and, thus, safe operation temperatures are considerably lower after long-term usage than after short-term usage. Thermal stability of a compound is typically characterized by the decomposition temperature determined from TGA. Various ways can be used to evaluate the decomposition temperature from TGA data,33 but the general concern is that all these determined temperatures do not correspond to the “real” decomposition temperature but comply with a mass loss of at least 10% for all classic evaluation methods. In other words, since 10% of the substance has already decomposed at the given decomposition temperature, the latter cannot be used for synthesis design.33,34,46 Nevertheless, it is still possible to apply a kinetic model to estimate the so-called maximum operation temperature (MOT) that corresponds to the mass loss of 1% for a certain period of time.47 The used kinetic model has already been applied for the calculation of MOT for some ILs.48,49

In this study, we evaluated the stability of 1-alkyl-3-methylimidazolium halide ILs in a comprehensive way by different methods. As far as the short-term thermal stability is concerned, this is the first report that approaches decomposition scenarios of ionic liquids by the TGA/DSC-Skimmer-SPI-TOFMS method and uses the above-mentioned advantages of photoionization in order to resolve the ambiguities arising from the literature. Additionally, we performed tests in different atmospheres to find out whether evaporation of 1-alkyl-3-methylimidazolium halides takes place upon heating prior to their decomposition. Finally, we present a method for the determination of long-term application temperatures for these halides using dynamic thermogravimetric (TGA)-measurements.

Experimental

Short-term thermal stability of the considered ionic liquids was studied by means of TGA/DSC-Skimmer-SPI/EI-TOFMS measurements. For this reason, a thermal analysis – mass spectrometer setup (STA 409 CD with QMS 403/5 Skimmer®-Coupling, Netzsch-Geraetebau GmbH, Selb, Germany) was modified. The quadrupole analyzer of the commercial system was replaced by an orthogonal acceleration time-of-flight mass spectrometer (CTOF, Tofwerk, Thun, Switzerland). The instrumental setup was described in detail previously50,51. Briefly, the Skimmer® coupling allows the on-line wall-contact free analysis of the released gases that are transferred from atmospheric pressure of the STA into the high vacuum of the ion source through an intermediate vacuum chamber (40 mbar). For the photoionization, we applied an air-cooled deuterium lamp (*Hamamatsu Photonics K. K., Hamamatsu City, Japan*) generating VUV photons. The photon beam was focused on the path of the released gases at the ion source with mirror modules comprising two parabolic MgF2-coated mirrors. The local maximum of the wavelength–irradiance function of the used deuterium lamp lies at 122 nm, which corresponds to the 10.16 eV photon energy. The mass spectrometer was also operated at standard electron ionization with the applied ionization energy of 70 eV. For the detection of unknown reaction products, a time-of-flight mass spectrometer is more suitable than a quadrupole mass analyzer since the former allows to record a high number of mass spectra over the entire mass range and to record fingerprint-like mass-spectra that help to identify decomposition products of various ILs. The following measurement conditions were used for the TGA/DSC-Skimmer-SPI-TOFMS samples: the heating rate of 10 K min−1 in the 25–500 °C range; sample weight 5 mg in alumina crucibles with a lid and a pinhole in the lid; purge and protective gas: 30 mL min−1 nitrogen, helium, synthetic air (only for purge).

Long-term thermal stability has been determined by thermogravimetric analysis. Measurements for the determination of MOTs were performed with a simultaneous thermal analyzer (STA 449 F3 Jupiter) manufactured by *Netzsch*. The experiments were carried out from ambient temperature to 500 °C at the rates of 1, 2, 5, 7, 10 and 20 K min−1 under the nitrogen flow with the rate of 20 mL min−1 in uncovered alumina crucibles. The weighing of 1-butyl-3-methylimidazolium halides (Cl, Br, I) samples used in different measurements was 10 mg. The decomposition temperatures were determined at the onset of the DTG curve of the respective thermal effect.

Ionic liquid substances have been used for thermal measurements as follows: 1-ethyl-3-methylimidazolium halides, [C2mim]*X*: [C2mim]Cl with purity over 98% from Sigma-Aldrich (St. Louis, Missouri, USA); [C2mim]Br (> 98%) and [C2mim]I (> 97%) purchased from Alfa Aesar (Ward Hill, Massachusetts, USA). 1-butyl-3-methylimidazolium halides [C4mim]*X*: all three halides (*X* = Cl, Br, I) supplied by Sigma-Aldrich with purity over 99%. All samples had been freed additionally from moisture at ambient temperature under dynamic vacuum (< 10−2 mbar) prior to use and were handled and stored in an argon-filled glove box [*c*(O2, H2O) ≤ 0.1 ppm, M. BraunLAB 130]. Other chemicals: imidazole (VWR, Radnor, USA), 1-methylimidazole and 1-ethylimidazole (Santa Cruz Biotech, Dallas, USA). The evaluation of data was performed with Proteus 5.1.0, Tofdaq 1.2.93 and Origin2017.

Results and discussion

Short-term thermal stability: Thermogravimetric analysis (TGA)

The results of a study of short-term thermal stability performed for [C2mim]*X* and [C4mim]*X* (*X* = Cl, Br, I) under nitrogen at the heating rate of 10 K min−1 are presented in Figure 1. As can be seen from the course of the TGA-curves, one decomposition step leading to the 100% mass loss was detected for all substances. The respective DSC curves showed three effects: the first, endothermal one with the temperature peak maximum below 100 °C that was attributed to melting, and the second and the third endothermal signals with the temperatures peak maximum over 200 °C that were associated with the thermal decomposition of the sample, which occurs by multiple possibly overlapping processes. The decomposition temperatures were extrapolated from the onset of the DTG-curves. Whereas the TGA-curve of [C4mim]I has only one step, the DTG-curve shows multistep decomposition with at least two overlapping peaks (in accordance to the respective DSC peaks), that cannot be separated from one another to evaluate the second one (Figure 1). Varying experimental conditions such as a smaller heating rate, a larger mass of the sample, and a different gas atmosphere had no influence on the shape of the DTG-curve.

**Figure 1.** Ramped temperature thermogravimetric (TGA) curves of [C2mim]*X* and [C4mim]*X* (*X* = Cl, Br, I) under nitrogen at the heating rate of 10 K min−1, DSC-curves and the first derivative (DTG).

In general, thermal stability is governed by a set of parameters, e. g. steric effects, nucleophilicity and basicity of the halogen. Thermal stability increases in order from [C2mim]Cl ˂ [C2mim]Br ≈ [C2mim]I as well as in the series of [C4mim]*X* (Cl ˂ Br ˂ I). This correlation can be explained by increasing polarizability in the series of halogens. However, [C2mim]Br and [C2mim]I exhibit similar decomposition temperatures, which may be caused by stronger influence of kinetic factors on the decomposition process. Elongation of the alkyl-chain from ethyl to butyl hampers the thermal stability. As a rule, the longer an alkyl-group, the lower the decomposition temperature of the substance. This observation can be rationalized by vanishing attraction between the tail part of an extended alkyl-chain and the ring of the molecule.

TGA/DSC-Skimmer-SPI/EI-TOFMS results for the determination of decomposition products

The TGA/DSC-Skimmer-SPI-TOFMS setup was used for the investigation of thermal behavior, for mapping structure-stability relations, as well as the decomposition products and patterns of 1-alkyl-3-methylimidazolium halides under various inert (argon, nitrogen, helium) and reactive (oxygen) gas flow. The thermal stability of [C2mim]*X* and [C4mim]*X* (*X* = Cl, Br, I) under different gas atmospheres was compared. Figure 2 illustrates thermal decomposition of [C2mim]Br under argon, nitrogen, helium and synthetic air at the heating rate of 10 K min−1. Other ILs investigated in this work have shown similar behavior. Table 1 summarizes decomposition temperatures extrapolated from the onset of the DTG curves of [C2mim]*X* and [C4mim]*X* (*X* = Cl, Br, I) under different gas atmospheres used in this work and literature data.

**Figure 2.** Ramped temperature thermogravimetric (TGA) and DSC-curves of [C2mim]Br at the heating rate of 10 K min−1 under different gas atmospheres.

The TGA-curves of [C2mim]Br measured under different gases (argon, nitrogen, helium and oxygen) are very close to each other (Figure 2). The observed course of the curves is an indirect indication that the decomposition process takes place during the heating of the 1-alkyl-3-methylimidazolium halides and prior to their evaporation. If the evaporation had been the dominating process, then the measured TGA-curve under helium would have been shifted toward significantly lower temperatures and the associated decomposition temperature of the substance would have been much lower. The DSC-curves of the [C2mim]Br have the same course until the start of decomposition. Only under synthetic air the melting occurs earlier, whereas under argon, helium and nitrogen the melting of [C2mim]Br occurs at the same temperature. The lower melting temperature could be caused by impurities, precisely by some moist contained in the synthetic air. The synthetic air may contain up to 2% of water according to the application form. The course of the DSC-curves under synthetic air and helium atmospheres during the decomposition of the [C2mim]Br is similar and the process of degradation is endothermal. The decomposition process under nitrogen is endothermal too and has a complicated character (overlapping effects), whereas the decomposition under argon proceeds exothermally.

**Table 1.** Decomposition temperatures of [C2mim]*X* and [C4mim]*X*, where *X* = Cl, Br, I at the heating rate of 10 K min−1 under different gas atmospheres

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Gas | onset-DTG\*, °C | | | | | |
| [C2mim]*X* | | | [C4mim]*X* | | |
| Cl | Br | I | Cl | Br | I |
| Ar | 269  26733 | 288  28933 | 288  29233 | -  24638 | -  26038 | -  23838 |
| Air | 269 | 272 | 293 | 248 | 260 | 277 |
| N2 | 260 | 283 | 279 | 250 | 255 | 265 |
| He | 253 | 279 | 284 | 251 | 266 | 277 |

\*All values are determined with a systematic error of ± 5K.

In the following, the mass spectrometric results of the ILs thermal decomposition are presented. Using the soft ionization mass spectrometry, we studied the decomposition products and elucidated possible pathways and mechanisms of thermal decomposition of the investigated ionic liquids. Thermoanalytical data (TGA/DSC) provides information complementary to the MS data.

Figure 3depicts the mass traces obtained during a TGA/DSC-Skimmer-SPI-TOFMS measurement of [C2mim]*X* (*X* = Cl, Br, I) in nitrogen atmosphere. On the contour plot, the *m/z* value, temperature, and signal intensity are shown on the axes. Figure 3a shows the detected mass traces upon heating of [C2mim]Cl: 1-ethylimidazole (*m/z* 96), 1-methylimidazole (*m/z* 82), and imidazole (*m/z* 68, very small amount, not shown in the figure). The masses corresponding to any chloride species were not detected. This holds for both isotopes, 35Cl and 37Cl, of the chloride ion as well as for alkyl chlorides, methyl chloride or/and ethyl chloride. Figure 3brepresents the mass traces of the molecules released upon heating of [C2mim]Br, namely two alkyl bromide species, methyl bromide (*m/z* 94, 96) and ethyl bromide (*m/z* 108, 110), each with both bromine isotopes, 79Br and 81Br, 1-ethylimidazole (*m/z* 96), 1-methylimidazole (*m/z* 82), and imidazole (*m/z* 68). Mass traces of isotopes of bromine (*m/z* 79, 81) were not found. The detected mass traces during decomposition of [C2mim]I (Figure 3c) suggest the formation of ethyl iodide (*m/z* 156) and methyl iodide (*m/z* 142), 1-ethylimidazole (*m/z* 96), 1-methylimidazole (*m/z* 82), and imidazole (*m/z* 68). The iodine ion was not detected just like in the case of chloride and bromide. The [C2mim]+ cation (*m/z* 111) was only detected in the [C2mim]I measurements that may suggest the formation of gaseous ion pairs.35 However, we did not detect any intact gaseous ion pairs under our experimental conditions.

**Figure 3.** Mass spectrometric traces of [C2mim]Cl, [C2mim]Br, [C2mim]I measured by TGA/DSC-Skimmer-SPI-TOFMS.

In the case of above-mentioned molecules the photoionization with vacuum ultraviolet photons (with energy of 10.16 eV) allows detection of molecular ions with no or less fragments. This is due to the photoionization energies of the molecules (imidazole 8.81 eV, C2H5I 9.33 eV and CH3I 9.53 eV). We did not found any literature data for 1-methylimidazole and 1-ethylimidazole). The alkyl halides which are formed from 1-ethyl-3-methylimidazolium chloride or bromide are difficult to detect, as their ionization energies are higher than the applied ionization energy (C2H5Cl 10.98 eV, CH3Cl 11.27 eV, CH3Br 10.53 eV, C2H5Br 10.29 eV).

Only a very small amount of the alkyl bromide can be ionized; for ionization of alkyl chlorides the applied ionization energy of 10.16 eV is not enough. In order to show that the applied photoionization has non-fragmenting character, we performed mass spectrometric measurements of pristine imidazole, 1-methylimidazole, and 1-ethylimidazole to show (Figure 4). Alternatively, it is possible to operate the device in the EI mode so that certain fragments imply the formation of compounds that cannot be investigated with photoionization. It is particularly useful for detecting of ethane and hydrogen halides: C2H6 10.50 eV, HCl 12.74 eV, HBr 11.68 eV, HI 10.38 eV (energies of ionization were taken from the database of NIST).

**Figure 4.** SPI-MS spectra of pristine (a) imidazole (*m/z* 68), (b) 1-methylimidazole (*m/z* 82), (c) 1-ethlyimidazole (*m/z* 96).

It is possible to deduce the decomposition pathways of [C2mim]*X* (*X* = Cl, Br, I) due to the fragment-free detection of the decomposition products. Scheme 1a illustratesthe formation of 1-ethylimidazole and methyl halide and Scheme 1b shows the formation of 1-methylimidazole and ethyl halide, respectively. The both reactions arise via the reverse Menshutkin reaction. The reaction of the halide anion with the quaternary ammonium cation leads to the formation of an alkyl halide and tertiary amine.52The reverse Menshutkin reaction occurs on both alkyl chains that is confirmed by the detected mass traces. For the [C2mim], a CH3 group is little more favored than a C2H5 chain, which is suggested by the formation of CH3I and 1-ethylimidazole at lower temperatures instead of C2H5I and 1-methylimidazole. In the case of the [C2mim]Br and [C2mim]Cl, this inclination is less obvious. The first step of the reverse Menshutkin reaction is a nucleophilic attack of the halide anion on an alkyl group. The next step is a C-N cleavage. It was described by *Chan et al.,*53 that the mechanism of nucleophilic substitution follows to SN2 mechanism in the case of dialkyl imidazolium halide salts. For allyl- and benzyl-substituted salts the observed mechanism was SN1. We made the comparison between products of the decomposition and their appearance from [C2mim]Cl, [C2mim]Br, [C2mim]I to analyze and to study the effect of changing the anion. The selectivity of the attack on CH3 group rather than on C2H5 in the SN2 mechanism decreases with the decreasing size of the nucleophile. Smaller anions show lower inclination for CH3 to C2H5 group. Our experimental results corroborate the SN2 mechanism since we detect 1-ethylimidazole and 1-methylimidazole released simultaneously from the [C2mim]Cl and [C2mim]Br in contrast to the above described case of the [C2mim]I.

According to *Chan et al.*53 the order of nucleophilicity is I− > Br− > Cl−, however according to *Lancaster et al*54 the order is I− > Cl− > Br−, where Cl−  is slightly more nucleophilic than Br-. Based on our experimental results (Table 1), we conclude that the bromide salt is to be the most stable one followed by the iodide (slight difference in the onset temperatures measured under nitrogen can be observed); and the chloride salt is the most vulnerable. As consequence, it also signifies that the degradation process and the stability cannot be interpreted only by the SN2 reaction. Elimination reaction should also be considered as a possible degradation pathway which takes place parallel to the SN2 reaction. Hofmann elimination reaction of a quaternary amine occurs by splitting off a C2H5-group in the form of ethene (Scheme 1c). The ethene cannot be detected by the photoionization, since its ionization energy is 10.50 eV. Therefore, we performed the STA-Skimmer-MS measurements with the ionization energy of 70 eV. Figure 5 depicts the mass traces of the decomposition of [C2mim]Cl with EI of 70 eV. The signal of (*m/z* 28) increases during the decomposition and the increase parallel to the signals of the degradation products. Together with the change in the mass spectrum this confirms the formation of ehtene. Moreover, the formation of hydrogen chloride also supports the Hofmann elimination reaction. The order of basicity is Cl− > Br− > I− which makes chloride salts more tend to elimination reaction. The detected molecule of imidazole indicates further degradation of 1-ethylimidazole due to a C-N bond cleavage. Besides ethane, imidazole can as well be dissociating products of 1-ethylimidazole. Additionally, ethyl halide and ethene can also be formed by elimination of C2H5I**.** Scheme 1d and 1e show further possible pathways of the decomposition scenario. We did not observe the decomposition of an imidazole ring under applied ionization energy.

**Scheme 1.** Proposed thermal decomposition pathways of [C2mim]*X* (*X* = Cl, Br, I).

**Figure 5.** Mass spectrometric scans of [C2mim]Cl under nitrogen with an ionization energy of 70eV.

Thermal degradation of the 1-butyl-3-methylimidazolium halides arises similarly to the way described for the 1-ethyl-3-methylimidazolium halides. Figure 6illustrates the mass spectrometric traces recorded during the TGA/DSC-Skimmer-SPI-TOFMS measurements of [C4mim]*X* (*X* = Cl, Br, I) under nitrogen atmosphere. The detected mass traces during decomposition of [C4mim]Cl (Figure 6a) suggest the formation of 1-butylimidazole (*m/z* 124), 1-ethylimidazole (*m/z* 96) and 1-methylimidazole (*m/z* 82). The mass traces of 1-butylimidazole (*m/z* 124), 1-ethylimidazole (*m/z* 96), 1-methylimidazole (*m/z* 82), methyl bromide (*m/z* 94, 96) with both bromine isotopes, 79Br and 81Br, and butene (*m/z* 56) are correspond to the decomposition of [C4mim]Br. The observed degradation products during the thermal decomposition of [C4mim]I are: 1-butylimidazole (*m/z* 124), 1-ethylimidazole (*m/z* 96), 1-methylimidazole (*m/z* 82) and imidazole (*m/z* 68), butyl iodide (*m/z* 184) and methyl iodide (*m/z* 142), and butene (*m/z* 56).

**Figure 6.** Mass spectrometric traces of [C4mim]Cl, [C4mim]Br, [C4mim]I under nitrogen atmosphere measured by TGA/DSC -Skimmer-SPI-TOFMS.

**Scheme 2.** Proposed thermal decomposition pathways of [C4mim]*X* (*X* = Cl, Br, I).

Decomposition of [C4mim]I proceeds via the reverse Menshutkin reaction (Scheme 2a and 2b) on both N-substituents; the nucleophilic attack on the methyl substituent is slightly more preferred because of the higher steric effect of the longer C4H9-chain. However, the favour is only slight. The 1-butylimidazole and butyl halides have not yet been detected by mass spectrometry during the decomposition of [C4mim]*X* (*X* = Cl, Br, I);34,52 their formation was only suggested. Soft photoionization with ionization energy of 10 eV enables direct detection of 1-butylimidazole and butyl iodide, as opposed to the TGA-EI-MS method described by *Hao et al*.34The detected butene could descend from the Hofmann elimination reaction (Scheme 2c)as well as from elimination of the hydrogen iodide from the C4H9I (Scheme 2f). Further degradation of the butyl iodide is not evident; the detected butene could also be formed by a C-N cleavage of the 1-butylimidazole (Scheme 2e).By a C-C cleavage of 1-butylimidazole, 1-ethylimidazole is formed (Scheme 2d). At higher temperatures imidazole was detected, like in the measurements of ethyl salt (Scheme 2e and 2h). We also detected propyl iodide (Scheme 2g). The same decomposition products with the corresponding halide (chloride or bromide) were found along the thermal decomposition of [C4mim]Cl and [C4mim]Br.

Since basicity decreases in the series Cl− > Br− > I−, chloride salts will show stronger vulnerability to elimination as well. With an increasing length of alkyl chain, this inclination will intensify.

The investigated ionic liquids and their main possible decomposition fragments are summarized in Table 2.

**Table 2.** Overview on investigated ionic liquid substances and their main possible fragments in mass spectrometric analysis

|  |  |  |  |
| --- | --- | --- | --- |
| *Substance* | *structural formula* | *molecular formula* | *significant mass of main fragment and isotope (m/z)* |
| *1-Ethyl-3-methylimidazolium halides* |  | *[C2mim]X* |  |
| 1-Ethyl-3-methylimidazolium chloride |  | [C2mim]Cl | 146 (35Cl)  148 (37Cl) |
| 1-Ethyl-3-methylimidazolium bromide | [C2mim]Br | 190 (79Br)  192 (81Br) |
| 1-Ethyl-3-methylimidazolium iodide | [C2mim]I | 238 |
| *1-Butyl-3-methylimidazolium halides* |  | *[C4mim]X* |  |
| 1-Butyl-3-methylimidazolium chloride |  | [C4mim]Cl | 174 (35Cl)  176 (37Cl) |
| 1-Butyl-3-methylimidazolium bromide | [C4mim]Br | 218 (79Br)  220 (81Br) |
| 1-Butyl-3-methylimidazolium iodide | [C4mim]I | 263 |
| *Imidazole and substituted (1-Alkylimidazoles)* |  |  |  |
| Imidazole |  | C3H4N2 | 68 |
| 1-Methylimidazole |  | C 4H6N2 | 82 |
| 1-Ethylimidazole |  | C5H8N2 | 96 |
| 1-Butylimidazole |  | C7H12N2 | 124 |
| *Butyl halides* |  | *C4H9X* |  |
| Butyl chloride |  | C4H9Cl | 92 (35Cl)  94 (37Cl) |
| Butyl bromide | C4H9Br | 136 (79Br)  138 (81Br) |
| Butyl iodide | C4H9I | 184 |
| *Propyl halides* |  | *C3H7X* |  |
| Propyl chloride |  | C3H7Cl | 78 (35Cl)  80 (37Cl) |
| Propyl bromide | C3H7Br | 122 (79Br)  124 (81Br) |
| Propyl iodide | C3H7I | 170 |
| *Ethyl halides* |  | *C4H9X* |  |
| Ethyl chloride |  | C2H5Cl | 64 (35Cl)  66 (37Cl) |
| Ethyl bromide | C2H5Br | 108 (79Br)  110 (81Br) |
| Ethyl iodide | C2H5I | 156 |
| *Methyl halides* |  | *CH3X* |  |
| Methyl chloride |  | CH3Cl | 50 (35Cl)  52 (37Cl) |
| Methyl bromide | CH3Br | 94 (79Br)  96 (81Br) |
| Methyl iodide | CH3I | 142 |
| *Hydrogen halides* |  | *HX* |  |
| Hydrogen chloride |  | HCl | 36 (35Cl)  37 (37Cl) |
| Hydrogen bromide | HBr | 80 (79Br)  82 (81Br) |
| Hydrogen iodide | HI | 128 |
| *Hydrocarbons* |  |  |  |
| Ethane |  | C2H6 | 30 |
| Ethene |  | C2H4 | 28 |
| Butene |  | C4H8 | 56 |

Determination of maximum operation temperature (MOT)

In the previous experiments of the short-term stability of the ionic liquids based on imidazolium and pyrrolidinium considerable reduction in mass was observed at lower temperatures, thus hinting at much lower decomposition temperature than typically assessed by such method.33,55-57 Various methods for determination of decomposition temperatures from the TGA curves has been discussed earlier.33 The main issue is the discrepancy between the measured and the “real” decomposition temperatures caused by the fact that all classic evaluation methods lead to the mass loss of at least 10%. The measurements of the long-term stability are time-consuming, but the notion of maximum operation temperature (MOT) is meant to ameliorate this problem. MOT corresponds to the maximum mass loss of 1% over a given period of time (eq 1). The model of MOT estimation is applicable under an assumption that evaporation of the substance is negligible and is based on the kinetic analysis of several dynamic TGA measurements with different heating rates (Figure 7).

(1)

(*E*a: activation energy; *R*: ideal gas constant; *k*0: frequency factor; *t*max: certain period of time or operation time)

Figure 7. Ramped temperature thermogravimetric (TGA) curves of [C4mim]Br at a heating rate of 1, 2, 5, 7, 10 and 20 K min−1, and the first derivative (DTG).

In order to calculate the maximum operation temperature, the kinetic parameters from the *Arrhenius* equation have to be determined. At the first step, activation energy is determined according to the recommendations of *ICTAC* for applications of isoconversional methods.58-61 Activation energy in the series of different turnover ratios *α* (taken as a constant for various heating rates *β*i) can be evaluated by the integrated isoconversional method, employing the Kissinger-Akahira-Sunose equation:

(2)

: heating rate; *T*α,i: temperature at the considered conversion *α* reached at *i*th heating rate)

The dependency between the activation energy and the turnover ratio gives an indirect hint to whether the decomposition process occurs in one or multiple stages.60 Figure 8 illustrates the dependence of the activation energy *E*a on the conversion degree α during thermal decomposition of [C4mim]*X* (*X* = Cl, Br, I).

**Figure 8.** Activation energy *E*a for the thermal decomposition of [C4mim]*X* (*X* = Cl, Br, I) in dependence on the conversion degree α.

As a result, [C4mim]Cl shows a dependence of *E*a on α with the values increasing from 105 to 145 kJ mol−1. The dependences *E*a on α for [C4mim]Br and for [C4mim]I demonstrate an increase followed by a quick fall. This complex behavior is associated with weak effects such as steric ones and nucleophilicity of the ILs. Their existence gives rise to different mechanisms of initiation of the thermal decomposition. There are no systematic trends in activation energies *E*a (for α = 0.01) of [C2mim]*X* and [C4mim]*X*, *X* = Cl, Br, I (Table 3).

As the second step, the pre-exponential factor that corresponds to the 1% mass loss in activation energy is calculated by

(3)

(*m*: sample mass)

**Table 3.** Kinetic parameters *E*a (for α = 0.01) and *k*0 for decomposition processes of [C2mim]*X* and [C4mim]*X*, where *X* = Cl, Br, I

|  |  |  |  |
| --- | --- | --- | --- |
| Substance | | Kinetic parameter | |
| *E*a, kJ mol−1 | *k*0, min−1 |
| [C2mim]*X,*33  *X* = | Cl | 120 | 2.3∙1010 |
| Br | 125 | 1.9∙1010 |
| I | 111 | 1.0∙109 |
| [C4mim]*X*,  *X* = | Cl | 105 | 7.0∙108 |
| Br | 127 | 5.8∙1010 |
| I | 121 | 2.1∙1010 |

Using the kinetic parameters received from the TGA-experiments it is possible to estimate the maximum operation temperature for any period of time for long time applications. MOT of [C2mim]*X* and [C4mim]*X* (*X* = Cl, Br, I) estimated according to the eq 1 for 1 day and 1 year, respectively, are summarized in Table 4.

**Table 4.** Maximum operation temperature (MOT) of [C2mim]*X* and [C4mim]*X*, where *X* = Cl, Br, I

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Substance | | MOT, °C | | | |
| 1 day | 1 week | 1 month | 1 year |
| [C2mim]*X*,33  *X* = | Cl | 132 | 112 | 97 | 76 |
| Br | 149 | 131 | 115 | 90 |
| I | 139 | 114 | 100 | 77 |
| [C4mim]*X*,  *X* = | Cl | 118 | 95 | 80 | 57 |
| Br | 143 | 122 | 107 | 85 |
| I | 133 | 113 | 99 | 76 |

Comparison of the decomposition temperatures that are derived from the onset of DTG-curves, and of the maximum operation temperatures estimated for 1 day via eq 1, yields a difference of roughly 100 K. These examples show clearly that the “real” decomposition temperature in the sense of MOT should be assessed for the long-time applications.

The established maximum operation temperature increases from the chloride to the iodide in the [C4mim]*X* (*X* = Cl, Br, I) series. The observed trend can be attributed to increasing polarizability of the halogens from the chloride anion to the iodide anion and to decreasing basicity in this order. This correlation is not observed for [C2mim]*X* (*X* = Cl, Br, I).

Conclusions

Ionic liquids, among them the investigated 1-alkyl-3-methylimidazolium halides, are being increasingly applied on a large scale, for example as synthesis media, also at elevated temperatures. Thus, it is crucial to describe their thermal behavior at high temperatures and find out their reliable operation temperatures.

Based on the reported data it was shown that the TGA/DSC-Skimmer-SPI-TOFMS method is well applicable for identification of degradation products of the ionic liquids as a consequence of the non-fragmenting character of photoionization. We elucidated to which extent the applied technology provides additional benefits, in contrast with those already described in the literature. It is possible to unambiguously identify products of thermal decomposition whose formation was earlier only suggested from the EI data or predicted by the quantum chemical calculations.

From the detected gas species during the thermal degradation, we derived the patterns of decomposition of the investigated in this work 1-alkyl-3-methylimidazolium halides. Their degradation via the reverse Menshutkin reaction and various elimination reactions results in alkyl imidazoles, alkyl halides and hydrogen halides, and alkenes. It was found that the 1-ethyl- and 1-butyl-3-methyl-imidazolium chlorides are increasingly prone to decomposition due to the reverse Menshutkin reaction and Hofmann elimination reaction. Hofmann elimination reaction in the bromide and iodide salts cannot also be excluded, obviously contributes to a lesser extent. We evaluated the structure-decomposition relationship with the respect to the alkyl-chain length and the type of the halide anion. Amongst the detected decomposition products, alkyl halides are critical for environmental and medical reasons, e. g. bromine released into the atmosphere during alkyl bromide photolysis is destructive to stratospheric ozone than chlorine.

The suggested maximum operation temperatures (MOTs) for 1 day and 1 year are found to be 100–200 °C lower than the decomposition temperatures determined via single TA-MS runs.

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Note

The authors declare no competing financial interest.

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**Figure 1.** Ramped temperature thermogravimetric (TGA) curves of [C2mim]X and [C4mim]X (X = Cl, Br, I) under nitrogen at the heating rate of 10 K min−1, DSC-curves and the first derivative (DTG).

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**Figure 1.** Ramped temperature thermogravimetric (TGA) curves of [C2mim]X and [C4mim]X (X = Cl, Br, I) under nitrogen at the heating rate of 10 K min−1, DSC-curves and the first derivative (DTG).

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**Figure 2.** Ramped temperature thermogravimetric (TGA) and DSC-curves of [C2mim]Br at the heating rate of 10 K min−1 under different gas atmospheres.

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**Figure 3.** Mass spectrometric traces of [C2mim]Cl, [C2mim]Br, [C2mim]I measured by TGA/DSC-Skimmer-SPI-TOFMS.

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**Figure 4.** SPI-MS spectra of pristine (a) imidazole (*m/z* 68), (b) 1-methylimidazole (*m/z* 82), (c) 1-ethlyimidazole (*m/z* 96).

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**Scheme 1.** Proposed thermal decomposition pathways of [C2mim]*X* (*X* = Cl, Br, I).

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**Figure 5.** Mass spectrometric scans of [C2mim]Cl under nitrogen with 70eV.

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**Figure 6.** Mass spectrometric traces of [C4mim]Cl, [C4mim]Br, [C4mim]I under nitrogen atmosphere measured by TGA/DSC -Skimmer-SPI-TOFMS.

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**Scheme 2.** Proposed thermal decomposition pathways of [C4mim]*X* (*X* = Cl, Br, I).

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Figure 7. Ramped temperature thermogravimetric (TGA) curves of [C4mim]Br measured at a heating rate of 1, 2, 5, 7, 10 and 20 K min−1, and the first derivative (DTG).

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**Figure 8.** Activation energy *E*a for the thermal decomposition of [C4mim]*X* (*X* = Cl, Br, I) in dependence on the conversion degree α.